



The Role of Flame Retardants in Reducing the Rate of Fire Spread

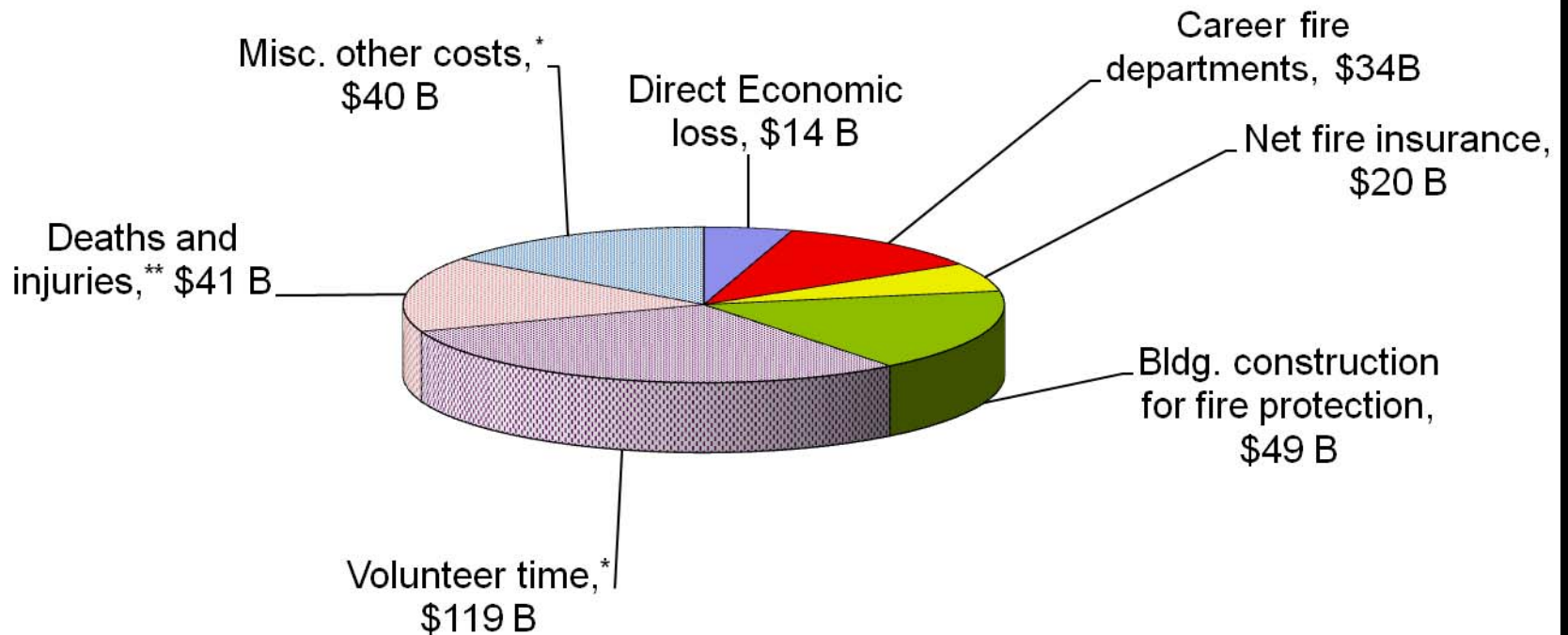
Jeffrey W. Gilman
Leader, Materials Flammability Group
NIST

September 30, 2009

A one-day meeting on "Fire Retardants and their Potential Impact on Fire Fighter Health"

What is the problem ?

Year	Reported Fires	Civilian Deaths	Civilian Injuries	Firefighter Deaths	Firefighter Injuries	Core Cost of Fire (\$ B In 2006 dollars)*
1980	3,000,000	6,505	30,200	138	98,070	\$69
1990	2,250,000	5,195	28,600	108	100,300	\$80
2000	1,750,000	4,045	22,350	103	84,550	\$95



Annual Fire Losses from Home Structure Fires from 2003 through 2006, Grouped by First Item Ignited

First Item Ignited	Fires	Deaths	Injuries	Property Damage (\$ B)
Upholstered furniture	7,400	590	900	0.4
Mattress/bedding	11,200	380	1,390	0.4
Thermoplastics ^A	29,400	280	1,160	0.7
Structural member, component, insulation	32,500	240	620	1.3
Other furniture or utensils	6,000	170	500	0.2
Confined cooking fire/materials ^B	134,900	130	3,670	0.3
Interior wall covering	8,200	120	340	0.3
Subtotal of Above Categories	228,100	1,730	7,520	3.6
Totals ^C	378,600	2,850	13,090	6.1

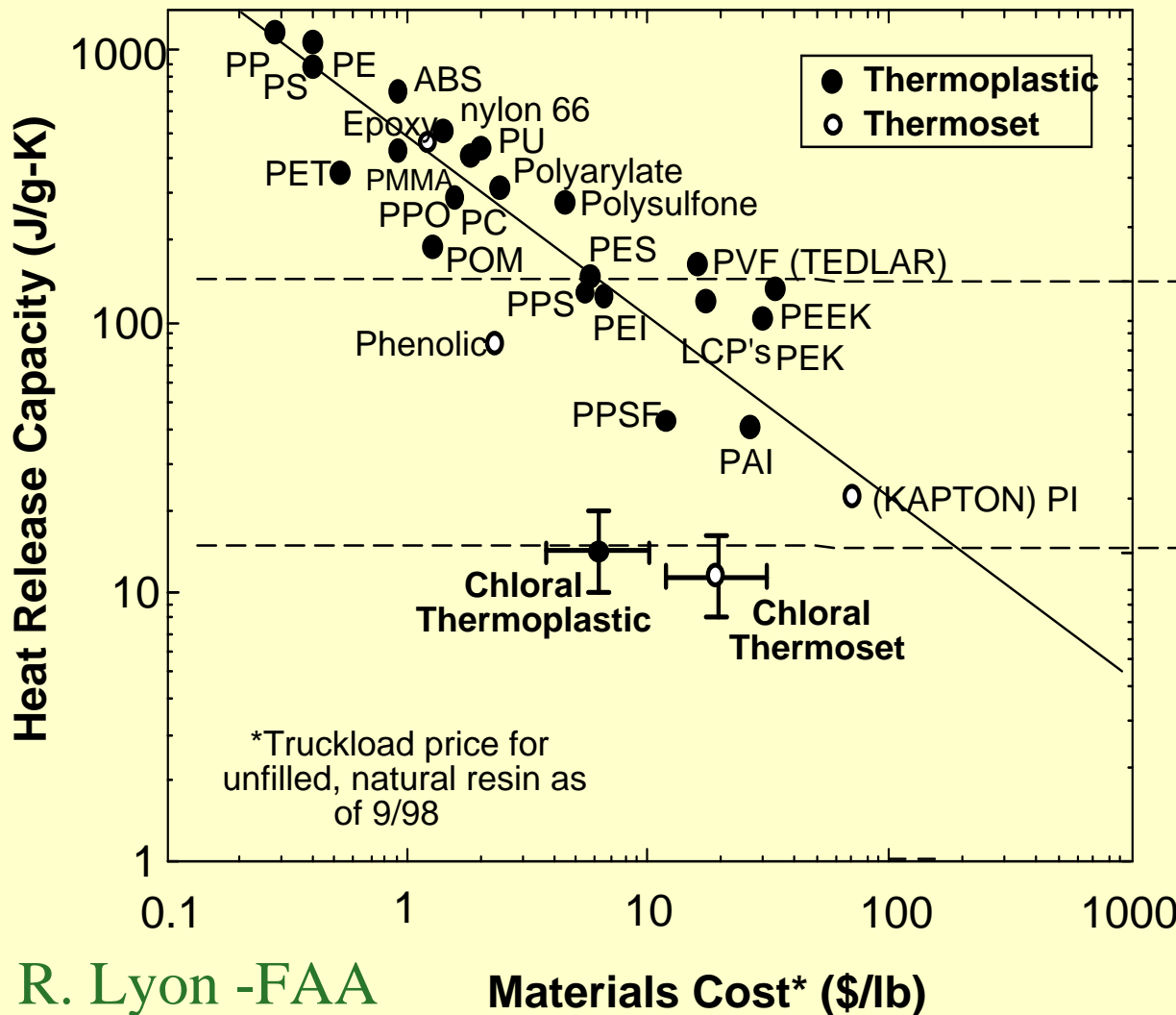
A. It is assumed that the overriding reason that the items (in the categories for curtains, wire insulation, carpeting, and appliance housings) first ignited was due to thermoplastic content.

B. Cooking could also lead to ignition of cabinetry and interior wall coverings (not included here).

C: Includes results for all sources, not just those listed here; does not include unknown sources.

Current:
 25% of injuries and property damage, 40 % of deaths are due to burning of polymer based products
Future:
 use of low cost, bio-based, highly flammable polymers is increasing in all product classes

Polymer Flammability vs Cost



Markets

World
Retardant
Chemical
Market :
\$3B/yr

World
Flame
Retarded
Product
Market:
\$100B/yr

R. Lyon -FAA

GENERAL FLAME RETARDANT APPROACHES FOR POLYMERS

I- Gas Phase Flame Retardants

- Reduce Heat of Combustion (ΔH_c) resulting in incomplete combustion.
- Inherent Drawbacks: Negative Public Perception!

II- Endothermic Flame Retardants

- Function in Gas Phase and Condensed Phase
- Via endothermic release of H_2O , polymer cooled and gas phase diluted.
- Inherent Drawback: High loadings (30-50%) degrade mechanical properties.

III- Char Forming Flame Retardants

- Operate in Condensed Phase
- Provides thermal insulation for underlying polymer and a mass transport barrier, preventing or delaying escape of fuel into the gas phase.
- Inherent Drawback: High loadings (20-50%) degrade mechanical properties.

Goal: develop cost effective, environmentally friendly approaches to reduce flammability and improve physical properties

NIST Multi-scale Flammability Comparison of FR and Non-FR Products

Goals

- To determine if FR products reduced the overall fire hazard relative to non-FR products
- to determine if bench-scale flammability measurement methods could enable validated screening of new FR approaches

NBS Special Publication 749

Fire Hazard Comparison of Fire-Retarded and Non-Fire-Retarded Products

Vytenis Babrauskas, Richard H. Harris, Jr., Richard G. Gann, Barbara C. Levin, Billy T. Lee, Richard D. Peacock, Maya Paabo, William Twilley, Margaret F. Yoklavich, and Helene M. Clark

Fire Measurement and Research Division
Center for Fire Research
National Bureau of Standards
Gaithersburg, MD 20899

Sponsored by:
Fire Retardant Chemicals Association
Lancaster, PA 17604

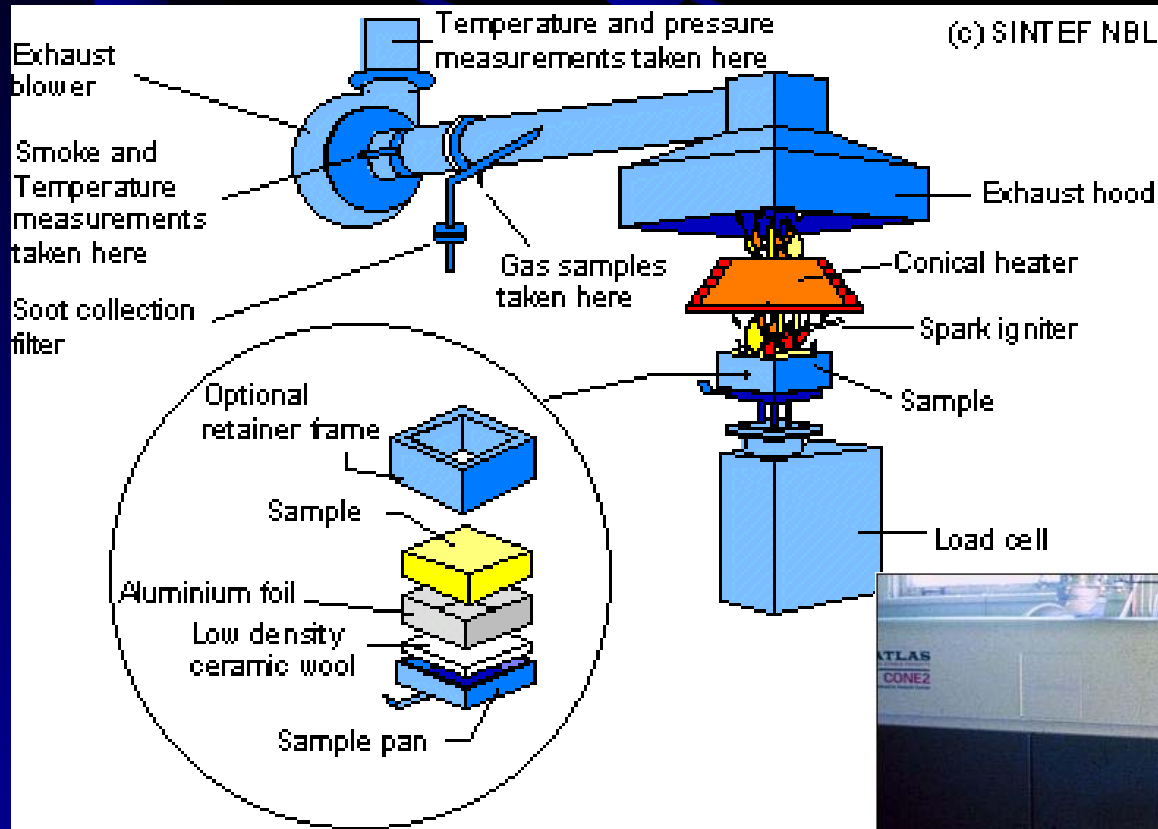


July 1988

U.S. Department of Commerce
C. William Verity, Secretary

National Bureau of Standards
Ernest Ambler, Director

CONE CALORIMETRY



- Oxygen consumption calorimetry



NIST Multi-scale Flammability Comparison of FR and Non-FR Products

Furniture Calorimeter

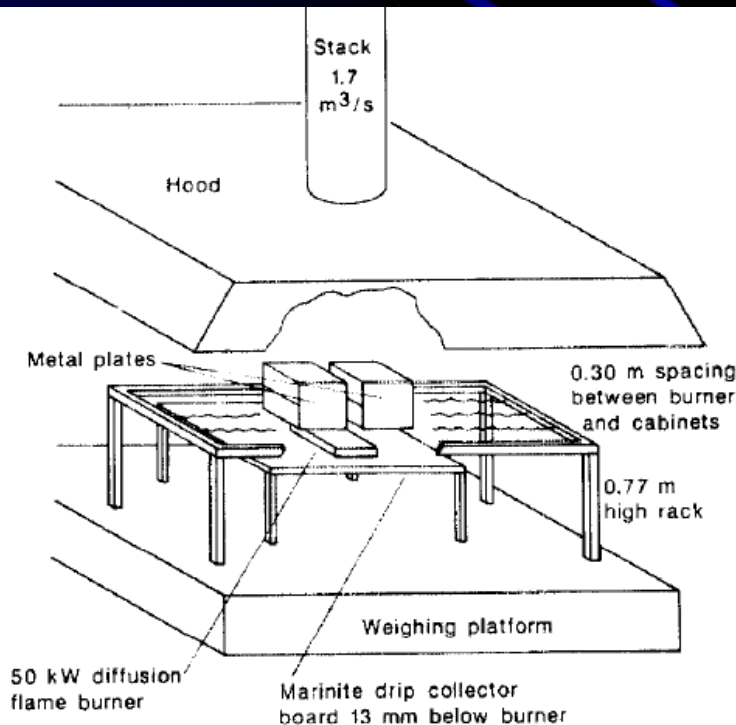


Figure 9. Furniture Calorimeter test of business machines and TV cabinets.

Business Machines

NBS Special Publication 749

*Fire Hazard Comparison of
Fire-Retarded and
Non-Fire-Retarded Products*

NIST Multi-scale Flammability Comparison of FR and Non-FR Products

Large Scale Test Room-Corridor-Room Fire using Large Calorimeter

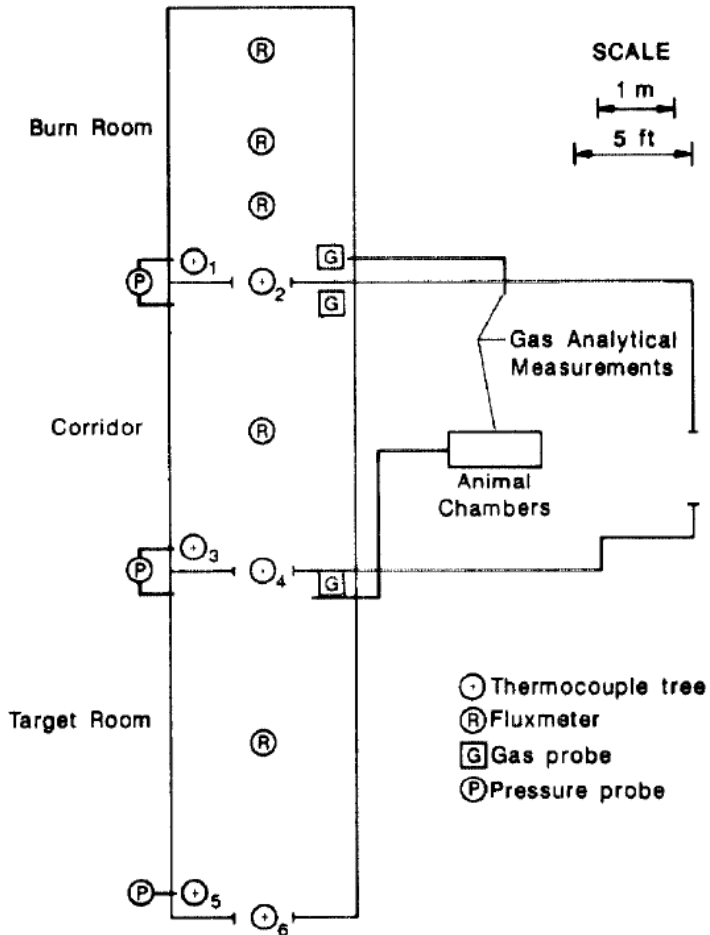


Figure 29. Plan view of large-scale test arrangement B.

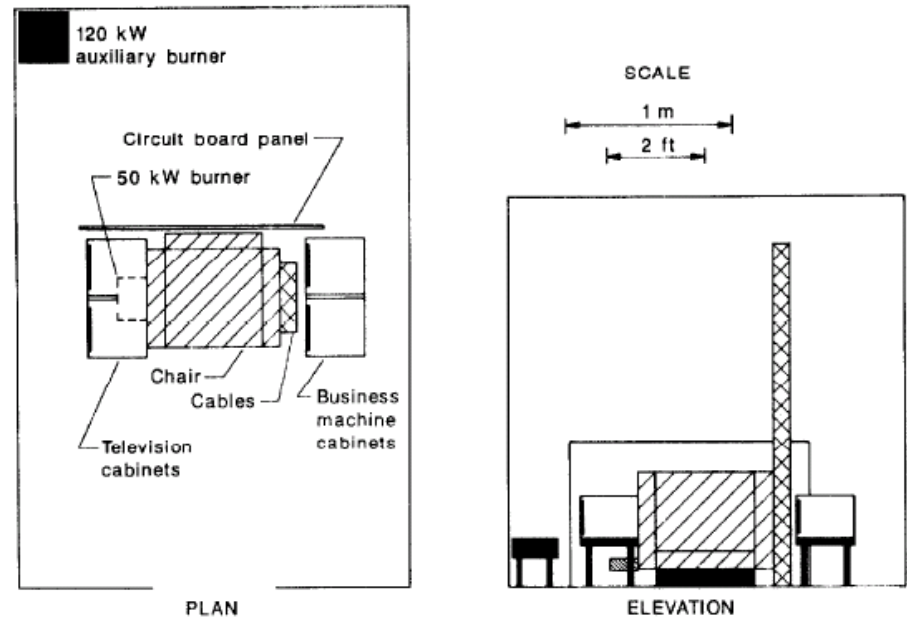


Figure 30. Arrangement B of test items in the burn room.

NIST Multi-scale Flammability Comparison of FR and Non-FR Products

Furniture Calorimeter

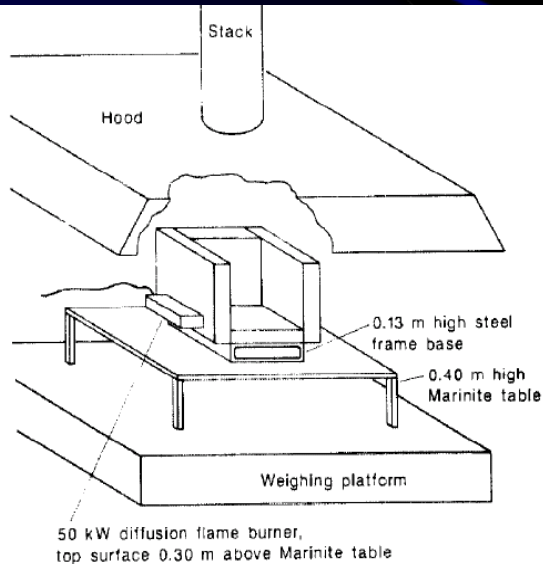


Figure 10. Furniture Calorimeter test of chairs.

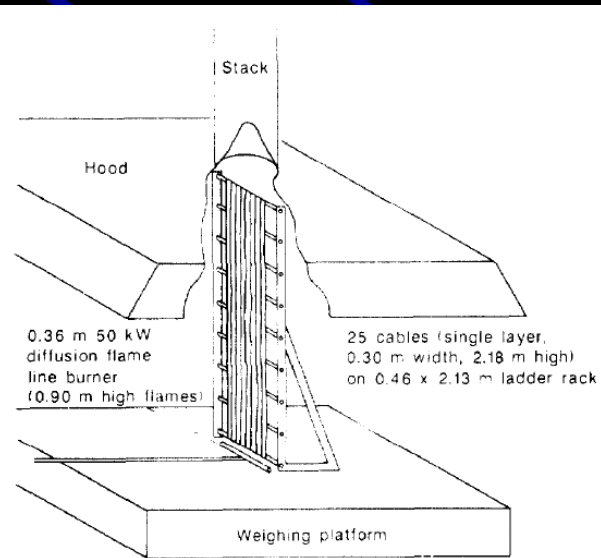


Figure 12. Furniture Calorimeter test of cables (vertical array).

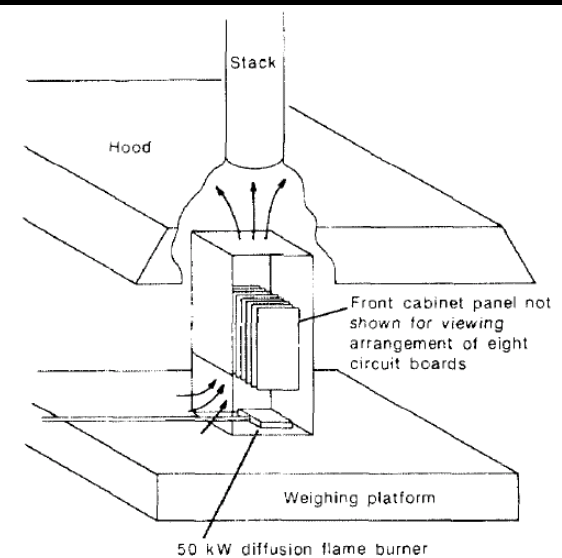


Figure 13. Furniture Calorimeter test of circuit boards.

PU-foam, Nylon
Chair Mock-up

EVA Cables

PE/Glass
Circuit Boards

High Impact Polystyrene TV housings, PPO Computer housings

NIST Multi-scale Flammability Comparison of FR and Non-FR Products



Fire Hazard

- Rate of Heat Release
- Smoke Obscuration
- Smoke Toxicity

NIST Multi-scale Flammability Comparison of FR and Non-FR Products

Goals

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- to determine if bench-scale flammability measurement methods could enable validated screening of new FR approaches

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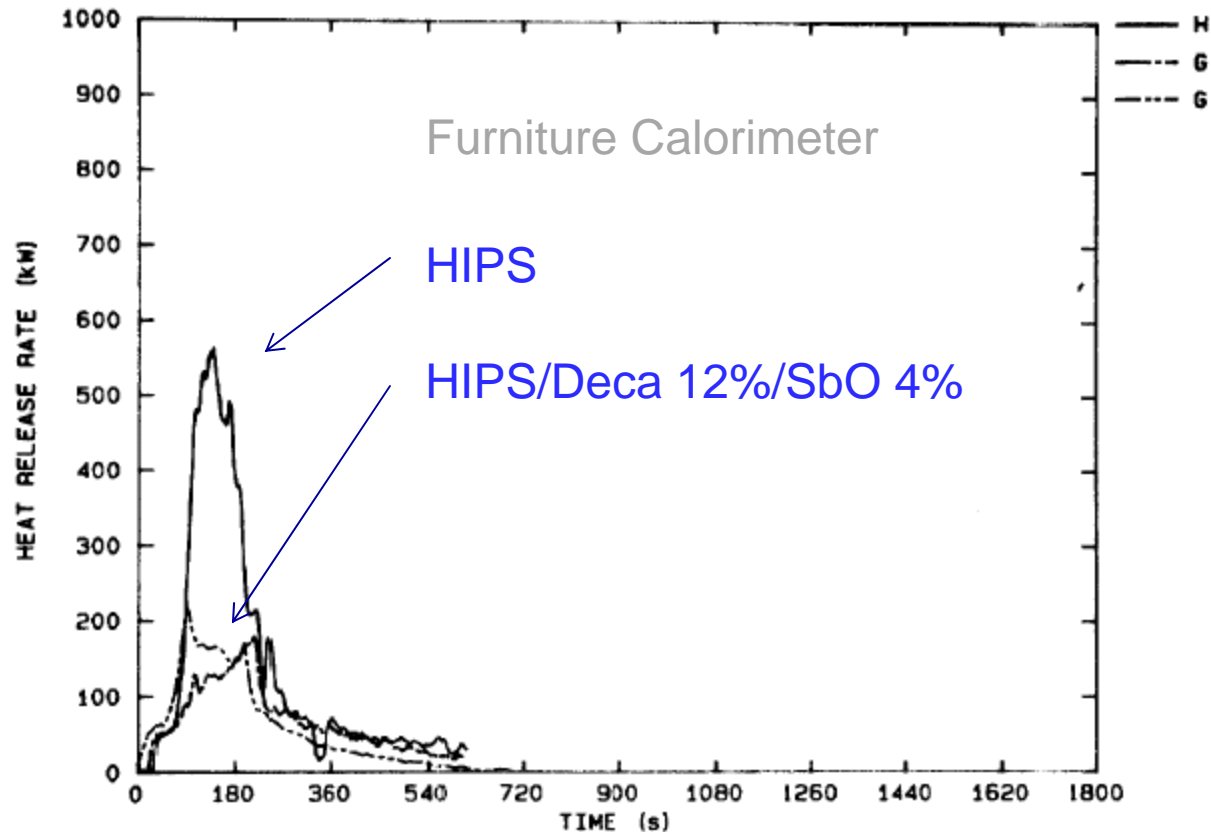
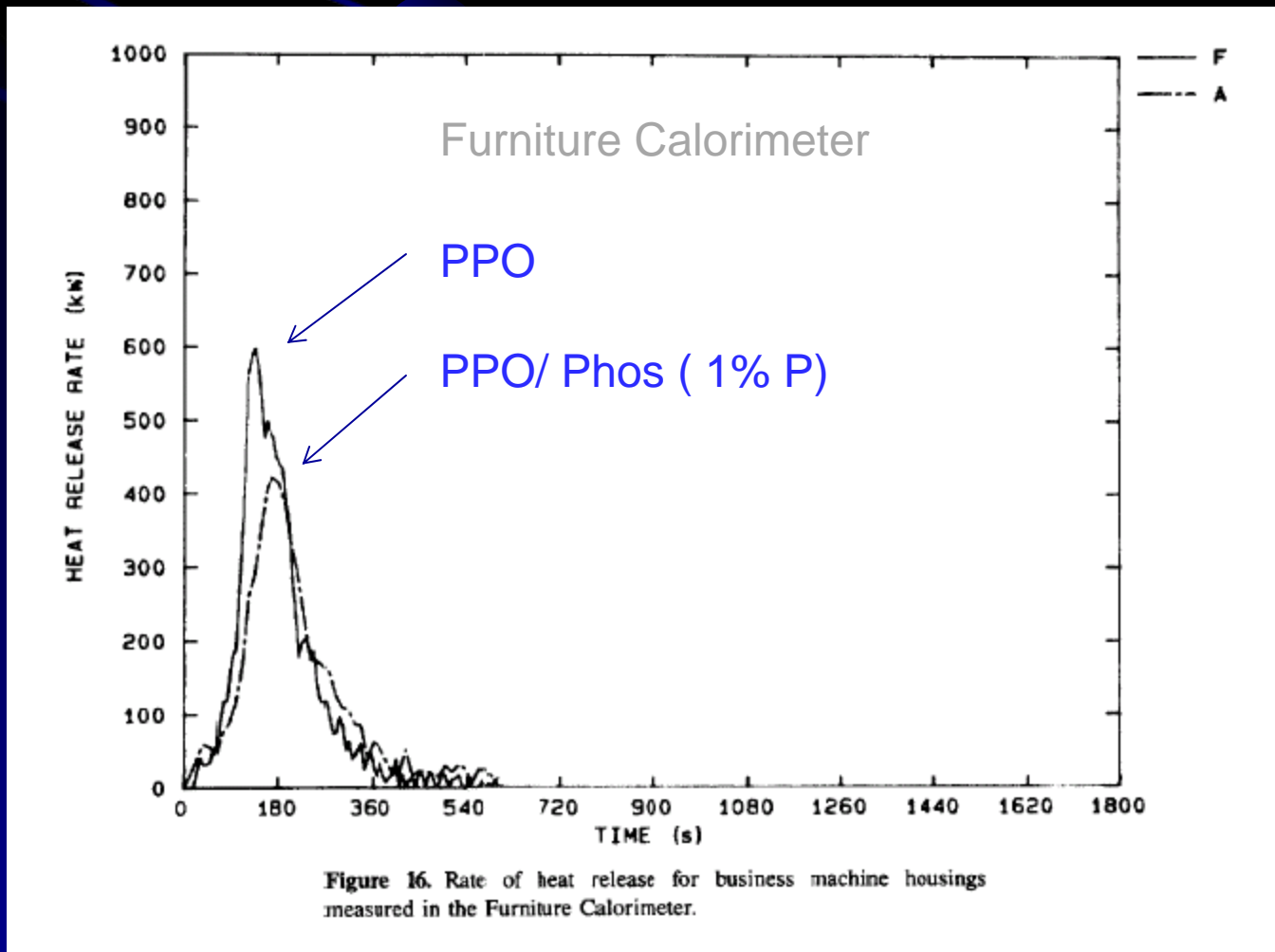


Figure 15. Rate of heat release for TV cabinets measured in the Furniture Calorimeter.

- Rate of Heat Release

NIST Multi-scale Flammability Comparison of FR and Non-FR Products



- Rate of Heat Release

NIST Multi-scale Flammability Comparison of FR and Non-FR Products

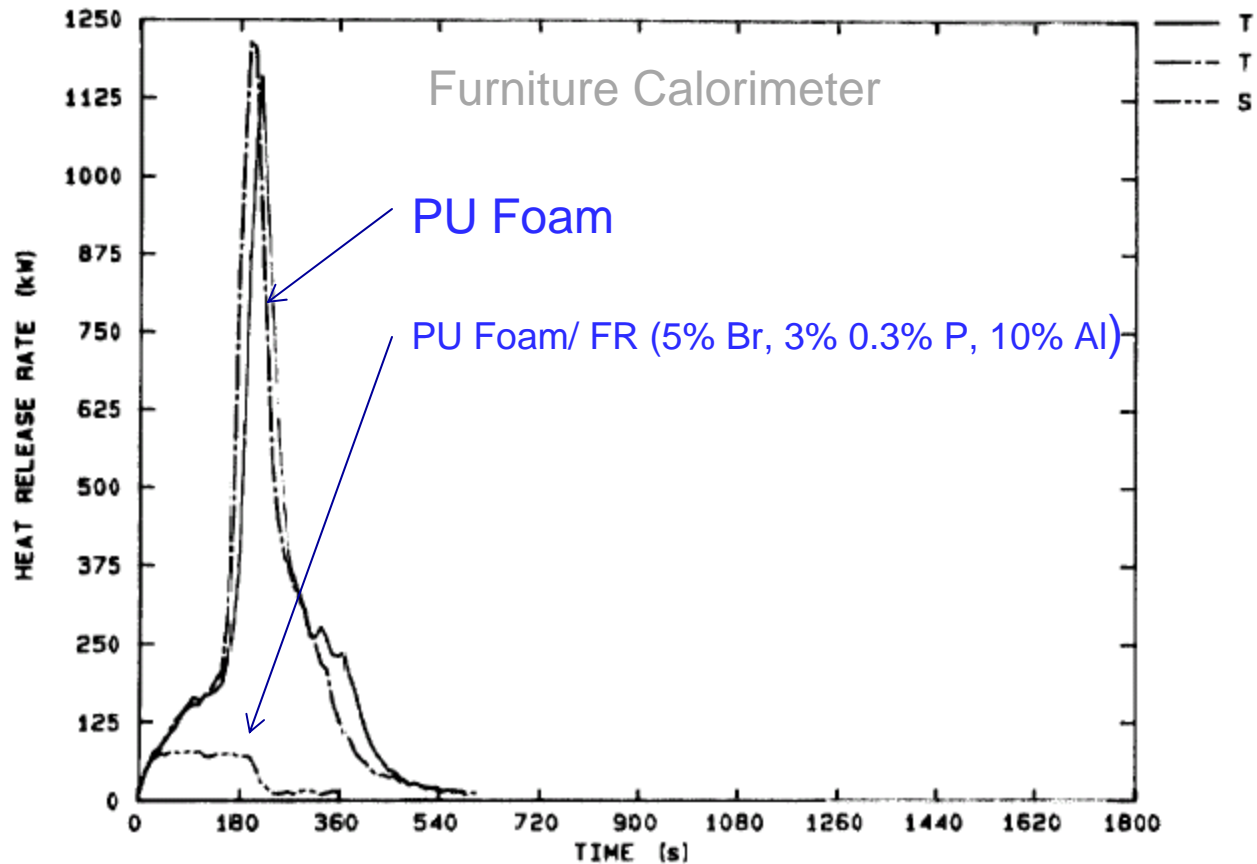


Figure 17. Rate of heat release for upholstered chairs measured in the Furniture Calorimeter.

- Rate of Heat Release

NIST Multi-scale Flammability Comparison of FR and Non-FR Products

Large Scale Test Room-Corridor-Room Fire using Large Calorimeter

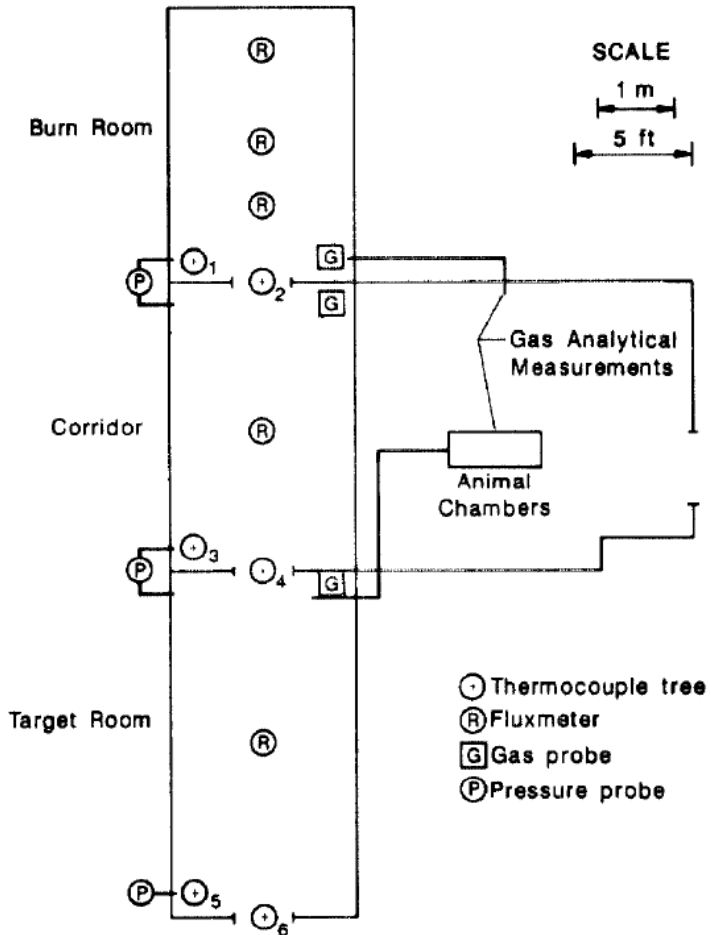


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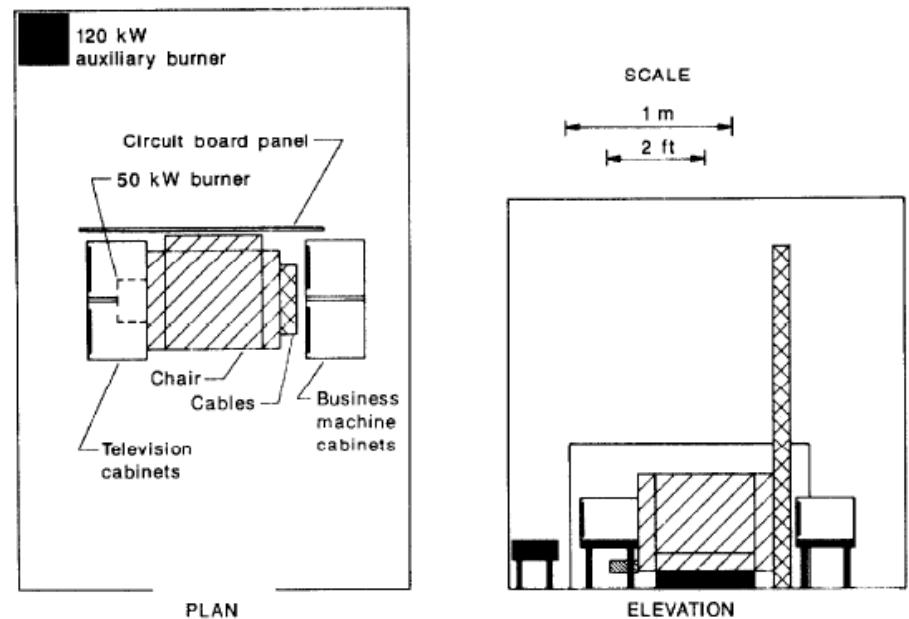


Figure 30. Arrangement B of test items in the burn room.

NIST Multi-scale Flammability Comparison of FR and Non-FR Products

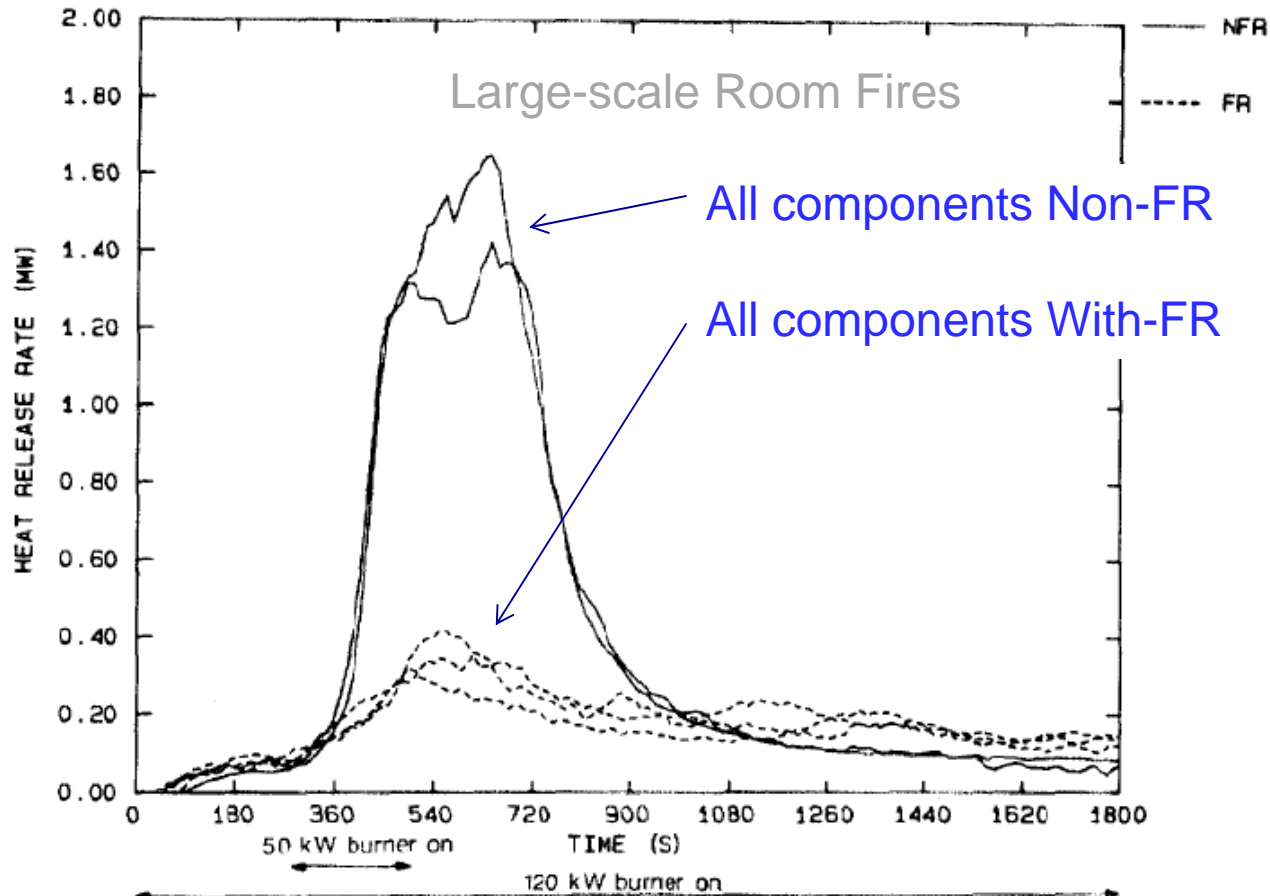


Figure 47. Heat release rates in the large-scale room/corridor/room tests with the auxiliary burner.

- Rate of Heat Release

NIST Multi-scale Flammability Comparison of FR and Non-FR Products

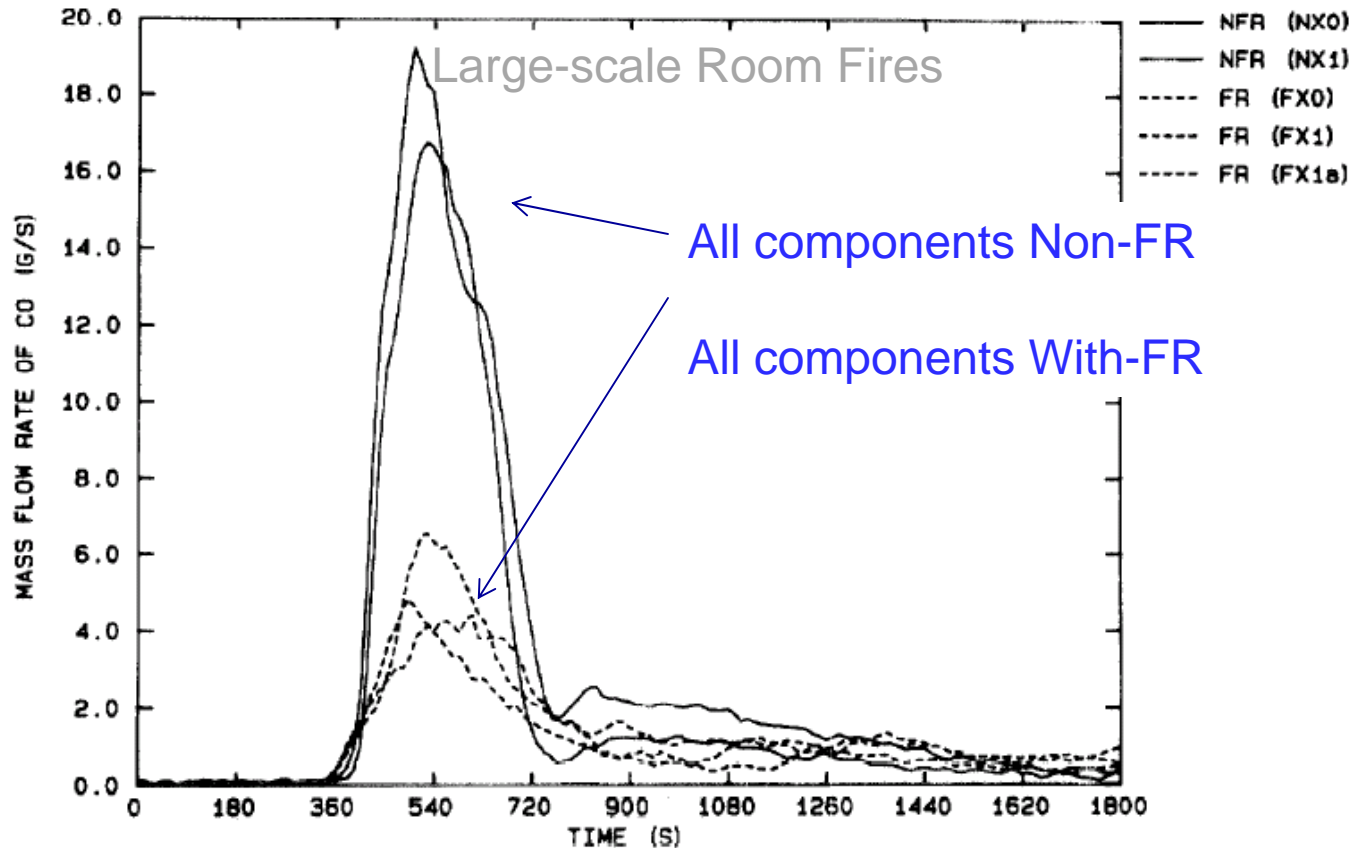


Figure 49. Mass flow rate of CO in the large-scale room/corridor/room tests with the auxiliary burner.

- CO generated in Room Fires

NIST Multi-scale Flammability Comparison of FR and Non-FR Products

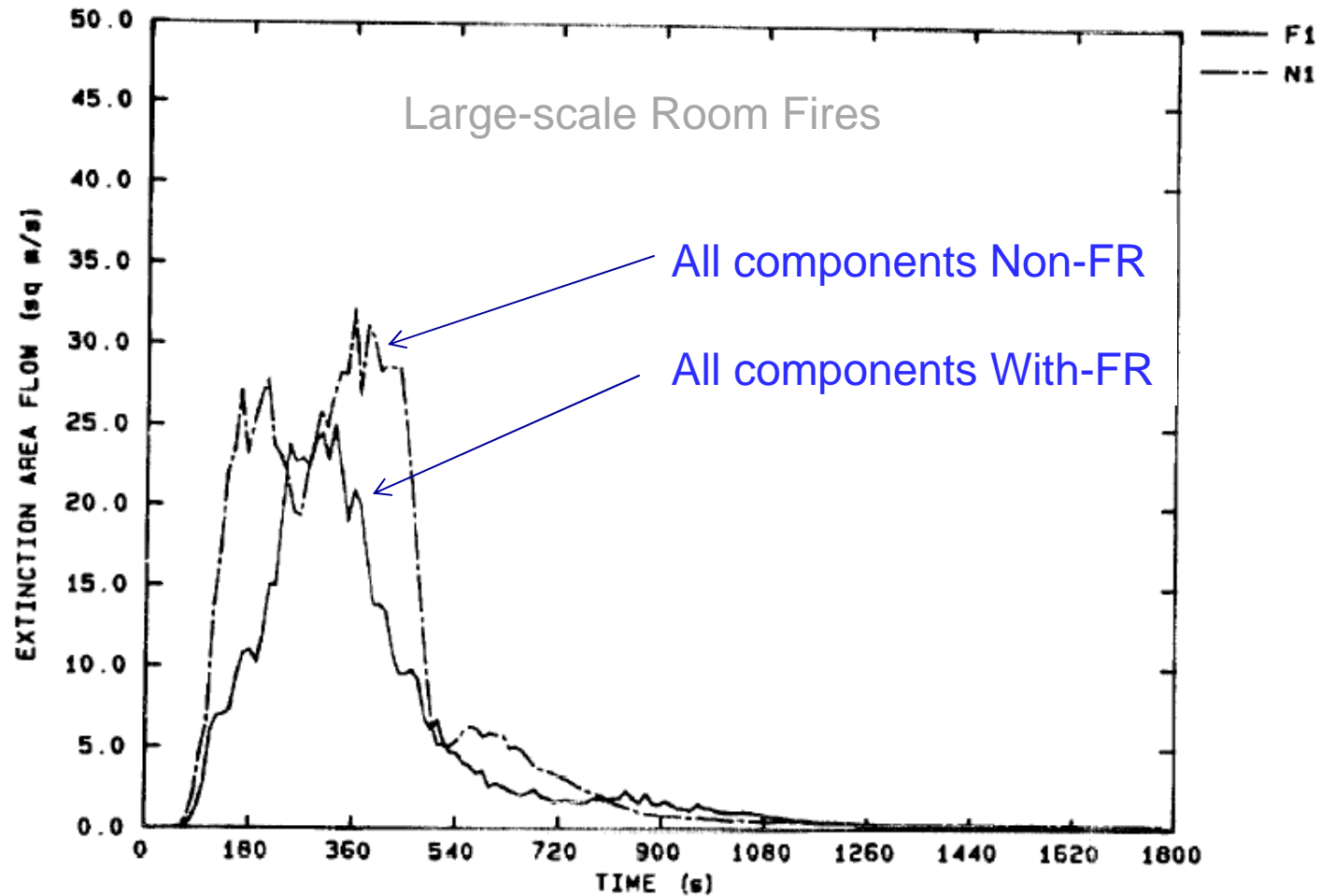


Figure 52. Smoke flow rates in the large scale room/corridor/room tests without the auxiliary burner.

- Smoke Generated in Room Fires

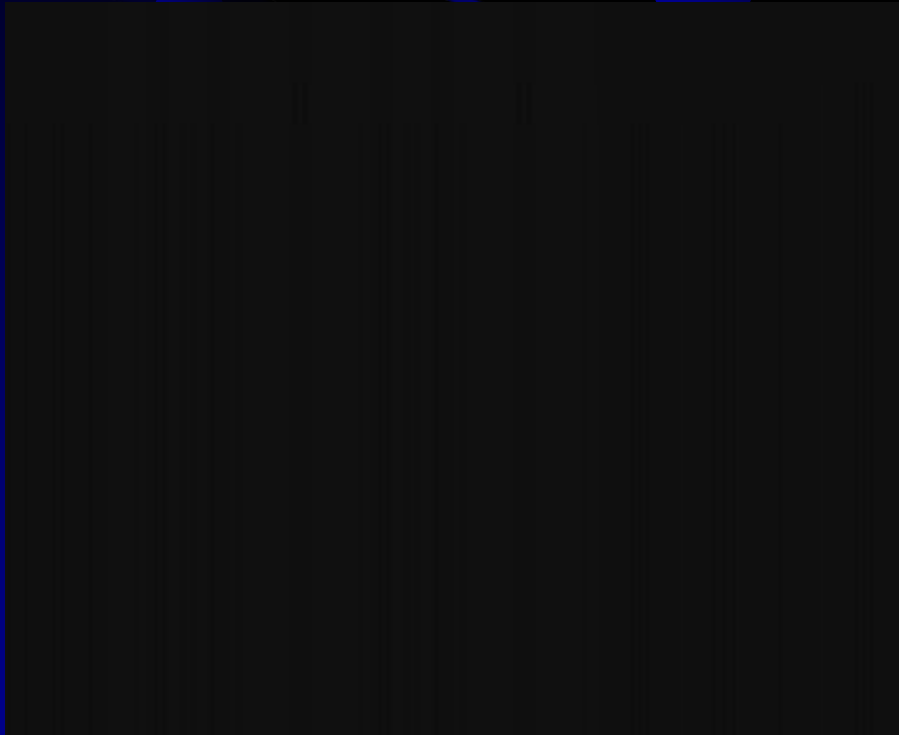
NIST Multi-scale Flammability Comparison of FR and Non-FR Products

Summary of Large Scale Room Fires

1. FR product tests had a 3 to 4 times less lower heat release rate and lower quantity of toxic gases relative to the Non-FR product tests
2. The smoke production was not significantly different between the FR tests and Non-FR product tests
3. FR products studied provide a 15 x greater escape time compared to the Non-FR products

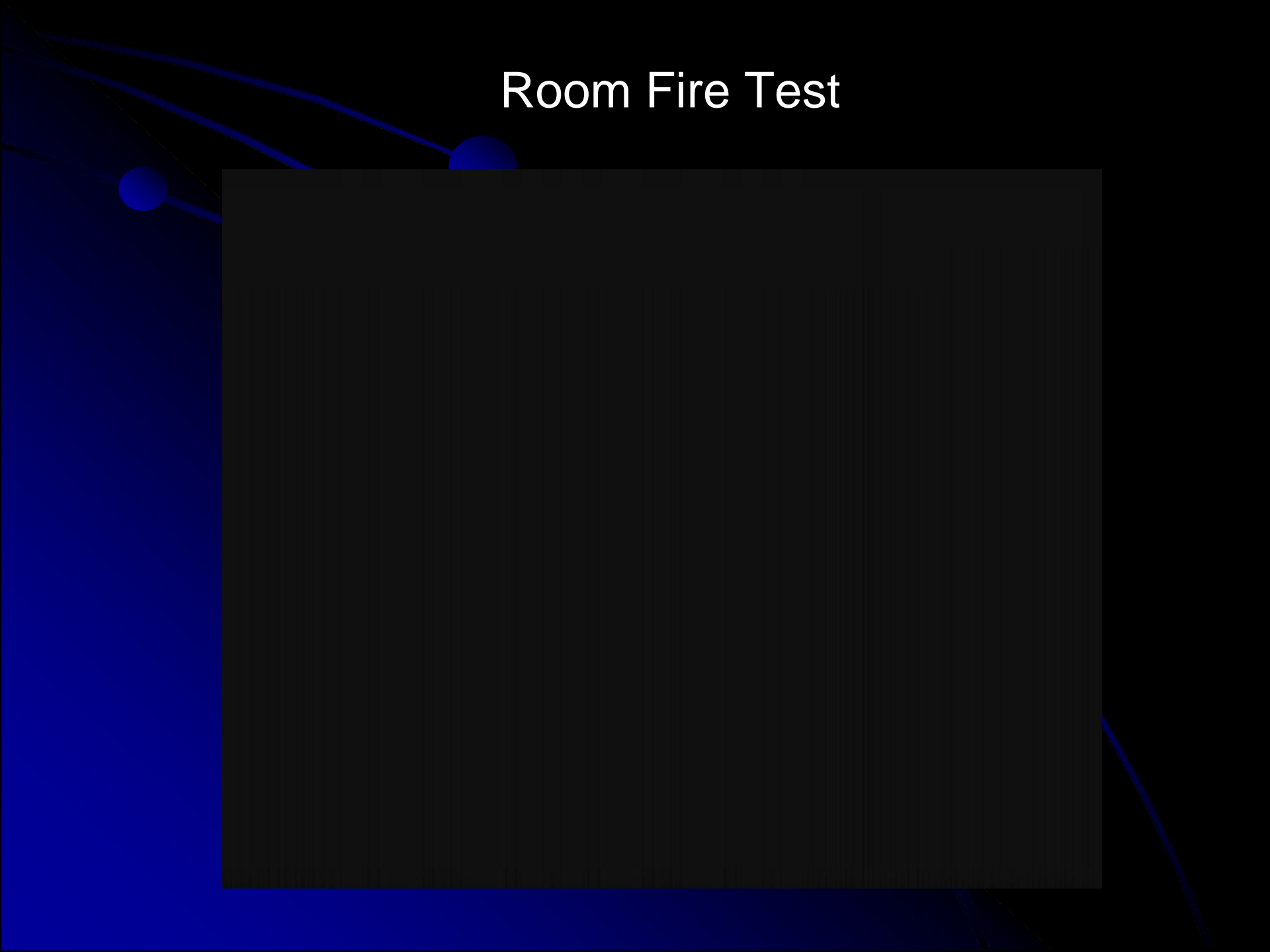
Flame Retarded Sofa

Non Flame Retarded Sofa



*SP Swedish National Testing and Research
Institute, Sweden,*

Room Fire Test



ECOLABEL

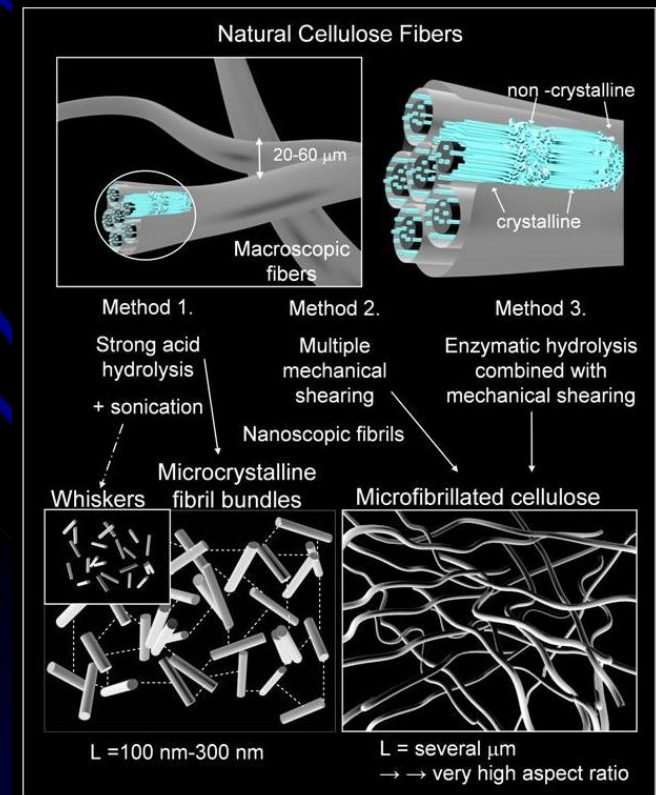
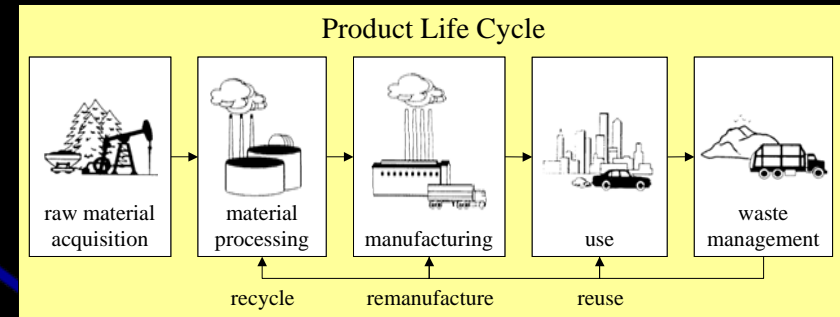


- **Flame retardants used in the entire mattress**
- **Only flame retardants that are chemically bound into mattress materials or onto the materials surfaces (reactive flame retardants) may be used in the product.**
- If the flame retardants used have any of the R-phrases listed below, these reactive flame retardants should, on application, change their chemical nature to no longer warrant classification under any of these R-phrases. (Less than 0.1% of the flame retardant may remain in the form as before application.)
- R40 (limited evidence of a carcinogenic effect), R45 (may cause cancer), R46 (may cause heritable genetic damage), R49 (may cause cancer by inhalation), R50 (very toxic to aquatic organisms), R51 (toxic to aquatic organisms), R52 (harmful to aquatic organisms), R53 (may cause long-term adverse effects in the aquatic environment), R60 (may impair fertility), R61 (may cause harm to the unborn child), R62 (possible risk of impaired fertility), R63 (possible risk of harm to the unborn child), R68 (possible risk of irreversible effects), as laid down in Council Directive 67/548/EEC on the approximation of the laws, regulations and administrative provisions relating to the classification, packaging and labeling of dangerous substances, and its subsequent amendments.
- **Flame retardants which are only physically mixed into the mattress materials or coatings are excluded (additive flame retardants).**
- Alternatively, classification may be considered according to Regulation (EC) No 1272/2008 of the European Parliament and of the Council of 16 December 2008 on classification, labeling and packaging of substances and mixtures, amending and repealing directives 67/548/EEC and 1999/45/EC, and amending Regulation (EC) No 1907/2006. In this case no substances or preparations may be added to the raw materials that are assigned, or may be assigned at the time of application, with and of the following hazard statements (or combinations thereof): H351, H350, H340, H350i, H400, H410, H411, H412, H413, H360F, H360D, H361f, H361d, H360FD, H361fd, H360Fd, H360Df, H341.
- *Assessment and verification: The applicant shall provide a declaration that additive flame retardants have not been used and indicate which reactive flame retardants, if any, have been used and provide documentation (such as safety data sheets) and/or declarations indicating that those flame retardants comply with this criterion.*

Sustainable Fire Safe Products

Evaluate new “green” flame retardants (FRs) and biopolymers

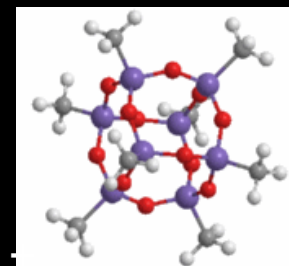
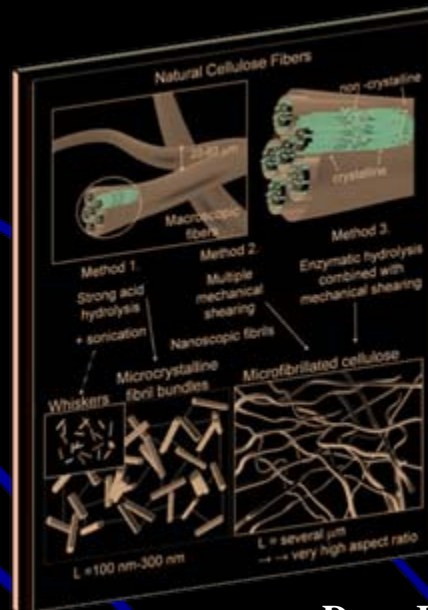
- Bio-based polymers, as well as nanomaterials such as cellulose nanofibrils, graphene, and LDH clays
 - Evaluate flammability performance (foams, thermoplastics and composites)
 - Form Sustainable Fire Safe Products Consortium
 - Investigate biopolymer flammability and FR mechanisms
 - Evaluate ageing effects on flammability (dark-side, MALDI MSEL)
 - Gather inventories of environmental inputs and outputs across all life cycle stages—raw material acquisition, manufacture, transportation, use, and waste management—for one new system/yr
 - Score inventories for the new system using BEES
 - Include economic performance data in sustainability
- Outcomes:** new knowledge on sustainable FRs and polymers, tools for assessing sustainable fire safe products



Natural Polymer Nanocomposites: Plans

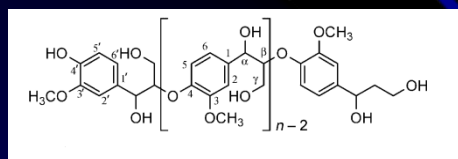
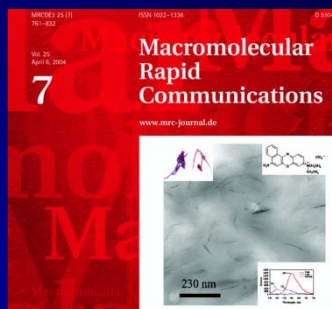
Goals

- 1) Characterize effects of aspect ratio, surface chemistry and processing on nanoparticle network formation in natural polymer nanocomposites.
- 2) Use ionic liquids, natural surfactants, to prepare and process sustainable nanoparticles.



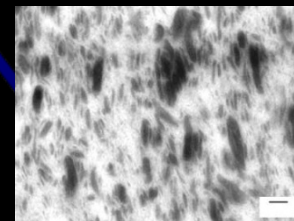
POSS
functionalized
cell-NF

Doug Fox – American University



Lignin

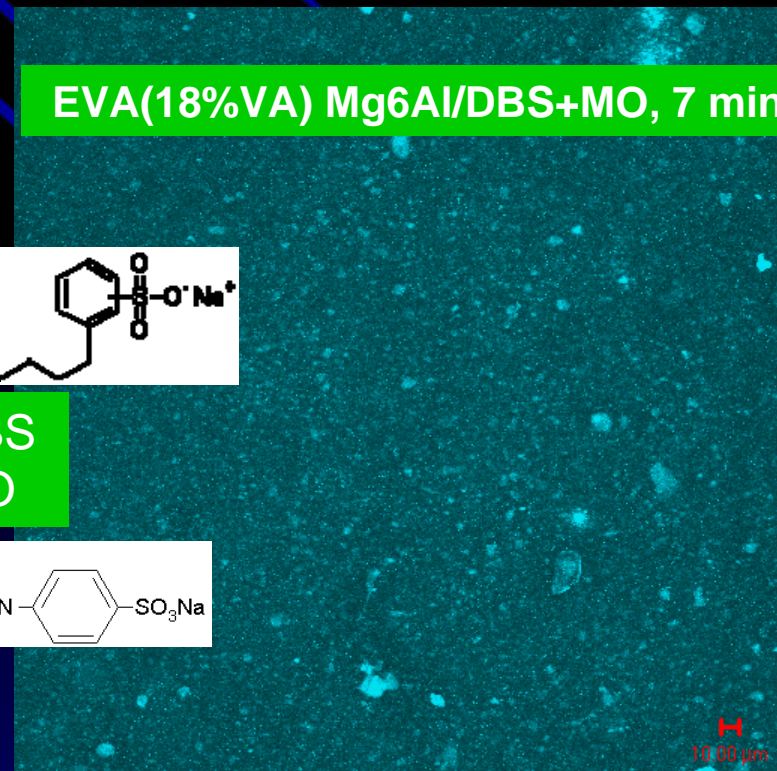
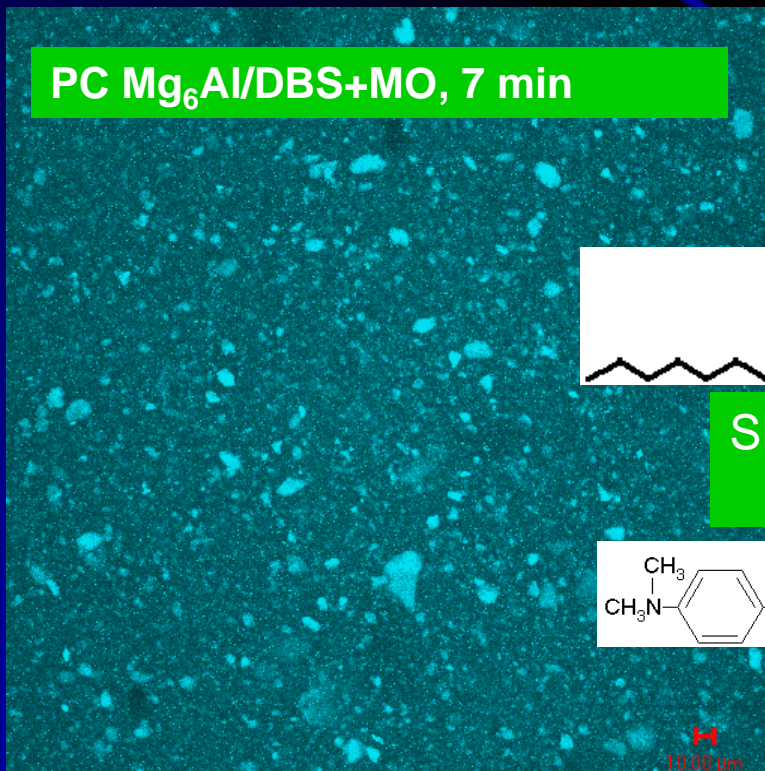
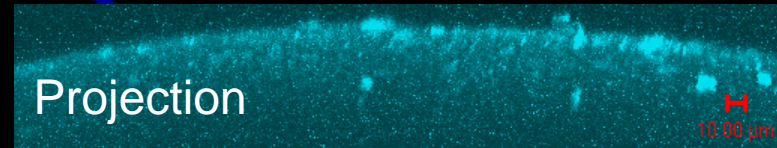
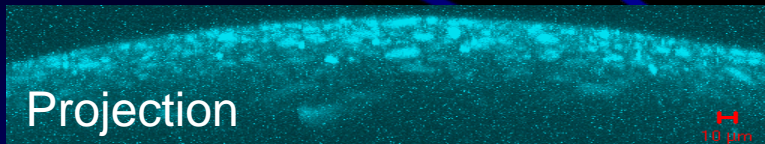
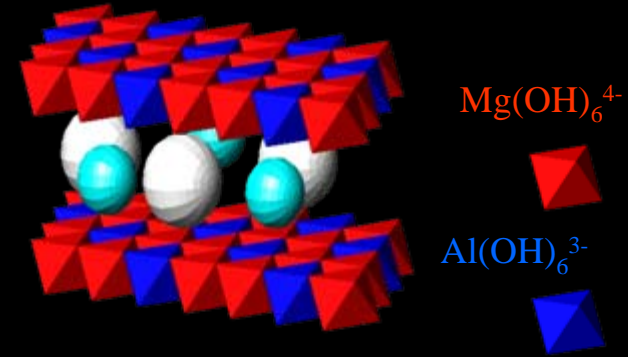
Layered Double Hydroxide



P. Mather; U. Conn



Confocal Imaging of LDH Nanocomposites



NANOPOARTICLE RELEASE



- Foam and fabric
 - Mechanical release as aerosol
 - Simulated body fluids
 - Following combustion

UCCEIN

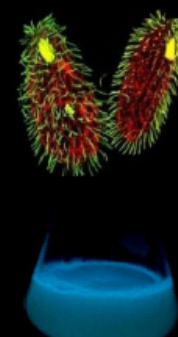
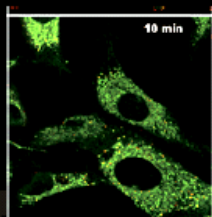
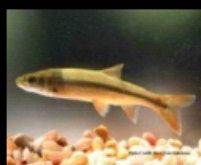
Center for Environmental
Implications of NanoTechnology

University of California, Center for the
Environmental Implications of Nanotechnology,
UC-CEIN <http://cein.ucla.edu>



Center for the Environmental Implications of
NanoTechnology, CEINT
<http://www.ceint.duke.edu/ICEIN09>

High Throughput Screening and Data Mining based on QSAR relationships that can be used to rank NM for risk and priority *in vivo* testing



100's/year

1000's/year

10,000's/day

100,000's/day

Immediate Relevance

High Throughput Bacterial,
Cellular or Molecular Screening

Prioritize *in vivo* testing
at increasing trophic levels

IRG 5: High Throughput Screening, Data Mining, and Quantitative Structure-Activity Relationships for NM Properties and Nanotoxicity

Group Leader: **Ken Bradley (UCLA)**

Participants:

Damoiseaux

Nel

Hoek

Keller

Cherr



Establish HTS methodologies

Perform HTS

Data Mining & QSAR profiling