Environmentally-friendly inorganic fire retardants

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ITRI Limited, St Albans, UK

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Overview

1. Introduction
   - ITRI
   - Inorganic fire retardants

2. Recent FR projects at ITRI
   - FLAMTEX
   - HALFREE
   - ENFIRO
   - HYBRID
   - STEELPROST

3. ITRI facilities
   - Polymer processing & testing
   - Fire testing
   - Chemical analysis & characterisation

4. Summary
Organisation History

• 1932 – 1994 International Tin Research Institute
• Sponsored by the Governments of the tin-producing countries
• 1995 ITRI Limited established

• Privatised by tin-producer mining/smelting consortium
• 2003 New modernised facilities at Curo Park, St Albans, UK
Worldwide FR Consumption 2006

- Alumina trihydrate (38%)
- Chlorinated FRs (11%)
- Phosphorus FRs (16%)
- Antimony oxides (6%)
- Brominated FRs (18%)
- Magnesium hydroxide (2%)
- Melamine FRs (3%)
- Others (6%)

Total = ca. 1,600,000 tonnes
Inorganic Fire Retardants – Main Types

- **Hydrated fillers**
  - Alumina trihydrate (ATH)
  - Magnesium hydroxide (MH)

- **Phosphorus compounds**
  - Red phosphorus
  - Ammonium polyphosphate (APP)
  - Aluminium diethylphosphinate (AlPi)

- **Inorganic synergists**
  - Antimony trioxide (ATO)
  - Zinc borates (ZB)
  - Zinc stannates (ZHS/ZS)
  - Ammonium octamolybdate (AOM)

- **Nanoclays**
  - Montmorillonite (MMT, cationic clays)
  - Layered double hydroxides (LDH, anionic clays)

- **Expandable graphite**
FLAMTEX

- Tin-based flame-resistant treatments for aircraft cabin textiles
- DTI funded project under CARAD programme
- ITRI Ltd
- Keeling & Walker Ltd
- Replin Fabrics Ltd
- Britax Aircraft Interiors (UK) Ltd
- Wool – nylon blend fabric
- Problems with existing treatment (PFZ)
- Fluoride in effluent discharge
- Relatively high smoke emission
- Colloidal inorganic tin treatments
Flame Retardancy (LOI)

- Untreated wool
- Commercial PFZ system
- Colloidal tin system
Smoke Parameter

- Untreated wool
- Commercial PFZ system
- Colloidal tin system
Carbon Monoxide Yield

- Untreated wool
- Commercial PFZ system
- Colloidal tin system
• Commercial PFZ treatment – good FR, but high smoke & CO emissions

• Several tin-based treatments match or outperform PFZ at comparable uptake levels

• Marked reductions in smoke & CO emission levels

• Quantitative retention of FR elements in char – condensed phase action

• FR evaluation using industrial treatment process

• Production & testing of full-scale prototype aircraft seat assembly

• Assessment of economic & practical viability
Halogen-free FR systems for PCBs & encapsulated electronic components

DTI funded project – Sustainable Technologies Initiative (STI)

2 year programme

ITRI Ltd

Celestica

Joseph Storey Co Ltd

Keeling & Walker Ltd

Merlin Circuit Technology Ltd

Prestwick Circuits Ltd

RF Bright Enterprises Ltd
HALFREE – Background

- Brominated FRs widely used in the electronics industry, but concerns:
  - May persist in the environment?
  - May bio-accumulate in living organisms (e.g. animal tissue)?
  - May be detrimental to human health or toxic to wildlife?
  - May generate highly toxic species during combustion (e.g. dioxins)?

- EU Directives:
  - RoHS (2002/95/EC)
  - WEEE (2002/96/EC)
  - Marketing & Use of Dangerous Substances (2003/11/EC)

- Eco Labels:
  - German Blue Angel
  - Swedish TCO
  - Nordic Swan
  - EU Flower

- HALFREE – development of halogen-free epoxy compositions using novel inorganic FRs based on ITRI nano-particulate coating technology
## HALFREE – Encapsulating Resin

<table>
<thead>
<tr>
<th>Formulation</th>
<th>UL-94 Performance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control resin (non-halogenated)</td>
<td>FAIL</td>
</tr>
<tr>
<td>150phr ATH</td>
<td>V0</td>
</tr>
<tr>
<td>125phr ATH</td>
<td>V1</td>
</tr>
<tr>
<td>100phr ATH</td>
<td>FAIL</td>
</tr>
<tr>
<td>100phr ZHS-ctd ATH</td>
<td>V0</td>
</tr>
<tr>
<td>95phr ZHS-ctd ATH + 5phr ZB</td>
<td>V1</td>
</tr>
<tr>
<td>Comm. FR resin (Deca-BDE + Sb$_2$O$_3$)</td>
<td>FAIL</td>
</tr>
</tbody>
</table>
## HALFREE – PCB Resin

<table>
<thead>
<tr>
<th>Formulation</th>
<th>UL-94 Performance</th>
<th>Oxygen Index</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control resin (non-halogenated)</td>
<td>FAIL</td>
<td>23.5</td>
</tr>
<tr>
<td>100phr ZHS-ctd ATH</td>
<td>V0</td>
<td>30.0</td>
</tr>
<tr>
<td>95phr ZHS-ctd ATH + 5phr ZB</td>
<td>V0</td>
<td>30.5</td>
</tr>
<tr>
<td>90phr ZHS-ctd ATH + 10phr ZB</td>
<td>V0</td>
<td>32.5</td>
</tr>
<tr>
<td>Comm. Br resin (19% Br as TBBPA)</td>
<td>V0</td>
<td>29.0</td>
</tr>
</tbody>
</table>
HALFREE – PCB Resin

Cone: Peak RHR (kW/m²)

- Control
- 100 ZHS-ctd ATH
- 95 ZHS-ctd ATH + 5 ZB
- 90 ZHS-ctd ATH + 10 ZB
- TBBPA resin

AMI - Cologne Nov. 2007
HALFREE – PCB Resin

Cone: Smoke Parameter (MW/kg)

Control  100 ZHS-ctd ATH  95 ZHS-ctd ATH + 5 ZB  90 ZHS-ctd ATH + 10 ZB  TBBPA resin
HALFREE – PCB Resin

Cone: Carbon Monoxide Yield (kg/kg)

- Control
- 100 ZHS-ctd ATH
- 95 ZHS-ctd ATH + 5 ZB
- 90 ZHS-ctd ATH + 10 ZB
- TBBPA resin

AMI - Cologne Nov. 2007
HALFREE – Conclusions & Future Work

• Over 100 experimental epoxy formulations prepared & fire tested
• Best performing systems show clear benefits over commercial BrFR formulations, particularly markedly lower smoke & CO emissions
• ZHS-coated ATH alone or in combination with zinc borate (ZB)

• Fabrication of prototype PCBs containing HALFREE systems
• Industrial evaluation – electrical, physical, thermal stability, solderability
• Cost assessment (vs. current TBBPA-based FR-4 boards)
• Environmental impact – including recycling issues
ENFIRO

- Life cycle assessment of environment-compatible flame retardants (prototypical case study) – substitution options for brominated FRs
- FP7 Collaborative Project – 3 year programme (commenced Sept. 2009)
- VU University Amsterdam (Netherlands)
- Ulster University (UK)
- Clariant Produkte GmbH (Germany)
- IRIS Vernici srl (Italy)
- Procoat (Italy)
- IVAM (Netherlands)
- Stockholm University (Sweden)
- IRAS Utrecht (Netherlands)
- Swerea IVF AB (Sweden)
- University of Amsterdam (Netherlands)
- Callisto (UK)
- ITRI Ltd (UK)
<table>
<thead>
<tr>
<th>Base polymer</th>
<th>FR additives</th>
<th>Compounding</th>
<th>Moulding</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC/ABS</td>
<td>deca-BDE + Sb$_2$O$_3$, RDP, BDP, nanoclay</td>
<td>Twin-screw extruder</td>
<td>Injection</td>
</tr>
<tr>
<td>PPE/HIPS</td>
<td>deca-BDE + Sb$_2$O$_3$, RDP, BDP</td>
<td>Twin-screw extruder</td>
<td>Injection</td>
</tr>
<tr>
<td>PA66 – GF</td>
<td>Br-PS + Sb$_2$O$_3$, Al-DEP, mel-PP, ZS, ZB</td>
<td>Twin-screw extruder</td>
<td>Injection</td>
</tr>
<tr>
<td>PBT – GF</td>
<td>Br-PS + Sb$_2$O$_3$, Al-DEP, nanoclay</td>
<td>Twin-screw extruder</td>
<td>Injection</td>
</tr>
<tr>
<td>Epoxy resin (encapsulant)</td>
<td>deca-BDE + Sb$_2$O$_3$, DOPO, ZHS-coated ATH, ATH, ZHS, ZB, nanoclay</td>
<td>High-shear mixer (Silverson)</td>
<td>Cast into RTV silicone moulds, then heat cured</td>
</tr>
<tr>
<td>PE/EVA (cable)</td>
<td>deca-BDE + Sb$_2$O$_3$, ZHS-coated ATH, ATH, ZHS, ZB, nanoclay</td>
<td>Two-roll mill (or twin-screw extruder?)</td>
<td>Compression</td>
</tr>
</tbody>
</table>
• Novel tin – layered double hydroxide (Sn – LDH) hybrid fire retardants and their application in nano-composite cable formulations

• EUROSTARS Programme (Joint EUREKA / FP7 Initiative)

• 2 year programme (commenced February 2010)

• ITRI Ltd (UK)
• CimtecLab srl (Italy)
STEELPROST

- Innovative fire protective coatings for steel structures
- FP7 Research for SME Associations Project – 2½ year programme (commenced May 2010)
- European Convention of Construction Steelwork (Belgium)
- Asociacion de la Industria Navarra (Spain)
- Construction Cluster of Slovenia (Slovenia)
- Alcea srl (Italy)
- Bersch & Fratscher GmbH (Germany)
- Matherm SAS (France)
- Talleres Ruiz (Spain)
- Razpon D.O.O. (Slovenia)
- ITRI Ltd (UK)
- Tecnologias Avanzadas Inspiralia SL (Spain)
- Acciona SA (Spain)
STEELPROST – Objectives

• Development of a new generation of fire-protective coatings for steel panels

• Compared to conventional intumescent paint systems:
  ➢ Easier to paint on
  ➢ Cover a larger surface area faster
  ➢ Exhibit improved adhesion and quick drying properties
  ➢ Fire resistance compliant with grades R90 to R120 (BS 476 – Part 20)
  ➢ Significantly reduced smoke and toxic gas emissions
Polymer Laboratory

- Twin-screw extruder
- Two-roll mill
- Injection moulding
- Compression moulding
- High shear mixers
- Tensile tests
- Impact tests
Fire Test Laboratory
Fire Tests

- Cone Calorimeter
- Limiting Oxygen Index (LOI)
- NBS Smoke Chamber
- UL-94 Vertical & Horizontal Burning Tests
- Simultaneous Thermal Analysis (TG/DSC)
- Evolved Gas Analysis (by FTIR)
ITRI Laboratories - Chemical Analysis

- ICP – AES
- Wet chemical analysis
- FTIR
- UV/Vis/NIR
- Thermal analysis – TG/DSC
- Particle sizing
- Zeta potential
- BET surface area
- XRF
- XRD
- SEM – EDX
- Voltammetry
- Ion chromatography
Summary

- Many flame retardants now subject to increasing levels of environmental scrutiny & regulatory control

- Certain inorganic flame retardants finding increasing use as low toxicity alternatives for many polymer applications

- Novel nano-particulate & coating technologies developed to optimise synergistic interactions between multi-component systems

- Opportunities exist in a wide range of applications
  - Plastics
  - Rubbers
  - Foams
  - Fibres & textiles
  - Paints & coatings
  - Composite materials