

Commercially Available Halogen free Alternatives to Halogen-Containing Flame Retardant Systems in Polymers

1 Overview of flame retardants by polymer

This table gives an overview of commercially available non halogenated flame retardants. Often, combinations of the given substances are used. The individual formulation is up to the polymer compounder and often regarded as company know how. The abbreviations are listed at the end of the document. Please send any comments or information on new FRs and applications to jtroitzsch@troitzsch.com.

| Polymer | Application / Product | Fire Safety Requirement | Halogen-Containing FR System | Halogen free FR System |
|-----------------------|-----------------------|-------------------------|--|---------------------------------------|
| Thermoplastics | | | | |
| PE | E&E | UL94V0 | Deca / ATO DBDE / ATO EBTPI / ATO TBNPP / ATO CP / ATO | Intum P-based P-red / halfreeFR |
| | Building Films DE | UL94V2 | | P-red |
| | | DIN4102B2 | TBNPP / ATO DBDE / ATO | NorHals |
| | Wire & Cable | IEC 60332-3 | | ATH |
| PE / EVA | Wire & Cable | IEC 60332-3 | | ATH / Nano |
| PP | E&E | UL94V0 | Deca / ATO | Intum P-based |
| | | | DBDE / ATO | |
| | | | EBTPI / ATO | MOH |
| | | | TDPE / ATO | |

| Polymer | Application / Product | Fire Safety Requirement | Halogen-Containing FR System | Halogen free FR System |
|---------|-----------------------|-------------------------|---|-----------------------------------|
| | | UL94V2 | BEO / ATO CP / ATO HBCD / ATO TBNPP | |
| | Building Pipes DE | DIN4102B1 | TDPE | |
| | Building Films DE | DIN4102B2 | BEO / ATO | |
| | Building FR | NFP92507 M2 | TBNPP / ATO | Intum Pbased |
| | Wire & Cable | IEC 60332-3 | | ATH or MOH |
| HIPS | E&E | UL94V0 | Deca / ATO DBDE / ATO EBTPI / ATO BEO / ATO TBBPA / ATO CP / ATO | |
| | | UL94V2 | HBCD | RDP TPP BDP PolyDP |
| EPS | Building foam DE | DIN4102B1 | HBCD | |
| ABS | E&E | UL94V0 | Deca / ATO DBDE / ATO EBTPI / ATO BEO / ATO TBBPA / ATO | |
| PA | E&E | UL94V0 | Dech / ATO PBBPA / ATO BrPS / ATO BEO / ATO | P-red MC MPP MePh MOH |
| PET | E&E | UL94V0 | Deca / ATO DBDE / ATO BEO / ATO EBTPI / ATO TBBPA-CO / ATO | P-red MePh |
| | Fibres | BS5852Crib5 | | Dopo Oxa |
| PBT | E&E | UL94V0 | Deca / ATO | MePh |

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|-------------------|---|---|--|--|
| | | | DBDE / ATO EBTPI / ATO BEO / ATO TBBPA-CO / ATO | |
| PC | E&E | UL94V0 | Deca / ATO DBDE / ATO EBTPI TBBPA-CO / ATO TBBPA reactive | SulSalts TPP RDP BDP |
| PC / ABS | E&E | UL94V0 | Deca / ATO DBDE / ATO EBTPI / ATO TBBPA-CO / ATO BEO / ATO | RDP BDP TPP |
| PPE / HIPS | E&E | UL94V0 | Deca / ATO DBDE / ATO EBTPI / ATO TBBPA-CO / ATO | RDP BDP TPP |
| Thermosets | | | | |
| EP | E&E | UL94V0 | Deca / ATO DBDE / ATO EBTPI / ATO | ATH ATH / APP P-red PhPol |
| | | FR4 | TBBPA reactive | PhPol Dopo MePh PhPho Dopo |
| | Transport Air | | | |
| PIRrig | Building DE Building FR Building DE | DIN4102B1 NF P 92501 M1 DIN4102B2 | BrPol / TCPP P-red / TCPP | P-red APP |
| PURrig | Building DE | DIN4102B2 and SBI Class C | BrPol / TCPP | APP PhPol TEP DMPP |

| Polymer | Application / Product | Fire Safety Requirement | Halogen-Containing FR System | Halogen free FR System |
|---------|-----------------------|-------------------------|---|---|
| | Building USA | ASTM E84 | BrPol / TCPP | P-red |
| PURflex | Transport Auto | MVSS 302 | TCPP BrPol | PhPol CDP TCP APP APP / Intum |
| | Transport Air | KerosBurner | TCPP / Mel / EG | |
| | Building UphFur UK | BS5852Crib5 | TCPP / Mel TCPP / Mel | APP / Mel / EG |
| | USA | CalTB117 | | PhPol CDP TCP |
| UP | E&E | UL94V0 | Deca / ATO DBPE / ATO EBTPI / ATO TBBPA reactive CP / ATO HET-acid TCEP TCPP | ATH ATH / P-red ATH / APP DMPP DMPP+WMP |
| | Transport Sea | Flame Spread | | ATH |
| | Transport Rail DE | DIN 5510 | | APP |

2 Abbreviations

Applications

| | |
|-----------|-----------------------------------|
| UphFur | Upholstered furniture |
| E&E | Electrical & electronic equipment |
| Transport | Transportation |
| - Air | Aircraft |
| - Auto | Automotive |
| - Rail | Railways |
| - Sea | Ships |

Polymers

2.1 Thermoplastics

| | |
|----------|---|
| ABS | Acrylonitrile/butadiene/styrene terpolymer |
| EPS | Expandable polystyrene |
| HIPS | High impact polystyrene |
| PA | Polyamide |
| PBT | Polybutylene terephthalate |
| PC | Polycarbonate |
| PC/ABS | Polycarbonate/ABS blend |
| PE | Polyethylene |
| PET | Polyethylene terephthalate |
| PP | Polypropylene |
| PPE/HIPS | Polyphenylene ether/high impact polystyrene blend |

2.2 Thermosets

| | |
|---------|------------------------------|
| EP | Epoxy resins |
| PIRrig | Rigid polyisocyanurate foam |
| PURflex | Flexible polyurethane foam |
| PURrig | Rigid polyurethane foam |
| UP | Unsaturated polyester resins |

Flame retardants

Brominated flame retardants

| | |
|----------|-------------------------------------|
| BEO | Brominated epoxies |
| BrPS | Brominated polystyrene |
| BrPol | Brominated polyols |
| DBDE | Decabromodiphenyl ethane |
| Deca | Decabromodiphenyl ether |
| EBTPI | Ethylene bis(tetrabromophthalimide) |
| HBCD | Hexabromocyclododecane |
| PBB-PA | Poly(pentabromobenzyl acrylate) |
| TBBPA | Tetrabromobisphenol-A |
| TBBPA-CO | TBBPA carbonate oligomer |
| TBNPP | Tris(bromoneopentyl) phosphate |
| TDPE | TBBPA (2,3-dibromopropyl ether) |

Chlorinated flame retardants

| | |
|----------|--|
| CP | Chloroparaffin |
| Dech | Alicyclic chlorinated compound (Dechlorane plus) |
| HET-acid | Hexachloroendomethylenetetrahydrophthalic acid |
| TCEP | tris(chloroethyl) phosphate |
| TCPP | tris(chloropropyl) phosphate |

Organo phosphorous flame retardants

| | |
|--------|---|
| BDP | Bisphenol A bis(diphenyl phosphate) |
| CDP | Cresyldiphenyl phosphate |
| DMPP | Dimethylpropane phosphonate |
| Dopo | Dihydrooxaphosphaphenanthrene oxide |
| MePh | Metal phosphinate |
| Oxa | Oxaphospholane |
| PhPol | Phosphorous polyol |
| PolyDP | Polymeric diphenyl phosphate |
| RDP | Resorcinol bis(diphenyl phosphate) |
| TCP | Tricresyl phosphate |
| TEP | Triethyl phosphate |
| TPP | Triphenyl phosphate |
| WMP | Intumescent system based on ethylenediamino phosphate |

Nitrogen-containing flame retardants

| | |
|---------|-------------------------|
| MC | Melamine cyanurate |
| Mel | Melamine |
| MPP | Melamine polyphosphate |
| NorHals | N-alkoxy hindered amine |

Inorganic flame retardants

| | |
|---------------|---|
| APP | Ammonium polyphosphate |
| APP/intum | Intumescent system based on APP |
| ATH | Aluminium hydroxide |
| ATO | Antimony trioxide |
| EG | Expandable graphite |
| Intum P-based | Intumescent flame retardant system based on APP, MC, etc... |
| MOH | Magnesium hydroxide |
| Nano | Nanocomposite based on montmorillonite clays |
| P-red | Red phosphorous |

Other

| | |
|----------|-----------------|
| SulSalts | Sulfonate salts |
|----------|-----------------|

3 Overviews and environmental assessments of alternatives to specific halogen-containing flame retardants

There are some third party overviews / assessments of flame retardants from various consultants and environmental agencies. These reports sometimes come to different conclusions on the same products and are often seen as controversial by the FR producers. One controversial point is that the flame retardants deca-BDE, TBBPA and HBCD have undergone comprehensive risk assessments, while the substitution products often have not. However, this will change in the near future with the implementation of REACH, as extensive data will have to be provided for all flame retardants.

Examples are:

- German UBA (2001): Substituting Environmentally Relevant Flame Retardants: Assessment Fundamentals Volume I: Results and summary overview - <http://www.umweltbundesamt.de/uba-info-medien/dateien/1988.htm>
- Danish EPA: Environmental Project no. 1141 (2007): Deca-BDE and Alternatives in Electrical and Electronic Equipment <http://www2.mst.dk/Udgiv/publications/2007/978-87-7052-349-3/pdf/978-87-7052-350-9.pdf>
- Morose, Gregory (2006): An Overview of Alternatives to Tetrabromobisphenol A (TBBPA) and Hexabromocyclododecane (HBCD), Prepared for the Jennifer Altman Foundation, <http://sustainableproduction.org/downloads/AlternativestoTBBPAandHBCD.pdf>
- Illinois Environmental Protection Agency (2007): "Report on Alternatives to the Flame Retardant DecaBDE: Evaluation of Toxicity, Availability, Affordability, and Fire Safety Issues", <http://www.epa.state.il.us/reports/decabde-study/index.html>
- European Chemicals Bureau (2007): Review on production processes of decabromodiphenyl ether (Deca-BDE) used in polymeric applications in electrical and electronic equipment, and assessment of the availability of potential alternatives to Deca-BDE. http://ecb.jrc.it/documents/Existing-Chemicals/Review_on_production_process_of_decaBDE.pdf