

(b) The Effects of FR Agents on Polymer Performance

by

Vytenis Babrauskas

Flame-retarded or fire-retarded polymers — what are they? The explanation seems simple: they produce 'slower' fires. But, is it simple? And what is 'slower,' anyhow? Until very recently, to the polymer development chemist in the U.S., this performance did, indeed, seem simple. Such FR polymers were ones which performed better on the limiting oxygen index (LOI) [1] or the UL 94 [2] tests. Unfortunately, there has been no evidence to show that the LOI test has any correlation with actual fire performance. The UL 94 Bunsen burner test, by contrast, does represent fairly realistically the ignition of small plastic parts from small ignition sources. Despite this limitation, it is most commonly used as a general test for rating plastics, such as large sheets, which are associated with very different hazard issues. So, FR polymers show retarded fire development in some limited or irrelevant bench-scale tests. What about real fire performance? Can they show improved ignitability, flame spread rates, heat release rates, smoke evolution, etc.? There are no theoretical or systematic answers to these questions. Thus, in this section we will, instead, review some of the experimental data useful for answering such questions.

BENCH-SCALE MEASUREMENTS

Because of its ability to measure a number of realistic fire properties, the Cone Calorimeter was used from its earliest days in examining the performance of FR plastics. Table 1 shows the results from the first such study ever conducted where flexible polyurethane foams were examined. Four polyurethane foams, in the density range of 20 to 25 kg/m³, representing materials commercially used for furniture applications, were studied. Two of the foams had no fire retardants added (NFR), while two others were each similar to one of the non-retarded foams, but contained retardants. The retardant in one was bromine-based, while

Table 1

A comparison of the fire performance of several flexible polyurethane foams

Sample	FRs	Irrad. (kW/m ²)	Time to ign. (s)	Peak \dot{q}'' (kW/m ²)	60 s avg. \dot{q}'' (kW/m ²)
12	—	25	5.5	430	280
11 ^a	Br	25	39.3	440	280
13	—	25	5.2	470	270
14 ^b	P, Cl	25	15.0	470	230
12		50	3.3	1060	440
11		50	4.1	1030	460
13		50	3.3	880	470
14		50	4.1	840	430
12		75	1.3	1770	500
11		75	2.7	1430	550
13		75	NA	1800	650
14		75	2.9	1860	560

^a Sample has same formulation as sample 12, except includes FR.^b Sample has same formulation as sample 13, except includes FR.

the second had phosphorus and chlorine. Test results are shown in Table 1. At the lowest irradiance tested, 25 kW/m², both retarded products showed a very substantial improvement in time to ignition. The rates of heat release, both peak and average, however, were not improved. At higher irradiances, the effect of the retardants on ignition time became small. These products, thus, behaved in a manner similar to many other polymers where a small amount of retardant is added—the resistance to small ignition sources is noticeably improved, while actual fire performance, once ignited, is not much changed.

Polystyrene foams can be difficult to provide successfully with fire retardancy. Table 2 shows some results, including FR specimens using an experimental,

Table 2
Polystyrene Foams

FR	Irrad. (kW/m ²)	Ign. time (s)	Peak \dot{q}'' (kW/m ²)	Avg. Δh_c (MJ/kg)	Avg. CO (kg/kg)	Avg. HC (kg/kg)	Avg. smoke (m ² /kg)	Avg. soot (kg/kg)
No	25	141	410	28.9	0.08			
Yes	25	101	420	24.6	0.006	0.070	2570	0.156
No	50	35	680		0.10			
No ^a	50	32	600	25.1	0.066	0.085	1400	0.204
Yes	50	33	650	24.5	0.006	0.072	2750	0.166

^a Different supplier.Table 3
Polyurethane Foams

FR	Irrad. (kW/m ²)	Ign. time (s)	Peak \dot{q}'' (kW/m ²)	Avg. Δh_c (MJ/kg)	Avg. CO (kg/kg)	Avg. HC (kg/kg)	Avg. smoke (m ² /kg)	Avg. soot (kg/kg)
<i>Series A</i>								
No	35	7	910	23.1	0.030	0.0001	580	0.012
Yes	35	63	110	10.8	0.060	0.0010	210	0.093
<i>Series B</i>								
No	30	22	450	26.0	0.017	0.006	200	0.029
Yes	30	22	390	16.2	0.035	0.025	300	0.069
No	100	<1	1480	29.2	0.011	0.014	270	0.048
Yes	100	1.8	390	15.2	0.050	0.019	580	0.098
<i>Series C</i>								
No	25	7	420	25.6	0.013	0.0033	190	0.028
Yes	25	6	350	22.7	0.045	0.0133	510	0.061

proprietary, inorganic retardant. Since the tests were not all conducted at the same time, not all tabulated data columns are available for the earlier tests. The only beneficial effect of the FR treatment, in this case is seen to be a reduction of CO production. Whereas the data for polyurethane foams showed an improvement in ignitability—but not rate of heat release—characteristics—here the rate of heat release is unchanged, while ignitability is actually made worse.

Flexible polyurethane foams were studied at NIST numerous additional times, generally in connection with upholstered furniture flammability studies. In most such cases, the foams are covered by fabrics when in use. Test methodology then demands that the bench-scale heat release rate specimens also be tested as fabric/foam composites. To illustrate the behavior of polyurethane foams alone, however, several sets of test results are available where a complete set of gas analyzer data were recorded. These are shown in Table 3. The FR-treated foam in Series C was to normal industry specification, which is generally formulated to pass the California TB 117 test [3]. The FR foams in Series A and B were intended for institutional use, and were of the combustion-modified high resilience (CMHR) type (U.S. type, see discussion of CMHR foams in Chapter 14). The non-retarded foams in Series B and C, and the FR foam in Series C were all of the typical 22 to 23 kg/m³ density range. The CMHR foams comprising the FR specimens in Series A and B were much denser, being 95 kg/m³ in Series A and 70 kg/m³ in Series B. The non-FR foam in Series A was also a high-density foam, being 55 kg/m³.

Table 4
Performance of composite polyester/glass panels

FR	Thickness (mm)	Irrad. (kW/m ²)	Ign. time (s)	Peak time (s)	Values at peak				
					q" (kW/m ²)	m" (g/s m ²)	CO (kg/kg)	CO ₂ (kg/kg)	Smoke (m ² /kg)
None ^a	13	50	55	59	270	13.6	0.062	1.86	1080
None ^b	13	50	50	53	250	11.8	0.063	1.89	950
None ^c	13	50	45	59	270	12.7	0.064	1.95	1110
Br ^d	13	50	35	41	160	18.5	0.135	0.82	1010
Br ^e	13	50	45	59	180	17.6	0.137	0.86	1250
Br ^f	25	35	120	160	100	10.5	0.167	0.97	840
Br ^f	25	70	72	95	75	13.0	0.121	0.84	1160
Br ^f	25	75	25	50	100	17.5	0.111	0.75	1100

Reinforcement glass:

^a woven roving and chopped strand,

^b woven roving and mat,

^c woven roving and chopped strand,

^d woven roving and mat,

^e woven mat,

^f woven glass.

Results on two suppliers' naval cables, to the same specification

FR	Irrad. (kW/m ²)	Ign. time (s)	Peak q" (kW/m ²)	Avg. Δh _c (MJ/kg)	Avg. CO (kg/kg)	Avg. HC (kg/kg)	Avg. smoke (m ² /kg)	Avg. soot (kg/kg)
B	35	115	130	22.5	0.024	0.0126	210	0.170
	35	115	130	22.2	0.026	0.0151	200	0.165
C	35	143	130	12.9	0.129	0.141	240	0.073
	35	123	130	9.7	0.128	0.167	240	0.088
B	75	30	240	25.7	0.016	0.0052	490	0.189
	75	30	250	27.4	0.019	0.0056	470	0.192
C	75	34	230	22.7	0.018	0.0068	290	0.091
	75	33	230	23.1	0.015	0.0055	220	0.083

Table 5
Tests of polypropylene

FR additive	FR (%)	Peak q'' (kW/m ²)	Avg. Δh_c (MJ/kg)	Avg. CO ₂ (kg/kg)	Avg. CO (kg/kg)	Avg. HC (kg/kg)	Avg. soot (kg/kg)	Avg. smoke (m ² /kg)
<i>At 15 kW/m² irradiance</i>								
None	0	980	37.6	2.84	0.027	0.007	0.065	440
HBBCD-Sb ₂ O ₃	5	930	33.4	2.48	0.070	0.032	0.107	690
HBBCD-Sb ₂ O ₃	10	810	32.0	2.29	0.095	0.078	0.119	740
HBBCD-Sb ₂ O ₃	15	750	28.3	2.10	0.107	0.122	0.126	770
TBBPA-Sb ₂ O ₃	5	890	34.7	2.53	0.066	0.034	0.108	730
TBBPA-Sb ₂ O ₃	10	860	32.1	2.24	0.090	0.078	0.128	860
TBBPA-Sb ₂ O ₃	15	810	28.7	1.93	0.112	0.128	0.146	910
DBDPO-Sb ₂ O ₃	5	730	35.3	2.44	0.071	0.036	0.110	720
DBDPO-Sb ₂ O ₃	10	840	29.7	2.08	0.099	0.057	0.125	790
DBDPO-Sb ₂ O ₃	15	750	26.0	1.86	0.122	0.079	0.146	890

<i>At 30 kW/m² irradiance</i>								
None	0	1100	37.2	2.59	0.029	0.006	0.043	500
HBBCD-Sb ₂ O ₃	5	1080	32.8	2.19	0.072	0.042	0.110	780
HBBCD-Sb ₂ O ₃	10	1210	32.0	2.00	0.095	0.063	0.124	840
HBBCD-Sb ₂ O ₃	15	1230	28.6	1.69	0.101	0.081	0.134	840
TBBPA-Sb ₂ O ₃	5	1010	33.9	2.22	0.065	0.038	0.133	760
TBBPA-Sb ₂ O ₃	10	980	31.1	1.86	0.088	0.069	0.126	900
TBBPA-Sb ₂ O ₃	15	1010	28.3	1.64	0.108	0.096	0.149	1010
DBDPO-Sb ₂ O ₃	5	1290	32.6	2.12	0.073	0.049	0.107	750
DBDPO-Sb ₂ O ₃	10	980	27.0	1.80	0.097	0.074	0.112	930
DBDPO-Sb ₂ O ₃	15	990	25.3	1.52	0.113	0.100	0.152	960

Table 6
Tests on PMMA

FR additive	FR (%)	Peak \dot{q}'' (kW/m ²)	Avg. Δh_c (MJ/kg)	Avg. CO ₂ (kg/kg)	Avg. CO (kg/kg)	Avg. HC (kg/kg)	Avg. soot (kg/kg)	Avg. smoke (m ² /kg)
<i>At 15 kW/m² irradiance</i>								
None	0	490	21.8	2.05	0.010	0.003	0.025	150
HBCD-Sb ₂ O ₃	5	320	19.2	1.87	0.057	0.016	0.019	350
HBCD-Sb ₂ O ₃	10	280	17.4	1.70	0.092	0.022	0.069	430
HBCD-Sb ₂ O ₃	15	280	16.4	1.50	0.133	0.012	0.078	440
TBBPA-Sb ₂ O ₃	5	390	21.9	2.01	0.029	0.006	0.041	280
TBBPA-Sb ₂ O ₃	10	330	18.7	1.80	0.063	0.019	0.065	420
TBBPA-Sb ₂ O ₃	15	300	17.0	1.68	0.087	0.025	0.073	480
DBDPO-Sb ₂ O ₃	5	380	20.6	1.98	0.038	0.011	0.015	310
DBDPO-Sb ₂ O ₃	10	380	18.5	1.74	0.066	0.022	0.061	390
DBDPO-Sb ₂ O ₃	15	360	16.0	1.62	0.095	0.031	0.066	460

<i>At 30 kW/m² irradiance</i>								
HBCD-Sb ₂ O ₃	5	495	19.2	1.68	0.056	0.018	0.055	380
HBCD-Sb ₂ O ₃	10	510	17.9	1.48	0.094	0.032	0.068	450
HBCD-Sb ₂ O ₃	15	480	16.5	1.36	0.121	0.036	0.074	480
TBBPA-Sb ₂ O ₃	5	470	19.5	1.75	0.033	0.009	0.043	320
TBBPA-Sb ₂ O ₃	10	430	18.3	1.61	0.060	0.020	0.062	430
TBBPA-Sb ₂ O ₃	15	380	16.5	1.44	0.089	0.030	0.070	520
DBDPO-Sb ₂ O ₃	5	390	19.6	1.76	0.033	0.009	0.054	300
DBDPO-Sb ₂ O ₃	10	380	17.8	1.55	0.063	0.028	0.058	400
DBDPO-Sb ₂ O ₃	15	380	15.8	1.35	0.098	0.037	0.072	460

The results for Series C (Table 3) were distinctly unencouraging for the California T.B. 117 specification. The FR specimen showed only a very modest diminution in \dot{q}'' and Δh_c . The yields of CO, smoke, and soot were increased by factors of 2 to 3, however, while the HC yield was quadrupled. Keeping in mind that this is the lowest level of FR treatment, we can examine the data for Series B and A. The FR specimen in Series A clearly shows major improvements to both \dot{q}'' and to Δh_c . The CO, HC, and soot yields, while higher than for the untreated specimen, are still quite low. The smoke production is especially well-controlled. The FR specimen in Series A can, thus, be considered a true success. The FR specimen in Series B performed not quite as well, but still showed detectable improvements over the non-FR specimen in the same areas where the Series A FR specimen showed major improvements. We note that while the performance shown by California T.B. 117 type foams is unimpressive, there is also another, much more rigorous, test method in use in California. The very good performance of materials conforming to T.B. 133 is discussed in Chapter 14.

For **non-retarded** polyurethane foams, it has been noted [4] that, all other factors being equal, increased foam densities tend to be associated with increased rates of heat release. The performance of the non-retarded specimen in Series A shows an example of this.

The Cone Calorimeter is a sufficiently sensitive instrument that it can be used for comparative studies on products produced to the same specification, but made by different manufacturers [5]. Table 4 shows some results on cables produced by two different vendors, labeled "B" and "C," but made to the same MIL-C-24643/16 specification. In each instance, data for two separate runs are presented, to indicate the magnitude of purely random scatter. While the ignition times and peak \dot{q}'' values are nearly identical for both manufacturers, other quantities measured differed noticeably. Soot yields were about half for Brand C, as compared to Brand B under both levels of irradiance. Under the 75 kW/m² irradiance, smoke yield for C was also about half that for B, while CO and HC yields were essentially identical. At 35 kW/m² irradiance, however, Brand B showed a much lower heat of combustion and, correspondingly, much greater yields of CO and HC. It is evident, then, that there is no single, preferred product here. If performance at higher irradiances is important, then Brand C could readily be preferred. If performance at lower irradiances is crucial, however, then the each product has different strengths.

The most systematic study of fire-retarded products tested so far in the Cone Calorimeter has been the one by Drews and Jarvis [6] where specimens were especially prepared with varying, controlled amounts of several different fire retardants. The two base polymers used were polypropylene (PP) and polymethylmethacrylate (PMMA). The fire retardants used were a series of organobromine/antimony oxide preparations. Three different organobromines were

studied: hexabromocyclododecane (HBCD), tetrabromobisphenol-A (TBBPA), and decabromodiphenyl oxide (DBDPO). The proportions were in all cases such that there was a 3:1 ratio of Br to Sb atoms. Because of the requirements of the available molding machinery, the specimen size for this study was 50 mm by 100 mm by 10–12 mm thick, which is half the standard area. This fact does not influence the results qualitatively, and has only a modest quantitative effect. Two irradiance levels were used, 15 and 30 kW/m². Table 5 gives the results for the PP specimens, while Table 6 shows the PMMA data. From these tables one can see that all three retardants showed modest effects. When considering either the peak \dot{q}'' or Δh_c the retardants typically showed an effect about twice what would be achieved by simply substituting an equal amount of inert filler. The effect of retardant loading on these two main variables was seen to be roughly linear. The effect on smoke and soot, especially for PMMA, however, appeared strongly non-linear; i.e., adding 5% retardant typically doubled the yields for smoke and soot, while increasing the loading to 15% gave only a small additional increase. The effect on CO and HC was also non-linear, although somewhat less so. The purpose of studying these particular retardant systems was to elucidate some of the basic chemistry involved. If the systems had been proposed for commercial use, however, we would probably state that the modest benefits of reduced \dot{q}'' and Δh_c are outweighed by the roughly doubled emissions of CO, HC, smoke and soot.

EFFECTS ON REAL-SCALE FIRE HAZARD

Thus far in this section we have discussed those property measurements which are directly obtainable from the Cone Calorimeter. While we have confidence that the Cone Calorimeter is the best general-purpose measurement tool we have, there remains the broader context of the real-scale fire. As we have already seen, in some cases the yields of smoke, CO, etc., can actually be increased with FR materials. Thus, questions arise which can only be settled by conducting large-scale (real-scale) tests. A program of such tests was undertaken by NIST for the Fire Retardant Chemicals Association [7]. The two issues to be resolved in this study were:

- (1) For today's most commonly used FR/polymer systems, is the **overall** fire hazard reduced, when compared to similar non-fire retarded (NFR) items?
- (2) Since both the commercially popular FR chemicals and the base polymer formulations can be expected to change in the future, can appropriate bench-scale test methodologies be validated which would allow future testing to be quick and simple?

To answer these questions, experimental studies were conducted on 5 sets of

products, each in an NFR and an FR variant. The products were chosen to represent a wide spectrum of both base polymers and FR agents. In each case, the FR agent used was chosen to represent one of the better commercially available formulations. The products selected for testing were as follows.

- 1. TV Cabinet housing** These were plastic moldings, 3 mm thick.
 - Sample H (NFR)** — high impact polystyrene base formulation.
 - Sample G (FR)** — the same base formulation with decabromodiphenyl oxide (12 % by weight) and antimony oxide (4 %)
- 2. Business machine housing** These were plastic moldings, 3 mm thick.
 - Sample F (NFR)** — poly(2,6-dimethyl 1,4 phenylene) oxide; also includes polystyrene, polybutadiene, polyethylene, mineral oil, and stabilizer additives.
 - Sample A (FR)** — the same base formulation, with a triaryl phosphate ester based flame-retardant (to give 1% P by weight).
- 3. Upholstered chairs** The upholstered chairs were constructed of only two combustible materials: flexible polyurethane padding foam, and a cover fabric. Instead of a conventional frame, the chairs used a steel mock-up frame.
 - Sample T (NFR)** — The density of this foam was 25 kg/m³.
 - Sample S (FR)** — This foam contained an organic chlorinated phosphate, and organic brominated retardant and 35% alumina trihydrate. The loadings represented an elemental content of 4.75% Br, 2.6% Cl, 0.32% P, and 10.0% Al. The density of this foam was 64 kg/m³.

The same nylon fabric (250 kg/m²) was used as a cover for both samples. Since the cover fabric was not varied, it was not evaluated in certain of the bench-scale tests.
- 4. Cable array** Each electric cable contained five copper wires, each 14 AWG (1.63 mm dia.). The outside diameter of each insulated wire was 3.30 mm. The overall, outside diameter of the complete jacketed cable was 12.7 mm. Pieces of the cable approximately 250 mm long are shown in Fig. 4.
 - Sample D (NFR)** — wire insulation made of crosslinked ethylene/ vinyl acetate copolymer, with clay (18.9 parts per 100 resin), antioxidant (2 parts), processing aid (1 part), and catalyst (1.5 parts). Covered with a black outside jacket made of chlorosulfonated polyethylene containing Sb₂O₃. Elemental contents were 12.2% Cl and 2% Sb.
 - Sample K (FR)** — wire insulation made of polyethylene cross-linked with ethylene vinyl acetate, with clay (28 parts), chlorinated cycloaliphatic fire retardant (38 parts), Sb₂O₃ (18.9 parts), antioxidant (2 parts), processing aid (1 part), and catalyst (1.5 parts). Outside jacket identical to that for the NFR specimen.

The outer jackets, being the same in both instances, were not evaluated in detail in certain of the bench-scale tests.

- 5. Laminated circuit board** This material was intended to be representative of glass/polyester electric circuit boards. It contained, however, no copper traces and no electrical components. The thickness of the board was 6.4 mm.
 - Sample C (NFR)** — polyester resin (38% by weight), with CaCO₃ filler (44% by weight), and fiberglass reinforcement (18%).
 - Sample L (FR)** — polyester resin (39%), with decabromodiphenyl oxide (10%), Sb₂O₃ (3%), Al₂O₃·3H₂O (30%), and fiberglass reinforcement (18%).

Specimens of these products were first tested in the Cone Calorimeter, in the furniture calorimeter, and in a bench-scale test for toxic potency. The same products were then tested in a number of real-scale room fires. The real-scale

Table 7
Cone Calorimeter Data Summary—30 kW/m² Irradiance Tests

Sample	NFR /FR	Mass (g)	% Mass burned	Ign. Time (s)	Peak q" (kW/m ²)	Peak q" time (s)	Tot. q" (MJ/m ²)	Eff. Δh _c (MJ/kg)
TV Cabinet H	NFR	34	99	107	970	190	87	30
TV Cabinet G	FR	38	98	84	340	184	46	12
Bus. Machine F	NFR	37	88	108	650	168	96	30
Bus. Machine A	FR	39	81	134	380	370	65	21
Chair T ^a	NFR	23	89	14	470	113	54	27
Chair S ^a	FR	43	67	34	290	51	51	18
Chair T ^b	NFR	15	90	2	540	65	34	27
Chair S ^b	FR	36	61	25	180	—	32	15
Cable D	NFR	166	35	383	360	505	156	28
Cable K	FR	170	33	374	380	487	114	23
Cable D ^c	NFR	54	52	189	270	208	65	23
Cable K ^c	FR	53	54	169	280	185	68	23
Cable D ^d	NFR	103	22	137	740	280	91	39
Cable K ^d	FR	106	22	131	260	161	51	23
Circuit Bd. C	NFR	123	28	199	250	220	73	21
Circuit Bd. L	FR	117	36	315	100	368	55	13

^a Foam and fabric cover combination

^b Foam only, no cover

^c Cable jacket only

^d Wire alone; jacket stripped off

Table 8
Cone Calorimeter Data Summary—Test Average Data at 30 kW/m² Irradiance

Sample	NFR /FR	CO kg/kg	CO ₂ kg/kg	HCl kg/kg	HBr kg/kg	HCN kg/kg	Smoke m ² /kg
TV Cabinet H	NFR	0.015	2.284	—	—	—	1010
TV Cabinet G	FR	0.109	0.671	—	0.069	—	1880
Bus. Machine F	NFR	0.037	2.211	—	—	—	1710
Bus. Machine A	FR	0.055	1.604	—	—	—	1660
Chair T ^a	NFR	0.020	1.617	—	—	0.002	410
Chair S ^a	FR	0.051	0.964	0.022	—	0.005	480
Chair T ^b	NFR	0.016	1.711	—	—	0.002	270
Chair S ^b	FR	0.055	0.809	0.022	—	0.002	280
Cable D	NFR	0.041	1.773	0.112	—	—	1010
Cable K	FR	0.060	1.337	0.131	—	—	880
Cable D ^c	NFR	0.029	2.190	—	—	—	690
Cable K ^c	FR	0.135	1.004	0.095	—	—	1030
Cable D ^d	NFR	0.030	2.208	0.128	—	—	710
Cable K ^d	FR	0.142	0.991	0.136	—	—	1000
Circuit Bd. C	NFR	0.014	2.070	—	—	—	560
Circuit Bd. L	FR	0.103	0.868	—	0.022	—	400

^a foam and fabric cover combination

^b foam only, no cover

^c wire alone; jacket stripped off

^d cable jacket only

tests were conducted in a full-scale test facility, which comprised a burn room, a corridor, and then a target room wherein hazard measurements were made.

The bench-scale Cone Calorimeter data are summarized in Tables 7 through 11. The data clearly reflect the difference between these particular specimens and some of the 'nominally treated' FR specimens discussed above. Substantial improvements in heat release rate performance were seen not only at the 30 kW/m² irradiance, but also at the very high 100 kW/m² level. The yields of smoke and toxic gas species, however, were in many cases higher. Thus, it was important to examine the behavior at more realistic scales.

Table 12 shows the results obtained in the Furniture Calorimeter, while Table 13 compares those values against Cone Calorimeter measurements. Here we find that

Table 9
Cone Calorimeter Data Summary—100 kW/m² Irradiance Tests

Sample	NFR /FR	Mass (g)	% Mass burned	Ign. Time (s)	Peak q" (kW/m ²)	Peak q" time (s)	Tot. q" (MJ/m ²)	Eff. Δh _c (MJ/kg)
TV Cabinet H	NFR	32	97	15	1400	68	93	29
TV Cabinet G	FR	36	95	13	480	55	39	10
Bus. Machine F	NFR	37	88	11	1100	46	95	29
Bus. Machine A	FR	35	87	11	570	41	60	20
Chair T ^a	NFR	22	93	5	1460	52	58	28
Chair S ^a	FR	45	72	5	760	22	56	18
Chair T ^{bd}	NFR	14	88	<1	1580	35	37	29
Chair S ^{bd}	FR	37	66	2	310	15	35	14
Cable D	NFR	170	38	8	550	225	159	26
Cable K	FR	173	35	10	380	32	119	21
Cable D ^c	NFR	102	23	16	1280	93	88	38
Cable K ^{cd}	FR	106	23	16	490	45	50	21
Circuit Bd. C	NFR	127	29	32	250	160	71	18
Circuit Bd. L	FR	116	43	49	147	128	74	14

^a Foam and fabric cover combination

^b Foam only, no cover fabric

^c Wire alone; jacket stripped off

^d Only one test value

some, but not all of the data trends can be predicted by the Cone Calorimeter. The reason for this is not surprising. A successful correlation scheme should involve a significantly more complex data treatment than a simple plot of peak values one against each other [8]. Such predictive correlations are only now beginning to be obtained (e.g., see the Chapters on furniture and wall linings), and typically include only heat release rate and not additional variables.

The arrangement of the test articles in the real-scale room fire tests is shown in Figure 1. The items were not tested individually, but, rather, in full-furnished test rooms, one all-FR, and one all-NFR. A 120 kW burner was used to provide added heat flux to the specimens, especially the upholstered chair mock-up at the start of the test. This was done so that the FR room would be sure to be fire-involved and would not simply show a no-flame-spread response. Figure 2 shows the heat release rates obtained for the two sets of rooms. The maximum rate produced by the FR room was about 1/4 of that from the NFR room (Table 14).

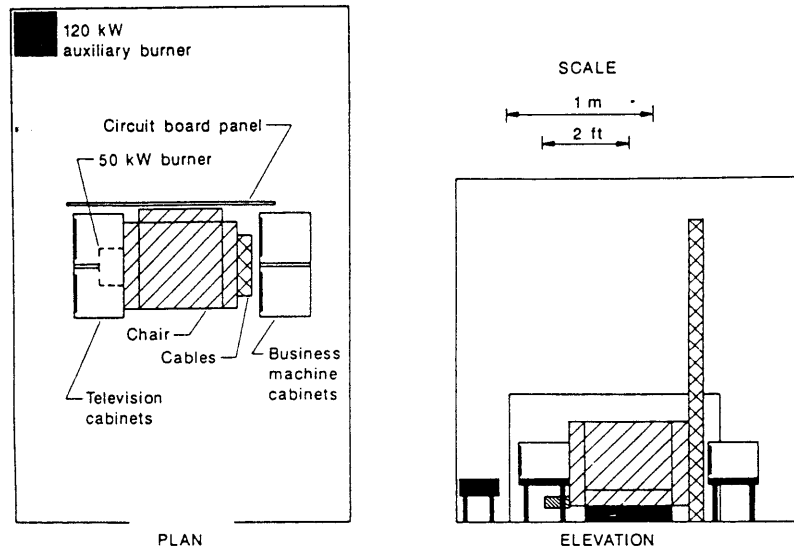


Figure 1. Set-up used in real-scale FRCA tests

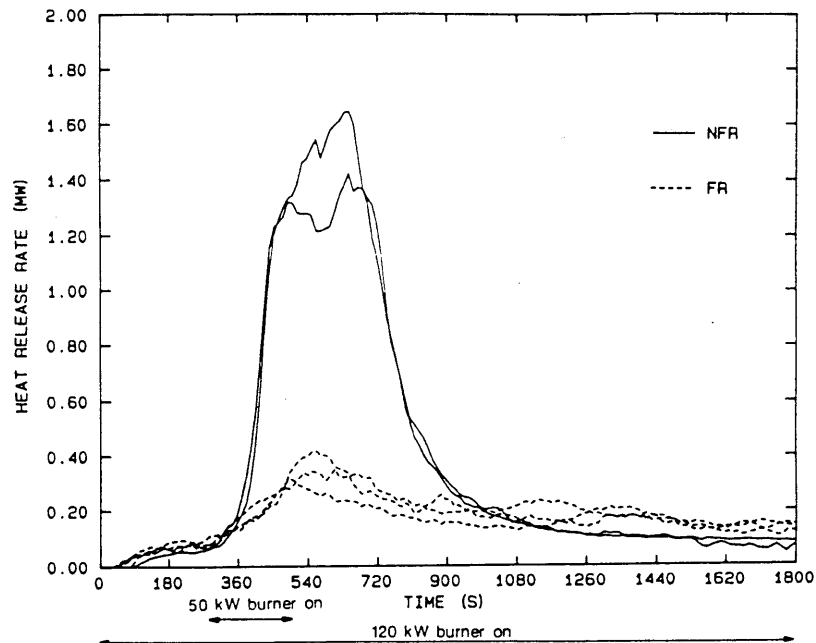


Figure 2. Heat release rates measured in the real-scale FRCA tests

Table 10
Cone Calorimeter Data Summary—Test Average Data at 100kW/m² Irradiance

Sample	NFR /FR	CO kg/kg	CO ₂ kg/kg	Smoke m ² /kg
TV Cabinet H	NFR	0.063	2.121	1430
TV Cabinet G	FR	0.074	0.564	2010
Bus. Machine F	NFR	0.060	1.627	1530
Bus. Machine A	FR	0.096	1.165	2120
Chair T ^a	NFR	0.021	1.828	340
Chair S ^a	FR	0.063	0.965	500
Chair T ^{bd}	NFR	0.018	1.889	450
Chair S ^{bd}	FR	0.052	0.895	420
Cable D	NFR	0.007	1.566	1270
Cable K	FR	0.025	1.245	1210
Cable D ^{cd}	NFR	0.035	2.148	760
Cable K ^{cd}	FR	0.101	0.910	1290
Circuit Bd. C	NFR	0.012	1.697	780
Circuit Bd. L	FR	0.012	1.221	410

^a Foam and fabric cover combination

^b Foam only, no cover fabric

^c Wire alone; jacket stripped off

^d Only one test value

Another way of quantifying the relative fire hazard is according to the time it takes to reach untenable conditions in the burn room or in the target room. Table shows this comparison. Table 15 shows this hazard comparison. A comparison of smoke and CO yields is shown in Tables 16 and 17.

We can now summarize the hazard findings from that study:

- The average available escape time was more than 15-fold greater for the FR products in the room burn tests.
- The amount of material consumed in tests of the FR products was less than half the loss in the NFR tests.
- FR products, on the average, gave 1/4 the heat release of NFR products.
- The production of CO for the FR tests was about half of that for the NFR ones.
- The production of smoke was not significantly different in room fire tests between FR and NFR products.

Table 11
Irradiance Threshold Limit for Foam S with Nylon Fabric Cover

Irrad. (kW/m ²)	Mass (g)	% Mass burned	time (s)	Peak q" (kW/m ²)	Ign. time (s)	q" (MJ/m ²)	Peak Δhc (MJ/kg)	Total CO (kg/kg)	Eff. CO ₂ (kg/kg)	Smoke (m ² /kg)	Soot (kg/kg)
7	43	—	NI	—	—	—	—	—	—	—	—
10	43	14.3	541	180	580	9.6	15.7	0.035	1.558	350	0.056
10	43	—	NI	—	—	—	—	—	—	—	—
11	44	20.5	341	190	370	13.1	14.6	0.035	0.677	380	0.052
11	43	—	NI	—	—	—	—	—	—	—	—
11	42	16.9	527	50	815	5.6	7.8	0.053	0.558	590	0.103
11	43	19.8	264	180	295	13.4	15.7	0.031	0.573	380	0.052
15	43	41.2	173	280	210	22.0	12.5	0.036	0.888	420	0.039

Table 12
Summary of Furniture Calorimeter Results

Product:	TV		Bus. machine		Chair		Cable (vertical configuration)		Cable (Z configuration)		Circuit board			
	FR		FR		FR		FR		FR					
	NFR	FR	NFR	FR	NFR	FR	NFR	FR	NFR	FR				
Specimen code	H	G	F	A	T	T	S	D	K	Jacket	D	K	C	L
Test no.	3	4	1	2	16	18	17	19	20	21	5	6	10B	11
Total mass (kg)	3.7	3.7	3.5	3.5	5.5	5.3	11.9	11.35	11.52	3.5	17.5	18.2		
Combustible mass (kg)	3.7	3.7	3.5	3.5	5.5	5.3	11.9	6.24	6.45	3.5	9.6	10.2	36.6	34.8
Mass loss (kg)	3.6	2.1	3.2	2.5	5.2	5.1	**	4.6	1.60	2.0	3.5	2.2	13.4	1.9
Peak heat release rate (kW)	515	180	560	380	1160	1205	50*	400	75*	140	245	130	205	100*
Time of occurrence (s)	139	216	88	138	218	208	209	858	1208	265	839	1402	396	1863
Total heat (MJ)	83	40	40	75	136	135	*	188	*	67	124	75	238	*
Average heat of combustion (MJ/kg)	23	20	20	28	26	27	**	41	*	34	35	34	18	*
Average CO (kg/kg)	0.12	0.48	0.26	0.13	0.01	0.01	**	0.12	0.10	0.13	0.25	0.30	0.10	0.10
Average CO ₂ (kg/kg)	1.39	0.72	0.75	1.61	1.88	1.89	**	1.61	1.04	1.48	1.89	0.70	1.71	1.36
Average HCl (kg/kg)								0.12*	0.13*					
Average HBr (kg/kg)								0.12*	0.13*					
Average HCN (kg/kg)								0.001 ^a						
Average smoke extinction area (m ² /kg)	1320	2690	2910	1145	1280	165	180	280	235	560	375	545	285	115

* Not reliable. Specimen heat release rate accuracy of ± 25 kW

** Not reliable. Specimen weight loss comparable to noise level of instrumentation

^a Determined by ion chromatography

Table 13
Comparison of Cone Calorimeter versus Furniture Calorimeter Data

Sample	NFR/FR	Pk q" (kW/m ²) ^a		Δh _c (MJ/kg)		% burned		Avg. CO (kg/kg)		Avg. CO ₂ (kg/kg)	
		Cone	Furn. ^b	Cone	Furn. ^b	Cone	Furn. ^b	Cone	Furn. ^b	Cone	Furn. ^b
TV Cabinet H	NFR	970	520	30	23	99	97	0.015	0.12	2.28	1.39
TV Cabinet G	FR	340	180	12	20	98	57	0.109	0.37	0.67	0.74
Bus. Machine F	NFR	650	560	30	24	88	91	0.037	0.13	2.21	1.61
Bus. Machine A	FR	380	380	21	28	81	71	0.055	0.29	1.60	1.45
Chair T	NFR	470	1180	27	27	89	96	0.020	0.01	1.62	1.89
Chair S	FR	290	50	18	c,d	67	d	0.051	d	0.96	d
Cable D	NFR	360	400	28	41	35	41	0.041	0.12	1.77	1.61
Cable K	FR	380	80	23	c	33	14	0.060	0.10	1.34	1.04
Circuit Bd. C	NFR	250	210	21	18	28	37	0.014	0.10	2.07	1.71
Circuit Bd. L	FR	100	100	13	c	36	5	0.103	0.10	0.87	1.36

Sample	NFR/FR	Pk q" (kW/m ²) ^a		Δh _c (MJ/kg)		% burned		Avg. CO (kg/kg)	
		Cone	Furn. ^b	Cone	Furn. ^b	Cone	Furn. ^b	Cone	Furn. ^b
TV Cabinet H	NFR	NM	NM	NM	NM	NM	NM	1010	1320
TV Cabinet G	FR	NM	NM	0.07	0.08	NM	NM	1880	2800
Bus. Machine F	NFR	NM	NM	NM	NM	NM	NM	1710	1150
Bus. Machine A	FR	NM	NM	NM	NM	NM	NM	1660	1280
Chair T	NFR	NM	NM	NM	NM	0.002	0.001	410	190
Chair S	FR	0.02	NM	TR	NM	0.005	d	480	180
Cable D	NFR	0.11	0.12	NM	NM	NM	NM	1010	280
Cable K	FR	0.13	0.13	NM	NM	NM	NM	880	240
Circuit Bd. C	NFR	NM	NM	NM	NM	NM	NM	560	290
Circuit Bd. L	FR	NM	NM	0.02	d	NM	NM	400	120

NOTE: All Cone Calorimeter data refer to 30 kW/m² irradiance tests.

^a Values for the Cone Calorimeter refer to peak q" (kW/m²); values for the Furniture Calorimeter refer to peak q (kW).

^b Values obtained from the following Furniture Calorimeter tests:

H: 3; G: 4,15; F: 1; A: 2; T: 16,18; S: 17; D: 19; K: 20; C: 10B; L: 11

^c Not reliable. Specimen heat release rate accuracy of ± 25 kW

^d Not reliable. Specimen weight loss comparable to noise level of instrumentation

NM Not measured

TR Trace

Table 14
Peak Heat Release and Total Heat Release

Test number	Peak heat release (kW)	Total heat release (MJ) large scale ^a			
		Individual	Average	Furn.	Cone
N1	1590	639 } 479 } 507 }	542	730	752
NX0	1540				
NX1	1790				
FX0	370	141 } 116 } 105 }	121	— ^b	199 ^c
FX1	350				
FX1a	450				

^a Corrected for auxiliary burner (252 MJ) and igniting torch (10 MJ)

^b TV cabinet and chair only two items involved in fire; since Δh_c for chair could not be determined from Furniture Calorimeter tests, the result is indeterminate.

^c Computed from TV cabinet and portion of chair consumed at 1800 s for F1 and 2100 s for FX0, FX1, and FX1a.

Table 15
Times to Reach Untenable Conditions in Large-Scale Tests

Test number	Burn room		Target room
	Flashover ^a (s)	CO FED (s)	CO FED (s)
	NX1	110	164
NX0	112	167	215
NX1	116	168	226
FX0	∞ (273) ^c	1939	∞ (0.40) ^d
FX1	∞ (285) ^c	2288	∞ (0.29) ^d
FX1a	∞ (334) ^c	1140	1013

^a Time when temperature reached 600°C.

^b Auxiliary burner output exceeds this flux.

^c Maximum burn room temperature (°C).

^d Maximum CO FED attained.

FED fractional effective exposure-dose.

Thus, briefly put, it was demonstrated that if sufficiently effective FR agents are used, any effects of increased yields of smoke or CO are more than compensated by the decreased burning rates. But how do we know if an FR agent being used is a sufficiently effective FR agent? Real-scale tests answer this question, but, in general, at an extremely high cost. Bench-scale tests can do this much cheaper and easier, if we know how to interpret and apply the results. At the moment, we do not have universal predictive techniques; the best we can do is establish

Table 16
Comparison of Smoke from Large-Scale Fires with Furniture Calorimeter and Cone Calorimeter Calculated Values

Test	Large-scale				Furn. cal. smoke yield (m ² /kg)	Cone cal. smoke yield (m ² /kg)
	Smoke prod. (m ²)	Average	Smoke yield (m ² /kg)	Average		
N1	10540	9900	351	330	486	780
NX0	8795		293			
NX1	10360		345			
FX0	12630	12400	1089	1038	638	725
FX1	12800		1103			
FX1a	11890		922			

Table 17

Comparison of Average CO from Large-Scale Fires with Furniture Calorimeter, Cone Calorimeter, and Toxicity Test Calculated Values

Test Number	Large-scale				Furn. cal. CO yield (kg/kg)	Cone cal. CO yield (kg/kg)	Tox. Test CO yield (kg/kg)
	CO prod. (kg)	Average	CO yield (kg/kg)	Average			
N1	6.6	5.5	0.22	0.18	0.09 ^a	0.02	0.074
NX0	5.5		0.18				
NX1	4.3		0.14				
FX0	2.6	2.8	0.23	0.23	— ^b	0.06	0.155
FX1	2.7		0.23				
FX1a	3.0		0.23				

^a Based on high values from Furniture Calorimeter which cannot be explained.

^b TV cabinet and chair only two items involved in fire; since CO for chair could not be determined from Furniture Calorimeter tests, the result is indeterminate.

methods which successfully predict one particular performance variable for one particular category of combustibles. Most of the other chapters in Part II of this monograph are addressed to precisely this question.

REFERENCES

1. Standard Test Method for Measuring the Minimum Oxygen Concentration to Support Candle-like Combustion of Plastics (Oxygen Index). ASTM D 2863, American Society for Testing and Materials, Philadelphia.

2. Tests for Flammability of Plastic Materials for Parts in Devices and Appliances (UL 94). Underwriters Laboratories, Northbrook.
3. Technical Bulletin 117 — Requirements, Test Procedure and Apparatus for Testing the Flame Retardance of Resilient Filling Materials Used in Upholstered Furniture, State of California, Bureau of Home Furnishings, North Highlands, CA (1980).
4. Babrauskas, V., and Krasny, J.F., Fire Behavior of Upholstered Furniture (NBS Monograph 173). [U.S.] Natl. Bur. Stand. (1985).
5. Braun, E., Shields, J.R., and Harris, R.H., Flammability Characteristics of Electrical Cables Using the Cone Calorimeter (NISTIR 88-4003). [U.S.] Natl. Inst. Standards and Technology, Gaithersburg, MD (1989).
6. Drews, M.J., Jarvis, C.W., and Lickfield, G.C., Ternary Reactions Among Polymer Substrate-Organohalogen-Antimony Oxides under Pyrolytic, Oxidative, and Flaming Conditions (NIST-GCR-89-558), [U.S.] Natl. Inst. of Standards and Technology, Gaithersburg MD (1989).
7. Babrauskas, V., Harris, R.H., Jr., Gann, R.G., Levin, B.C., Lee, B.T., Peacock, R.D., Paabo, M., Twilley, W., Yoklavich, M.F., and Clark, H.M., Fire Hazard Comparison of Fire-Retarded and Non-Fire-Retarded Products (NBS Special Publication SP 749). [U.S.] Natl. Bur. Stand. (1988).
8. Babrauskas, V., and Krasny, J.F., Fire Behavior of Upholstered Furniture (NBS Monograph 173). [U.S.] Natl. Bur. Stand. (1985).