SCREENING FLAME RETARDANT ADDITIVES FOR PLASTICS USING MICROSCALE COMBUSTION CALORIMETRY

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SCREENING PLASTICS FOR FLAMMABILITY

PROBLEM

Need Small Scale (milligram) Screening Test for FR Additives to Reduce Development Costs and Accelerate Discovery.

APPROACH

• Measure Properties of Complete Combustion using Microscale Combustion Calorimetry.

• Use a “Burning Efficiency” to Account for Incompleteness of Flaming Combustion.

• Account for Uncertainty Using Probability.

RESULTS

CONCLUSIONS
THE GOAL OF THE FR ADDITIVE APPROACH

Flammability ($\eta_c$), J/g-K

Materials Cost* ($/lb)

Commodity Plastics

Engineering Plastics

Heat Resistant Plastics

Intrinsically Flame Resistant

*Truckload Prices, 2001
FLAME RETARDANTS WORK IN TWO WAYS

Need to quantify the efficiency of these modes of action
APPROACH

1) Reproduce elements of flaming combustion in non-flaming test

Gases analyzed for residual oxygen to compute heat release rate

2) Measure thermal combustion properties of materials

3) Relate thermal combustion properties to fire and flame tests using deterministic and probabilistic models
MICROSCALE COMBUSTION CALORIMETER (MCC)

Heat release rate by oxygen consumption
AUTOMATED / HIGH THROUGHPUT MCC

Combustor with oxygen consumption attached to TGA with automated sampling

Capable of ≈ 50 tests/day
Designation: D 7309 – 07


1. Scope
   1.1 This test method, which is similar to thermal analysis techniques, establishes a procedure for determining flammability characteristics of combustible materials such as plastics.
   1.2 The test is conducted in a laboratory environment using controlled heating of milligram specimens and complete thermal oxidation of the specimen gases.
   1.3 Specimens of known mass are thermally decomposed in an oxygen-free (anerobic) or oxidizing (aerobic) environment at a constant heating rate between 0.2 and 2 K/s.
   1.4 The heat released by the specimen is determined from the mass of oxygen consumed to completely oxidize (combust) the specimen gases.
   1.5 The heat released by combustion of the specimen gases produced during controlled thermal or thermochemical decomposition of the specimen is computed from the rate of oxygen consumption.
   1.6 The specimen temperatures over which combustion heat is released are measured.
   1.7 The mass of specimen remaining after the test is measured and used to compute the residual mass fraction.
   1.8 The specimen shall be a material or composite material in any form (fiber, film, powder, pellet, droplet). This test method has been developed to facilitate material development and research.
   1.9 This test standard is used to measure and describe the response of materials, products, or assemblies to heat and flame under controlled conditions, but does not by itself incorporate all factors required for fire hazard or fire risk assessment of the materials, products, or assemblies under actual fire conditions.
   1.10 This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

Note 1 — There is no ISO equivalent to this test method.

2. Referenced Documents
   2.1 ASTM Standards:
   D 883 Terminology Relating to Plastics
   D 5965 Test Method for Gross Calorific Value of Coal and Coke
   E 176 Terminology of Fire Standards
   E 1591 Guide for Obtaining Data for Deterministic Fire Models

3. Terminology
   3.1 Definitions:
   3.1.1 For definitions of terms relating to plastics, refer to Terminology D 883.
   3.1.2 For definitions of terms relating to fire, refer to Terminology E 176.
   3.2 Definitions of Terms Specific to This Standard:
   3.2.1 combustion efficiency — the fraction of the heat of combustion of the specimen that is released as heat during the test.
   3.2.2 combustion temperature at which the specimen is heated, n — the temperature of the specimen at the beginning of combustion.

   3.2.3 heat release rate, n — the constant rate of temperature rise of the specimen during the test.
   3.2.4 heat release temperature, n — the temperature at which the specific heat release rate is a maximum during the test.

For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For Annual Book of ASTM Standards volume information, refer to the standard’s Document Summary page on the ASTM website.
Heat Release Rate (J/g-K) vs. Temperature (°C)

- **Heat Release Capacity,** $\eta_c$ (J/g-K)
- **Total Heat Release,** HR (J/g)
- **Temperature at Max HRR,** $T_{\text{max}}$ (°K)
- $\phi = \text{Pyrolysis residue (Char fraction)}$
FORCED AND UNFORCED COMBUSTION

Cone Calorimeter (ASTM E 1354)

OSU Calorimeter (14 CFR Part 25)

Vertical Flame Test (ASTM D 3801)

Unforced Combustion

Forced Combustion

Oxygen Index (ASTM D 2863)
FLAMING COMBUSTION: Gas Phase Chemistry

Complete Combustion (Oxidation) of Fuel Gases

\[
C_{cH_{n}O_{m}N_{n}X_{x}} + m O_2 \xrightarrow{900 \, ^\circ C \, 10 \, \text{sec}} CO_2 + H_2O + N_2 + HX
\]

Incomplete Combustion of Fuel Gases in Diffusion Flame

\[
C_{cH_{n}O_{m}N_{n}X_{x}} + n O_2 \xrightarrow{\text{Flame}} CO_2 + H_2O + N_2 + HX
\]
\[+ CO + C_xH_y + \text{soot}\]

Flaming Combustion Efficiency,

\[
\chi = \frac{n O_2}{m O_2} \quad < 1
\]
FLAMING COMBUSTION: Condensed Phase Physics

Heat Transfer Efficiency, $\theta = \frac{\left\{ -\kappa(\Delta T/\Delta x) \right\}_{\text{char layer}}}{\left\{ -\kappa(\Delta T/\Delta x) \right\}_{\text{resin}}} = \frac{q''_{\text{net}}}{q''^0_{\text{net}}}$
Heat Release Rate (HRR) for Steady Burning:

\[
HRR = \chi \frac{H_c^0}{L_g} \theta (q''_{\text{flame}} - q''_{\text{rerad}}) + \chi \frac{H_c^0}{L_g} \theta q''_{\text{ext}}
\]

**Cone Calorimeter Data**

- \( H_c^0 = \text{Heat of Combustion Of Fuel Gases} \)
- \( \chi = \text{Combustion Efficiency in Flame} \)
- \( \theta = \text{Heat Transfer Efficiency at Surface} \)
Heat Release Capacity

\[ HRP = \chi \theta \frac{H_c^0}{L_g} = \chi \theta \frac{\eta_c}{\eta_g} \]

Flaming Combustion Efficiency

\[ \eta_c \eta_g \frac{h_g}{\Delta T_p} \]

Heat Release Rate:

\[ HRR = \frac{\eta_c}{\eta_g} (q_{\text{flame}}'' - q_{\text{rerad}}'') + \frac{\eta_c}{\eta_g} q_{\text{ext}}'' \]
Fire Response
HEAT RELEASE RATE: Macro Vs. Micro

At large external heat flux, HRR $\propto \eta_c$

- Natural Plastics
- Micro-composites
- Nano-composites
- GFRP (PA6, PBT, PC, PPS)
- PC/ABS Blends
- FR Compounds

![Cone Calorimeter Image](image-url)
OSU HEAT RELEASE RATE: Macro Vs. Micro

OSU Peak HRR, kW/m² vs. Heat Release Capacity, J/g-K

- Thermoset Composites (single ply)
- Thermoplastic Sheet (1.6 mm)

FAR 25.853(a-1) Maximum

ASTM E 906/OSU Rate of Heat Release Apparatus
Flame Resistance
Flame Extinction Occurs at Critical HRR:

\[
HRR^* \approx \begin{cases} 
100 \text{ kW/m}^2 \ (\text{Downward Burning}) \\
60 \text{ kW/m}^2 \ (\text{Upward Burning})
\end{cases}
\]

- **MACRO Extinction Criterion for Flame Tests**

\[
HRP \leq \frac{HRR^*}{(q''_{\text{flame}} - q''_{\text{loss}})}
\]

- **MICRO Extinction Criterion for Flame Tests**

\[
\eta_c \leq \frac{\eta_g HRR^*}{(q''_{\text{flame}} - q''_{\text{rerad}})} = \eta_c^*
\]
Limiting Oxygen Index (LOI) = \([O_2^*]\)

\[ \text{HRR}^* = 100 \text{ kW/m}^2 \text{ (downward burning)} \]

\[
q''_{\text{flame}} \propto [O_2] = a [O_2] \quad q''_{\text{rerad}} = \sigma T_{\text{max}}^4 \approx 17 \text{ kW/m}^2
\]

\[ a = 1.4 \text{ kW/m}^2\%O_2 \]

\[
\eta_g = \frac{h_g / \Delta T_p}{\chi \theta} = \frac{(2 \text{ kJ/g})/(50 \text{ K})}{\chi \theta} = \frac{40 \text{ J/g - K}}{\chi \theta}
\]

**LOI Extinction Condition:**

\[
[O_2^*] = \frac{q''_{\text{rerad}}}{a} + \frac{\text{HRR}^* \eta_g / a}{\eta_c} \approx 12\% + \frac{2.8 \text{ kJ/g - K}}{\theta \chi \eta_c} \%
\]
EFFECT OF BURNING EFFICIENCY ON L.O.I.

\[ \text{LOI} = 12\% + \frac{2.8 \text{kJ/g-K}}{\theta \chi \eta_c} \] (%)

\[ \theta \chi = 1 \quad 0.6 \quad 0.3 \]

Limiting Oxygen Index, % v/v

Heat Release Capacity \( \eta_c \), J/g-K

\( \bigcirc \) Halogen containing

w/ FR Additives
FLAME RESISTANCE: UPWARD BURNING

Comparative Burning Characteristics of Plastics in Vertical Position (UL 94 V or ASTM D 3801):

\[ HRR^* = 60 \text{ kW/m}^2 \]

\[ q''_{\text{rad}} = CHF \approx \varepsilon \sigma T_{\text{max}}^4 \]

\[ q''_{\text{flame}} \approx 30 \text{ kW/m}^2 \]

\[ \eta_g = \frac{h_g / \Delta T_p}{\chi \theta} = \frac{(2 \text{ kJ/g})/(50\text{K})}{\chi \theta} = \frac{40 \text{ J/g - K}}{\chi \theta} \]

**UL 94 V EXTINCTION CONDITION:**

\[ \eta_c \leq \frac{HRR^* \eta_g}{\chi \theta (q''_{\text{flame}} - \varepsilon \sigma T_{\text{max}}^4)} \approx \frac{2.4 \text{ MW J m}^{-2} \text{ g}^{-1} \text{K}^{-1}}{\chi \theta (q''_{\text{flame}} - \varepsilon \sigma T_{\text{max}}^4)} \]
EFFECT OF $\chi^\theta$ AND $T_{\text{max}}$ ON EXTINCTION $\eta_c$

Burning Efficiency

Extinction $\eta_c$, J/g-K

Decomposition Temperature $T_{\text{max}}$, °C

UL 94 V Flame Test
EFFECT OF BURNING EFFICIENCY ON UL 94

UNCERTAINTY DUE TO BURNING EFFICIENCY

Heat Release Capacity, J/g-K

NR / Burns
V-2
V-1
V-0 / 5V

Flammability

UL 94 V Rating

Bromine FR
Natural Plastics
Phosphorus FR
Gas Phase FR
Condensed Phase FR

EFFECT OF BURNING EFFICIENCY ON UL 94
Assume that *Odds of Burning* is related to HRR and probability of burning, \( p_B \)

\[
\text{Odds of Burning} = \frac{p_B}{1 - p_B} = \left( \frac{\text{HRR}}{\text{HRR}^*} \right)^3
\]

Then,

\[
p_B = \frac{(\text{HRR}/\text{HRR}^*)^3}{1 + (\text{HRR}/\text{HRR}^*)^3}
\]

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<th>( \frac{\text{HRR}}{\text{HRR}^*} )</th>
<th>( p_B )</th>
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</table>
ODDS OF BURNING AND THERMAL COMBUSTION PROPERTIES

\[
HRR = \chi^\theta \frac{\eta_c}{\eta_g} q_{net}''; \quad HRR^* = \frac{\eta_c^*}{\eta_g} q_{critical}'' \approx 60 \text{ kW/m}^2
\]

Then,

\[
\frac{p_B}{1-p_B} = \left( \frac{HRR}{HRR^*} \right)^3 = \left( \chi^\theta \frac{\eta_c}{\eta_c^*} \right)^3 \left( \frac{q_{net}''}{q_{critical}''} \right)^3 \approx \left( \chi^\theta \frac{\eta_c}{\eta_c^*} \right)^{3/\chi^\theta}
\]

And:

\[
p_B = \frac{(\chi^\theta \eta_c / \eta_c^*)^{3/\chi^\theta}}{1 + (\chi^\theta \eta_c / \eta_c^*)^{3/\chi^\theta}}
\]

Depends only on burning efficiency \((\chi^\theta)\) and heat release capacity \((\eta_c)\)
MEASURE PROBABILITY OF BURNING, $\rho_B$

- $\bullet = \text{Burn (HB / NR / V-2 / V-1)}$
- $\bigcirc = \text{No Burn (V-0 / 5V)}$

HRC bin width of $\approx 50 \text{ J/g-K}$ gives statistically valid sample ($n \geq 5$)

$\rho_B = \text{Fraction of Burn}$

Results in HRC Bin

**UL 94 V Rating**

- NR / HB
- V-2
- V-1
- V-0 / 5V

**Heat Release Capacity, $\eta_c$ (J/g-K)**

184 test results
Heat Release Capacity, $\eta_c$ (J/g-K)

Probability of Burning, $p_B$

\[
p_B = \frac{\left(\chi^\theta \eta_c / 325\right)^{3/\chi^\theta}}{1 + \left(\chi^\theta \eta_c / 325\right)^{3/\chi^\theta}}
\]

EFFECT OF BURNING EFFICIENCY ON PROBABILITY OF BURNING

- $\chi^\theta = 1$
- $\chi^\theta = 0.8$
- Best Overall Fit ($p_B \pm 0.11$)
- $\chi^\theta = 0.6$ (FR Compounds)
CONCLUSIONS

- **Deterministic Models** using thermal combustion properties appear adequate for *forced flaming combustion*.

- **Probabilistic Models** are required to reconcile MCC data with *flame resistance* tests because
  
  \[ \begin{align*}
  \cdot \text{Intumescence, charring} & (\theta) \\
  \cdot \text{Gas phase inhibition} & (\chi) \\
  \cdot \text{and Dripping} \\
  \end{align*} \]

  are comparable in magnitude and effect to thermal combustion properties at extinction.