A NOVEL APPROACH TO MANAGE THE IMPLEMENTATION OF MORE SUSTAINABLE FLAME RETARDANTS

Presented by Marshall Moore
Director, Technology, Advocacy & Marketing

Fire Retardants in Plastics 2013
June 13-14 · Denver, CO
- Global specialty chemical company listed on the New York Stock Exchange (“CHMT”)
- Major markets served are energy & electronics, transportation, and agriculture
- Committed to global sustainability and engineering chemical solutions that meet our customers’ evolving needs
- More than 4,300 employees worldwide
- Manufactures in 31 countries and sells products in over 100 countries
- Global headquarters in Philadelphia, Pennsylvania
- Regional headquarters and shared service centers in Sao Paulo, Brazil; Shanghai, China; Middlebury, Connecticut; and Manchester, United Kingdom
Great Lakes Solutions, an Industry Leader

INDUSTRIES SERVED

- Electrical & Electronics
- Insulation & Furniture
- Automotive
- Fine Chemical/Pharmaceutical
- Energy: Oilfield & Mercury Control
- Fumigation
- Biocides
- Automotive Tires

KEY BUSINESSES

- Flame Retardants
- Brominated Performance Products

KEY GROWTH DRIVERS

- Mercury control
- Greener innovation
- Rapid growth in electronics
- Flame retarded energy efficient thermal insulation
- Increased global fire safety standards

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Trade Association Membership

- Chemtura is proud to be a member of:
  - Bromine Science and Environmental Forum
    - Working in Europe, Canada, China, Japan, and India
  - North American Flame Retardant Alliance
  - European Flame Retardants Association
  - Flame Retardant Chemicals Association of Japan
  - China Flame Retardant Society
  - ABICHAMA, Brazil
  - International Antimony Association (i2a)

- Communicating the essential role of flame retardants in fire safety
- Contributing our expertise to fire safety standards development
- Advocating for chemical management policies to be based on sound, scientific risk assessments

Members companies of these organizations represent the world's largest producers of both halogenated and non-halogen flame retardants
Greener Innovation

How Do We Move Towards Environmentally Friendly, Sustainable FR Solutions?

Chemtura is applying a “Greener is Better” philosophy...
Greener FR Design Strategy

- Greener Alternatives That
  - Achieve targeted fire safety standards
  - Meet or exceed baseline performance and manufacturability
  - Are cost effective based on total system cost
  - Minimize transition costs

- Strive for zero environmental release
  - VECAP to prevent release from manufacture to fabrication
  - Durable & recyclable to allow low-risk rework and recycling

- Structures that are inherently
  - Not migratory
  - Not bioavailable
  - Not toxic
DecaBDE Phase-out

- US Phase-Out commitment, but global implications
- Primary phase out in U.S. completed by end of 2012
- EPA SNUR pending, but additional state-level restrictions being enacted
- Continued, ongoing development of alternate formulations
EMERALD INNOVATION™ 1000

VERSATILE, EFFICIENT, SUSTAINABLE FLAME RETARDANT SOLUTION FOR IGNITION RESISTANT HIPS AND POLYOLEFINS
EMERALD INNOVATION™ 1000

- The polymeric structure of Emerald Innovation™ 1000 makes it not readily bioavailable\(^1\), thus addressing the environmental concerns that threaten the sustainability of many current products.
- Emerald Innovation™ 1000 is an efficient, sustainable replacement for decabromodiphenyl oxide (DE-83R™) and decabromodiphenyl ethane (Firemaster® 2100R), providing comparable or better properties.
- The high bromine content of Emerald Innovation™ 1000 makes it more efficient than other alternatives.
- Emerald Innovation™ 1000 offers an excellent balance of physical properties, flammability performance and processability.
- Emerald Innovation™ 1000 cost-effectively provides UL-94 V-0 performance in HIPS and Polyolefin formulations.

1. 49 Federal Register 46066 (Nov. 11, 1984), 40 CFR 723.250

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**Emerald Innovation™ 1000 Typical Properties**

**Emerald Innovation™ 1000 is a polymeric brominated flame retardant designed for use in a broad spectrum of applications**

<table>
<thead>
<tr>
<th>Property</th>
<th>Emerald Innovation™ 1000</th>
</tr>
</thead>
<tbody>
<tr>
<td>Appearance</td>
<td>Off-white powder</td>
</tr>
<tr>
<td>Bromine, %</td>
<td>78</td>
</tr>
<tr>
<td>Average particle size, (µm)</td>
<td>5-6</td>
</tr>
<tr>
<td>5% wt loss, 0°C</td>
<td>410°C</td>
</tr>
<tr>
<td>(Thermogravimetric Analysis (@ 10 0C/min under N₂)</td>
<td></td>
</tr>
</tbody>
</table>

*High bromine content with excellent thermal stability*
**EMERALD INNOVATION™ 1000 PERFORMANCE COMPARISON IN HIPS**

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**Excellent balance of impact, melt flow and thermal properties**

All formulations contain 4.0% antimony trioxide  
*afterglow*

---

### Excellent impact performance
- Efficiency at equal or lower load levels
- Equivalent Vicat softening performance
- Melt flow similar to DE-83R™, superior to Firemaster® 2100R

---

<table>
<thead>
<tr>
<th></th>
<th>Emerald Innovation 1000</th>
<th>FR-1</th>
<th>FR-2</th>
<th>FR-3</th>
</tr>
</thead>
<tbody>
<tr>
<td>FR Load, %</td>
<td>12.0</td>
<td>12.0</td>
<td>12.0</td>
<td>14.9</td>
</tr>
<tr>
<td>UL-94 @ 1.6 mm</td>
<td>V-0</td>
<td>V-0</td>
<td>V-0</td>
<td>V-1*</td>
</tr>
<tr>
<td>Notched Izod Impact, J/m</td>
<td>151.7</td>
<td>123.9</td>
<td>101.5</td>
<td>130.8</td>
</tr>
<tr>
<td>Gardner Impact, J</td>
<td>6.9</td>
<td>1.5</td>
<td>1.5</td>
<td>4.3</td>
</tr>
<tr>
<td>MFI, g/10min, 200 ºC/5 kg</td>
<td>11.9</td>
<td>10.9</td>
<td>8.7</td>
<td>15.3</td>
</tr>
<tr>
<td>Vicat Softening Point, ºC</td>
<td>99.1</td>
<td>96.3</td>
<td>98.2</td>
<td>96.0</td>
</tr>
</tbody>
</table>

---

All formulations contain 4.0% antimony trioxide  
*afterglow*
The higher impact strength achieved with Emerald Innovation™ 1000 provides an opportunity to reduce impact modifier loading, and thus reduced formulation cost.
Implications for Plastics Producers

- Reformulation of DecaBDE based products with an alternative
  - Select an FR that provide equivalent performance, efficiency, and will be sustainable long term
  - Reformulate to match performance requirements
- Performance Validations
  - Internal... Customers... Customers’ Customers
- Decide on approach for material designation, i.e. product name
  - New product designation
  - Maintain same product designation
- Notify listing agencies, e.g. UL*, and complete recertification program

Maintaining the same product designation is often an advantage. Defined by UL as a Polymer Variation, specific rules apply.

*UL is a trademark of UL LLC
UL* Safety Standards for Polymeric Materials

- **UL 746A Polymeric Materials – Short Term Property Evaluations**
  - Includes mechanical properties, electrical properties, distortion under load, resistance to ignition, dimensional stability, chemical resistance, polymer identification tests

- **UL 746B Polymeric Materials – Long Term Property Evaluations**
  - Determination of Relative Thermal Index

- **UL 746C** Polymeric Materials - Use in Electrical Equipment Evaluations

- **UL 746D** - Standard for Polymeric Materials - Fabricated Parts

- **UL 746E** - Standard for Polymeric Materials - Industrial Laminates, Filament Wound Tubing, Vulcanized Fibre, and Materials Used In Printed-Wiring Boards

- **UL 746F** - Standard for Polymeric Materials - Flexible Dielectric Film Materials for Use in Printed-Wiring Boards and Flexible Materials Interconnect Constructions

- **UL 94 Tests for Flammability of Plastic Materials for Parts in Devices and Appliances**

*Standards applicable to the evaluation of changes in FR polymer formulations are primarily UL 746A, UL 746B, and UL 94

*UL is a trademark of UL LLC*
Testing Requirements for Polymer Variations


- Addition, deletion or replacement of a flame retardant requires:
  - Full side-by-side testing
  - UL 94 flame testing at min and max thickness at all flame ratings assigned to the original material formulation
  - UL 746A short term properties, High Current Arc Ignition (HAI), Comparative Tracking Index (CTI), Izod Impact (II), Heat Distortion Temperature (HDT), and Tensile Strength (TS)
  - UL 746B Long Term Thermal Aging only for materials with elevated RTI values based on LTTA testing
Online UL Tool to Determine Required Testing

Get Started at: http://data.ul.com/formula/polyvar1.htm

Note: This website is a guide only and UL 746A shall be referenced for the most up to date and correct information.
### Step 2: Formulation Variations
Please check any ingredients you will be altering.
(click on any ingredient for more information)

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>No Change</th>
<th>Addition</th>
<th>Deletion</th>
<th>Change in Level</th>
<th>Replacement</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid Acceptor (Scavenger)</td>
<td>nc</td>
<td></td>
<td>D</td>
<td>C</td>
<td>R</td>
</tr>
<tr>
<td>Antimicrobial</td>
<td>nc</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Antioxidant</td>
<td>nc</td>
<td></td>
<td>D</td>
<td>C</td>
<td>R</td>
</tr>
<tr>
<td>Antistatic Agent</td>
<td>nc</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Blowing Agent</td>
<td>nc</td>
<td></td>
<td>D</td>
<td>C</td>
<td>R</td>
</tr>
<tr>
<td>Catalyst</td>
<td>nc</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Colorant/Pigment (Inorganic)</td>
<td>nc</td>
<td></td>
<td>D</td>
<td>C</td>
<td>R</td>
</tr>
<tr>
<td>Colorant/Pigment (Organic)</td>
<td>nc</td>
<td></td>
<td>D</td>
<td>C</td>
<td>R</td>
</tr>
<tr>
<td>Compatibilizer</td>
<td>nc</td>
<td></td>
<td>D</td>
<td>C</td>
<td>R</td>
</tr>
<tr>
<td>Conductive Material</td>
<td>nc</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Copolymer</td>
<td>nc</td>
<td></td>
<td>D</td>
<td>C</td>
<td>R</td>
</tr>
<tr>
<td>Corrosion Inhibitor</td>
<td>nc</td>
<td></td>
<td>D</td>
<td>C</td>
<td>R</td>
</tr>
<tr>
<td>Coupling Agent</td>
<td>nc</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Crosslinking Agent</td>
<td>nc</td>
<td></td>
<td>D</td>
<td>C</td>
<td>R</td>
</tr>
<tr>
<td>Curing Agent</td>
<td>nc</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Drip Inhibitor</td>
<td>nc</td>
<td></td>
<td>D</td>
<td>C</td>
<td>R</td>
</tr>
<tr>
<td>Filler/Reinforcement</td>
<td>nc</td>
<td></td>
<td>D</td>
<td>C</td>
<td>R</td>
</tr>
<tr>
<td>Flame Retardant</td>
<td>nc</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Halogen Scavenger</td>
<td>nc</td>
<td></td>
<td>D</td>
<td>C</td>
<td>R</td>
</tr>
<tr>
<td>Heat Stabilizer</td>
<td>nc</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hydrolytic Stabilizer</td>
<td>nc</td>
<td></td>
<td>D</td>
<td>C</td>
<td>R</td>
</tr>
<tr>
<td>Impact Modifier</td>
<td>nc</td>
<td></td>
<td>D</td>
<td>C</td>
<td>R</td>
</tr>
</tbody>
</table>
Online UL Tool to Determine Required Testing

Step 3: Specific Variation Questions
Please answer the specific questions concerning the changes you are making to each ingredient
(if there are no questions, please click the continue button)

Continue  Reset

Required Testing

Based on the polymer variations you have selected, you must perform the test program indicated below. Unless otherwise stated below, successful completion of this test program will allow you to keep the same material designation.

Full Testing Required for UL 94, UL 746A: In order to keep the same material designation, side by side UL 94 flammability tests, identification tests and a full set of UL 746A performance characteristics are needed.
UL 746B: Long term Heat Aging (LTHA) is required.

Summary of Your Selections: You want to Keep the Same Material Designation

The Original Material:
- has been assigned UL 94 flammability ratings
- has been assigned UL 746A performance profile indexing
- has been assigned UL 746B elevated temperature levels
- has been evaluated for UL 746C ultraviolet light and water immersion

Formulation Variations:
Flame Retardant: Replacement

Full Testing Required for UL 94, UL 746: In order to keep the same material designation, side by side UL 94 flammability tests, identification test and a full set of UL 746A performance characteristics are needed.

Without consultation on a reduced testing program, a testing program on a portfolio of a dozen products requires full testing of twenty-four formulations!
Requirements to Be Considered Comparable

Per UL 746A grade designations may be maintained if:

1. The individual test results are within 10% of the test results obtained for the original material;

2. The UL 94 flammability ratings are the same; and

3. The UL 746B RTI values based on LTTA testing, if applicable, comply with Section 19 of UL 746B for related materials.
Reduced Testing Program Concept

- In an effort to establish a foundation for discussions with UL on a testing program, Great Lakes Solutions proposed a program to conduct a preliminary reduced testing program.

- The program would include testing generic HIPS and ABS formulations to demonstrate the performance equivalence of Emerald Innovation™ 1000 to DE-83R™ and Firemaster® 2100R.

- Once completed, a plastic producer would be able to refer to this program as a basis for their own discussions on a reduced testing program during the transition of a sub-group of products.

- Testing programs have been completed for:
  - Replacement of DE-83R™ with Emerald Innovation™ 1000 in HIPS
  - Replacement of DE-83R™ with Emerald Innovation™ 1000 in ABS
  - Replacement of Firemaster® 2100R with Emerald Innovation™ 1000 in ABS
UL 746A Tests For Polymer Identification
Thermogravimetric Analysis (TGA) of FR-HIPS

TGA shows only minor differences between FRs

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Differential Scanning Calorimetry (DSC) of FR-HIPS

DSC shows only minor differences between FRs
FT-Infrared Spectroscopy of FR-HIPS

Emerald Innovation™ 1000
In HIPS

DE-83R™
In HIPS

Firemaster® 2100R
In HIPS

FTIR fingerprint region provide UL tool to differentiate FR formulations

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UL 746A Short Term Property Testing
## Emerald Innovation™ 1000 vs DE-83R™ in FR-HIPS

<table>
<thead>
<tr>
<th>Property</th>
<th>Emerald Innovation 1000</th>
<th>DE-83R</th>
<th>% Change</th>
</tr>
</thead>
<tbody>
<tr>
<td>UL-94V 1.5mm</td>
<td>V-0</td>
<td>V-0</td>
<td>n/a</td>
</tr>
<tr>
<td>UL-94V 3.0mm</td>
<td>V-0</td>
<td>V-0</td>
<td>n/a</td>
</tr>
<tr>
<td>Tensile Strength, MPa</td>
<td>21.0</td>
<td>19.9</td>
<td>5.4%</td>
</tr>
<tr>
<td>Izod impact Strength, J/m</td>
<td>146.3</td>
<td>148.6</td>
<td>1.6%</td>
</tr>
<tr>
<td>Vicat, °C</td>
<td>98.2</td>
<td>94.6</td>
<td>3.7%</td>
</tr>
<tr>
<td>Hot Wire Ignition, (sec)</td>
<td>10.2</td>
<td>10.0</td>
<td>1.4%</td>
</tr>
<tr>
<td>Hot Wire Ignition, PLC</td>
<td>4</td>
<td>4</td>
<td>n/a</td>
</tr>
<tr>
<td>High Current Arc Ignition, (arcs)</td>
<td></td>
<td></td>
<td>See note</td>
</tr>
<tr>
<td>High Current Arc Ignition PLC</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Comparative Tracking Index (Volts)</td>
<td>388</td>
<td>422</td>
<td>8.8%</td>
</tr>
<tr>
<td>Comparative Tracking Index  PLC</td>
<td>2*</td>
<td>1</td>
<td>n/a</td>
</tr>
</tbody>
</table>

Note: HAI requirement waived within the scope of the evaluation due to high observed variation on controls across multiple laboratories.

*Data within 10% but different PLC (Performance Level Category)*

Note: UL LLC neither selected the samples nor determined whether the samples were representative of production samples. The test results apply only to the actual samples tested.

All properties meet criteria for equal or improved performance.
# Emerald Innovation™ 1000 vs DE-83R™ in FR-ABS

<table>
<thead>
<tr>
<th>Property</th>
<th>Emerald Innovation 1000</th>
<th>DE-83R</th>
<th>% Change</th>
</tr>
</thead>
<tbody>
<tr>
<td>UL-94V 1.5mm</td>
<td>V-0</td>
<td>V-0</td>
<td>n/a</td>
</tr>
<tr>
<td>UL-94V 3.0mm</td>
<td>V-0</td>
<td>V-0</td>
<td>n/a</td>
</tr>
<tr>
<td>Tensile Strength, Mpa</td>
<td>44.3</td>
<td>44.1</td>
<td>0.3%</td>
</tr>
<tr>
<td>Izod impact Strength, J/m</td>
<td>94.8</td>
<td>72.1</td>
<td>24%</td>
</tr>
<tr>
<td>Vicat, °C</td>
<td>104.2</td>
<td>103.3</td>
<td>0.9%</td>
</tr>
<tr>
<td>Hot Wire Ignition, (sec)</td>
<td>23.3</td>
<td>13.9</td>
<td>40%</td>
</tr>
<tr>
<td>Hot Wire Ignition, PLC</td>
<td>3</td>
<td>4</td>
<td>n/a</td>
</tr>
<tr>
<td>High Current Arc Ignition, (arcs)</td>
<td>86.6</td>
<td>86.6</td>
<td>0.0%</td>
</tr>
<tr>
<td>High Current Arc Ignition PLC</td>
<td>1</td>
<td>1</td>
<td>0.0%</td>
</tr>
<tr>
<td>Comparative Tracking Index (Volts)</td>
<td>389</td>
<td>393</td>
<td>1.0%</td>
</tr>
<tr>
<td>Comparative Tracking Index PLC</td>
<td>2*</td>
<td>2*</td>
<td>n/a</td>
</tr>
</tbody>
</table>

*Data within 10% but different PLC (Performance Level Category)*

*Note: UL LLC neither selected the samples nor determined whether the samples were representative of production samples. The test results apply only to the actual samples tested.*

All properties meet criteria for equal or improved performance.
## Emerald Innovation™ 1000 vs Firemaster® 2100R in FR-ABS

<table>
<thead>
<tr>
<th>Property</th>
<th>Emerald Innovation™ 1000</th>
<th>Firemaster® 2100R</th>
<th>% Change</th>
</tr>
</thead>
<tbody>
<tr>
<td>UL-94V 1.5mm</td>
<td>V-0</td>
<td>V-0</td>
<td>n/a</td>
</tr>
<tr>
<td>UL-94V 3.0mm</td>
<td>V-0</td>
<td>V-0</td>
<td>n/a</td>
</tr>
<tr>
<td>Tensile Strength, Mpa</td>
<td>44.3</td>
<td>42.9</td>
<td>3.1%</td>
</tr>
<tr>
<td>Izod impact Strength, J/m</td>
<td>94.8</td>
<td>58.0</td>
<td>38%</td>
</tr>
<tr>
<td>Vicat, °C</td>
<td>104.2</td>
<td>104.2</td>
<td>0.0%</td>
</tr>
<tr>
<td>Hot Wire Ignition, (sec)</td>
<td>23.3</td>
<td>15.3</td>
<td>34%</td>
</tr>
<tr>
<td>Hot Wire Ignition, PLC</td>
<td>3</td>
<td>3</td>
<td>n/a</td>
</tr>
<tr>
<td>High Current Arc Ignition, (arcs)</td>
<td>86.6</td>
<td>86</td>
<td>0.7%</td>
</tr>
<tr>
<td>High Current Arc Ignition PLC</td>
<td>1</td>
<td>1</td>
<td>0.0%</td>
</tr>
<tr>
<td>Comparative Tracking Index (Volts)</td>
<td>389</td>
<td>419</td>
<td>7.7%</td>
</tr>
<tr>
<td>Comparative Tracking Index PLC</td>
<td>2</td>
<td>1</td>
<td>n/a</td>
</tr>
</tbody>
</table>

*Data within 10% but different PLC (Performance Level Category)*

*Note*: UL LLC neither selected the samples nor determined whether the samples were representative of production samples. The test results apply only to the actual samples tested.

---

**All properties meet criteria for equal or improved performance.**
Reduced Testing Program for HIPS: Project 12CA31391

- Great Lakes DE-83R™ may be replaced with Emerald Innovation™ 1000 in combination with currently UL Recognized HIPS resins ONLY, following the test program outlined below:
  - Conduct Program Code C and D in UL 746A Table 9.2 on at least one key grade, and no more than 10% of those in a “common” sub-generic group using the DE-83R and the Emerald Innovation™ 1000.
    - Code D required if thermal aging was originally conducted on the grades tested.
  - The percentage of Emerald Innovation™ 1000 in the formulation need not be identical to the percent age of DE-83R in the formulation of the key grades chosen for testing.
  - If the test results are comparable within +/-10% between the DE-83R and Emerald Innovation™ 1000, that entire sub-group would be considered comparable.
    - New identification scans (IR, DSC and TGA) would need to be established and the model designation can remain the same.
  - If the results are not comparable within +/-10%, a new designation would be required for every material grade, and testing may be required for the specific material grade.
    - That new grade would be Recognized with a new model designation and with the ratings received through testing using the Emerald Innovation™ 1000.

Reduced Testing Program for ABS: Project 11CA32487

- Great Lakes DE-83R™ or Firemaster® 2100R may be replaced with Emerald Innovation™ 1000 in combination with currently UL recognized ABS resins ONLY, following the test program outlined below:
  - Conduct Program Code C and D in UL 746A Table 9.2\(^1\) on at least one key grade, and no more than 10% of those in a “common” sub-generic group using the DE-83R or Firemaster® 2100R and the Emerald Innovation™ 1000.
    - Code D required if thermal aging was originally conducted on the grades tested.
  - The percentage of Emerald Innovation™ 1000 in the formulation need not be identical to the original FR loading in the formulation of the key grades chosen for testing.
  - If the test results are comparable within +/-10% between the old and new grades, that entire sub-group would be considered comparable.
    - New identification scans (IR, DSC and TGA) would need to be established and the model designation can remain the same.
  - If the results are not comparable within +/-10%, a new designation would be required for every material grade, and testing may be required for the specific material grade.
    - That new grade would be Recognized with a new model designation and with the ratings received through testing using the Emerald Innovation™ 1000.

\(^1\) Refers to UL 746A, Sixth Edition, September 6, 2012
The New Work Flow

- **Traditional**

  - New FR Grade Formulation Development
  - Screening Testing
  - Consult with UL to Define Testing Plan
  - Run Test Plan
  - Recognition

- **With Pre-defined Testing Plan**

  - New FR Grade Formulation Development
  - Screening Testing
  - Refer to Great Lakes Test Program
  - Run Test Plan
  - Recognition
ACKNOWLEDGEMENTS AND THANKS

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- UL LLC
  
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- Applied Market Information Limited LLC

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