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Combustibility of Electrical Wire and Cable for Rail Rapid Transit Systems Volume II: Toxicity

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The relative toxicities of the thermal decomposition products of six electrical wiring insulations were evaluated using animal incapacitation and lethality as measures of toxicity. One-gram insulation samples were thermally decomposed in a quartz combustion tube connected in-line with a 12.6-L exposure chamber by an air recirculation assembly to form a closed exposure system. Each material was decomposed under two thermal conditions, the time-to-incapacitation for the "worst case" condition (shortest time) was used to rank the materials in order of their relative potential toxicity. A rank order for the six materials is presented on the basis of potential toxicity for equal weights of insulation. Relative ranking, by toxicity for equal lengths of conductor, is presented also for materials supplied on conductors of equal gauge.

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PREFACE

This report describes the results of a study of the relative toxicities of the gaseous thermal decomposition products from six electrical wiring insulations. The study was conducted by the Aviation Toxicology Laboratory at the FAA Civil Aeromedical Institute (CAMI). The project was funded by the Department of Transportation, Urban Mass Transportation Administration (UMTA), Office of Technical Assistance, and the program was initiated and monitored by the Transportation Systems Center (TSC). The insulation specimens were selected from a larger group of candidate materials in a study of fire-related properties, other than toxicity, performed by Factory Mutual Research of Norwood, Massachusetts. The work described herein was performed between December 1981 and March 1982. It consists of test criteria, animal response data, and a relative ranking of six insulation materials on the basis of the relative inhalation toxicity of their thermal degradation products.

The authors would like to acknowledge the assistance provided by G.D. Hanneman, D.V.M., and J.L. Sershon for experimental animal maintenance and handling. Acknowledgement is also made to I. Litant, TSC Technical Monitor, for his guidance throughout this project.

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METRIC CONVERSION FACTORS

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SYMBOLS AND ABBREVIATIONS

AWG American Wire Gauge,

t,

tr

tr

CO Chemical formula for carbon monoxide.

ECTFE Ethylene chlorotrifluoroethylene.

EPDM Ethylene-propylene-diene-monomer.

EPR Ethylene propylene rubber.

- Loss tr Loss time-to-response, the theoretical response time for a 200-g rat exposed to the gases from a sample of sufficient weight to produce a sample weight loss of exactly 1 g.
- Obs tr Observed time-to-response, the time elapsed between t and the experimental observation of animal response
- OD Optical Density (absorbance), the logarithm to the base 10 of the ratio of incident light intensity divided by transmitted light intensity.
- Std t_r Standard time-to-response, the Obs t_r corrected for the deviation between animal weight and 200 g, and for the deviation, if any, between the sample weight and 1 g. It is the Obs t_r normalized to the response of a 200-g rat to 1-g sample size.
- t d Time-to-death, the time elapsed between t and the time when visible signs of breathing cease in the experimental animal.
 - Time-to-incapacitation, the time elapsed between t_o and animal incapacitation, i.e., when the animal can no longer perform the coordinated act of walking in the rotating cage.
- t Time zero, the time at which thermal degradation of the insulation sample is initiated.
 - Time-to-response, the time elapsed between t_0 and animal response; responses recorded in this study were incapacitation and death. Calculated t_r (in minutes) for a 200-g rat exposed to the gases produced from the insulation on 1 meter of conductor.



EXECUTIVE SUMMARY

Six electrical insulation materials were evaluated for the relative toxic potential of their combustion products using the procedure developed at the Civil Aeromedical Institute (CAMI). See Table ES-1 for a description of the test specimens. Each of the materials was tested under flaming conditions at 750°C with hot-wire ignition, and under nonflaming conditions at 550°C.

For each thermal condition, the relative potential toxicity of the decomposition products from an equal weight of material was assigned a rank-order (from the least toxic to most toxic potential), based on the values of the experimentally observed times-to-incapacitation (t_i) . A rank order was also established for each of the normalized values for t_i , i.e., Std t_i and Loss t_i . The concept of "worst-case performance" was presented as a basis for rating relative toxic hazards of materials, and a rank-order based on this concept was determined for the materials tested.

Based on the "worst-case" results from equal 1-g quantities of insulation placed in the furnace, the relative rank-order of the six materials evaluated is shown in Table ES-2, in order of increasing toxicity.

An additional rank-ordering based on the relative potential toxicity of each insulation for equal <u>lengths</u> of conductor is presented for five of the materials as an example of how test results could be applied to end-use problems. (The sixth material (EPR/Hypalon, #8-14-8-1) was supplied on a different gauge conductor (14 AWG) and could not be compared logically with the other five (12 AWG) by this method.) The sequence, from least to most toxic for worst-case conditions, is shown in Table ES-3.

The authors feel compelled to express their reservations concerning the utilization of these or any relative toxicity data as the sole basis for regulating the selection or usage or polymeric materials. This concern is based on three problem areas associated with extrapolating small-scale laboratory test data to predictions of human incapacitation from smoke in large-scale, uncontrolled fires.

ES-1

These areas are: (i) The toxicity of smoke from any given polymer is highly dependent on the manner in which that polymer is thermally decomposed, and the thermal environment in a test may be significantly different from that in a fire. (ii) The relative toxic ranking of smokes from a set of polymers may be entirely different for humans than for the rodent species used in the small-scale tests. The potential noncorrespondence between species is of especial concern to us for the irritant components of smoke. (iii) The appropriate basis for comparing materials should be relative toxic <u>hazard</u> in a fire, not relative specific <u>toxicity</u>; it is the latter that is estimated by current laboratory tests. Selection of materials on relative toxicity alone could possibly result in substituting a material with a <u>greater</u> potential toxic hazard for one with a lesser hazard.

TABLE ES-1. TEST MATERIAL DESCRIPTION

MATERIAL NO.	DESCRIPTION
1-12-2-1	Single, 65-strand, 12 AWG, tinned copper conductor wrapped with paper and covered with silicone insulation bonded to a polyolefin outer jacket.
6-12-12-1	Single, 19-strand, 12 AWG, tinned copper conductor covered with a single layer of Halar insulation.
3-12-5-1	Single, 7-strand, 12 AWG, tinned copper conductor insulated with EPR, with an XLPO outer jacket.
8-14-8-1	Single, 7-strand, 14 AWG, tinned copper conductor insulated with EPR bonded to a Hypalon outer jacket.
9-12-13-1	Single, 7-strand, 12 AWG, tinned copper conductor insulated with EPDM bonded to a Hypalon outer jacket.
7-12-7-1	Single, 19-strand, 12 AWG, tinned copper conductor covered with a single layer of XLPO insulation.

RANK*	MATERIAL	THERMAL CONDITION	MEAN Std. t _i (Min)
1	1-12-2-1 (Silicone/PO)	550 ⁰ C, nonflaming	21.8
2	3-12-5-1 (EPR/XLPO)	750 ⁰ C, flaming	8.1
3	9-12-13-1 (EPDM/Hypalon)	750 ⁰ C, flaming	7.1
4	7-12-7-1 (XLPO)	750 ⁰ C, flaming	6.7
5	6-12-12-1 (Halar)	750 ⁰ C, flaming	6.4
6	8-14-8-1 (EPR/Hypalon)	750 ⁰ C, flaming	5.6

TABLE ES-2. MATERIAL RANK-ORDER BASED ON WORST-CASE PERFORMANCE FOR STANDARD t

Rank No. 1 is least toxic; No. 6 is most toxic.

TABLE ES-3.	RANK-ORDER EVALUATIONS OF TOXIC	ITY BASED
	ON EQUAL LENGTHS OF INSULATION	

RANK*	MATERIAL	WORST-CASE THERMAL MODE	t¦(×100)**
1	1-12-2-1 (Silicone/PO)	550 ⁰ C, nonflaming	127.7
2	6-12-12-1 (Halar)	750 ⁰ C, flaming	105.4
3	7-12-7-1 (XLPO)	750 ⁰ C, flaming	33.5
4	9-12-13-1 (EPDM/Hypalon)	750 ⁰ C, flaming	28.5
5	3-12-5-1 (EPR/XLPO)	750 ⁰ C, flaming	17.5
	(8-14-8-1 EPR/Hypalon)***	(750 ⁰ C, flaming)***	(6.1)***

*Rank No. 1 is least toxic; No. 5 is most toxic.

** t¦ represents the calculated response time (in minutes) for a 200-g rat exposed to smoke/gas from the insulation on 1 meter of conductor when decomposed in the worst-case thermal mode; see text for t¦ calculation.

*** EPR/Hypalon was supplied on a 14 AWG conductor and could not be ranked, by this method, with the other 5 (all 12 AWG conductors) materials.



1. INTRODUCTION

The purpose of this research was to determine the relative inhalation toxicity of the gases produced by thermal degradation of selected electrical insulation materials. The specific materials to be evaluated were supplied by Factory Mutual Research and were selected from a larger population on the basis of prior tests of properties other than toxicity.

The contract work-statement required that toxicity be evaluated utilizing the basic principles of a system, designed at the Civil Aeromedical Institute (CAMI), that was used for an earlier study of aircraft interior materials (1) and for a previous study of electrical wiring insulations (2). The thermal test parameters were to be established experimentally and were to include a minimum of two decomposition temperatures, as well as a flaming and nonflaming mode. Time-to-incapacitation and time-to-death were to be recorded for each animal; maximal exposure time was to be 30 minutes.

The final requirement was for a systematic and objective protocol for converting the experimentally measured animal response times to a rank-orderlisting of the test materials that would reflect the relative toxic potential of their volatile combustion products -- as generated under the specific laboratory conditions utilized.

1/2



2. METHODOLOGY

2.1 MATERIAL DESCRIPTION

The six test specimens, as received from Factory Mutual Research*, had each been assigned a four-unit identification number; these same numbers were retained throughout this report. A physical description of the weight composition of each conductor and its components, as measured in the CAMI laboratory, is presented in Table 1. The test specimen configurations are described in Table 2 and cross-sectional drawings of each specimen are shown in Figures 1-6.

2.2 SYSTEM DESIGN

The system previously used to rank the toxicity of combustion products from 75 aircraft cabin interior materials (1), with the modifications to the combustion assembly required for testing in flaming and nonflaming modes, was used for this study. This modified system has been described in detail in an earlier study of 14 wiring insulation specimens (2).

The only modification to the system that was not used previously was the substitution of a simple hot-wire igniter for the capacitive discharge assembly. This modification provided successful ignition with less chance for ozone formation and with no recorder disturbance from the high-intensity spark of the capacitive discharge unit. A description of the combustion/exposure system is repeated below for clarity.

The requirement that the materials be tested in both flaming and nonflaming modes necessitated the design of a reliable ignition device and the use of a larger diameter combustion tube than was used for the aircraft interior materials (1). The larger tube decreased the linear velocity of the evolved gases in the vicinity of the igniter and allowed a flammable gas concentration to occur. It also provided a larger mass of diffusible oxygen in the vicinity of the thermal degradation zone.

^{*}Factory Mutual Research

¹¹⁵¹ Boston-Providence Turnpike

Norwood, Massachusetts 02062

MATERIAL	LINEAR DENSITY WIRE & INSULN. (g/cm)	COMPOSITIC WIRE ONLY, INSU WT (%)	JN JLN. ONLY, √T (%)	LINEAR DENSITY INSUL. ONLY (g/meter)	LENGTH/UNIT WT INSUL. ONLY (cm/g)
1-12-2-1 (Silicone/PO)	0.4835	64.6	35.4	17.1	5.85
6-12-12-1 (Halar)	0.3548	82.8	17.2	6.1	16.39
3-12-5-1 (EPR/XLPO)	0.7465	38.3	61.7	46.1	2.17
8-14-8-1 (EPR/Hypalon)	1.0997	16.7	83.3	7.19	1.09
9-12-13-1 (EPDM/Hypalon)	0.4345	42.5	57.5	25.0	4.00
7-12-7-1 (XLPO)	0.4717	57.9	42.1	19.9	5.03

TABLE 1. PHYSICAL DESCRIPTION OF CONDUCTOR AND INSULATION

.

I.

TABLE 2. TEST SPECIMEN CONFIGURATION

MATERIAL	NUMBER OF CONDUCTORS	AWG	INSULATING MATERIAL(S)	REMARKS
1-12-2-1	1	12	Conductor wrapped with paper, covered with silicone bonded to polyolefin outer jacket	65-strand tinned copper conductor
6-12-12-1	1	12	Conductor covered with single layer of Halar insulation	19-strand tinned copper conductor
3-12-5-1	1	12	Conductor insulated with EPR, with XLPO outer jacket	7-strand tinned copper conductor
8-14-8-1	1	14	Conductor insulated with EPR bonded to Hypalon outer jacket	7-strand tinned copper conductor
9-12-13-1	1	12	Conductor insulated with EPDM bonded to a Hypalon outer jacket	7-strand tinned copper conductor
7-12-7-1	1	12	Conductor covered with single layer of XLPO insulation	19-strand tinned copper conductor



Silicone insulation, polylefin jacket. Outside diameter 4.5 mm.

- 1. Polyolefin outer jacket.
- 2. Silicone insulation.
- 3. Paper wrapping.
- 4. Tinned copper conductor, 65 strands.

FIGURE 1. CROSS-SECTION, SAMPLE NO. 1-12-2-1



Halar (ECTFE) Outside diameter 3.1 mm.

- 1. Halar insulation
- 2. Tinned copper conductor, 19 strands.

FIGURE 2. CROSS-SECTION, SAMPLE NO. 6-12-12-1



EPR insulation/XLPO jacket. Outside diameter 6.9 mm.

- 1. XLPO jacket.
- 2. EPR insulation.
- 3. Tinned copper conductor, 7 strands.

FIGURE 3. CROSS-SECTION, SAMPLE NO. 3-12-5-1



Outside diameter 8.8 mm.

- 1. Hypalon jacket.
- 2. EPR insulation.
- 3. Tinned copper conductor, 7 strands.

FIGURE 4. CROSS-SECTION, SAMPLE NO. 8-14-8-1



EPDM insulation/Hypalon jacket. Outside diameter 5.1 mm.

- 1. Hypalon jacket.
- 2. EPDM insulation.
- 3. Tinned copper conductor, 7 strands.

FIGURE 5. CROSS-SECTION, SAMPLE NO. 9-12-13-1



XLPO insulation. Outside diameter 4.5 mm.

- 1. XLPO insulation.
- 2. Tinned copper conductor, 19 strands

FIGURE 6. CROSS-SECTION, SAMPLE NO. 7-12-7-1

The final combustion-exposure assembly is shown in Figure 7. The modified combustion tube consisted of a 2-inch diameter section, 13 inches long, connected to a 3-inch long, 1-inch diameter section by a 2.5-inch long tapered segment. The combustion tube was quartz (Vycor). Total enclosed volume was 12.6 liters.

Thermal destruction of the sample was accomplished with two semicylindrical, electrically resistive heating elements* that were fitted around the combustion tube (see Figure 7 insert) and secured with metal bands. (We found that, even though the heaters encircled the sample, flame initiation could be observed from the chamber end of the furnace.) A thermocouple embedded in the lower heating element was calibrated against a thermocouple in the sample position to provide a reference point for controlling the furnace temperature.

Ignition of the gases evolved from heated samples was accomplished with a hot-wire igniter. This igniter consisted of a pair of stainless steel wire conductors sandwiched between polymethylmethacrylate (PMMA) plates and then extended down the center of the combustion tube. Two loose coils of smaller diameter resistance wires were suspended between the conductors and positioned over the downstream end of the combustion boat. When the external ends of the conductors were connected to a 12-Vdc source, the wire coils rapidly became incandescent and ignited the evolved gases. Combustion boats for containing the insulation samples were constructed from split sections of 1 5/8-inch quartz tubing, 3 inches in length, with the ends partially closed to prevent melted sample material from running into the unheated area of the combustion tube.

Relative smoke densities were measured with a photometer mounted on the upper recirculation tube assembly, about 3 inches downstream from the blower outlet. This smoke-density device consisted of a photodiode behind a Wrattan #25 filter, and was mounted diametrically across the tube from a 6-Vdc tungsten lamp. The light path was 24mm long. The instrument was calibrated with neutral density filters and the results (see Appendix A) are reported in optical density units (OD). The relative performances among materials, and among the various thermal modes, can be evaluated from the OD values reported in those tables. The OD for a 1-meter light path may be calculated by multiplying the OD for the 24-mm path (from tables) by the factor 41.7.

*Watlow Electric Mfg. Co. 12001 Lackland Road St. Louis, Missouri 63141



- 1. Gearmotor, model 3M126, 6 rpm, 1/20 hp; Dayton Manufacturing Company, Chicago, Illinois.
- 2. Animal Exposure Chamber.
- 3. Heating Unit, model NV2X6, 425 W at 57.5 V, semi-cylindrical; Watlow Electric Manufacturing Co., 12001 Lackland Road, St. Louis Missouri.
- 4. Same as No. 3.
- 5. Thermocouple, chromel-alumel; Omega Engineering Inc., Stamford, Connecticut.
- 6. Hot Wire Igniter.
- 7. Combustion Tube.
- 8. Combustion Boat.
- 9. Spring Clamps.
- 10. Smoke Detector.

FIGURE 7. COMBUSTION/EXPOSURE ASSEMBLY

2.3 SAMPLE PREPARATION

Insulation was removed from the single-conductor specimens in sections that were 1-cm to 4-cm long using a manual wire stripper (Stripmaster, Model C, Ideal Industries, Inc., Sycamore, Illinois). These pieces were conditioned for a minimum of 24 hours in a constant humidity chamber ($50 \pm 2\%$ relative humidity), then were cut into approximately 1-cm lengths and the required sample weights were weighed to the nearest 0.01 mg.

The weighed and conditioned pieces were placed in the rear (upstream) third of the semicylindrical combustion boat with the longitudinal axes of the insulation pieces parallel to the length of the boat. With all materials, a single layer of insulation was achieved with all pieces touching the sides/bottom of the combustion boat.

When the boat was pushed into the heated tube with a metal rod, the 1-inch segment containing the sample was centered in the hottest part of the furnace.

2.4 SAMPLE WEIGHT

We found in preliminary experiments that, for five of the six materials, a sample weight of 1.0 g was sufficient to ensure a response time within the 30minute exposure limit. The remaining material, silicone/polyolefin, had to be tested at a 2-g loading for the 750°C flaming mode test in order to obtain incapacitation in less than 30 minutes. This exception is discussed in more detail in Section 3. A 1-g sample weight represents a fuel load (concentration) of 80 mg per liter of enclosed chamber-furnace volume.

2.5 TEST PROCEDURE

Animal selection, fasting, and the general test procedures were essentially identical to those described previously (1). Briefly, the procedure was as follows.

Male rats (100-120 g), Sprague-Dawley derived, were procured from Charles River Breeding Laboratories, Wilmington, Massachusetts. They were held in isolation with 10-12 animals/cage for 8-14 days; for the first 4 days an antibiotic (sulfathiazole) was added to the drinking water. All food and water were removed the afternoon prior to the day of the test. Randomly selected animals were weighed and marked with an identifying color code. All survivors of each

experiment were returned to cages; they were weighed and observed daily for 3 days, or until they expired.

The combustion tube was stabilized at the desired temperature prior to insertion of the test specimen. Immediately on insertion of the sample boat, the recirculation tube was closed; the mixing fans and recirculation blower were turned on; cage rotation was started; thermocouple recorder, analytical systems, and master timer were activated simultaneously. The chamber atmosphere was continuously recirculated through the combustion tube at a rate of 4 L/min.

Oxygen concentration in the exposure system was monitored gas chromatographically and maintained above 19 percent (vol/vol) by manual addition of oxygen as needed. For samples burned in the flaming mode, the igniter was turned on from the initiation of the test until ignition occurred; it was then turned off.

2.6 EXPERIMENTAL DATA COLLECTION

The following measurements and observations were recorded during the course of each experiment.

<u>Animal Responses</u>: Time-to-incapacitation, t_i , was measured in minutes of elapsed time from initiation of thermal degradation (t_0) until the subject no longer exhibited coordinated physical activity in the rotating cage, i.e., until tumbling began.

Time-to-death, t_d , was measured in minutes from t_o until there were no visible signs of respiration.

<u>Smoke Production</u>: The output of the smoke detector was recorded continuously on a strip-chart recorder as a function of time. Three specific items of information from this record were entered into the data log for each experiment, namely, the time at which smoke was first detected, the time(s) at which smoke density peaked, and the magnitude of this maximum density.

<u>Flaming Ignition</u>: The time at which visible flames were first noted, and the time at which they went out, were recorded manually.

<u>Chamber Air Temperature</u>: The temperature was monitored with thermocouples from eight locations in the chamber and recorded throughout the experiment on a multipoint strip-chart recorder. The design protocol was such that chamber air

temperature never exceeded 35[°]C during an experiment, but the thermocouples provided verification of this during an experiment and also reflected the speed and adequacy of air mixing in the dynamic system.

<u>Gas Analyses</u>: A continuous stream of the experimental atmosphere was pumped from the chamber, via 1/8-inch Saran tubing, through gas chromatrographic sample loops and back into the exposure chamber. At approximately 1.8-minute intervals a gas chromatograph (GC) sampled this flowing stream. Carbon monoxide and oxygen were measured by this procedure throughout the experiment.

<u>Sample Weight Loss</u>: At 10 minutes the recirculation blower was shut off, the combustion assembly was disconnected from the chamber, and the chamber outlets were sealed. Observation continued until the third animal died or until 30 minutes had elapsed. The sample boat was removed from the furnace, cooled, and reweighed. The original sample weight minus this residual weight yielded the nominal weight of material lost during the decomposition.

2.7 DATA NORMALIZATION PROCEDURES

Animal response times, as measured experimentally, are referred to as <u>observed</u> (Obs) response times. Corrected response times that take into account the deviation of an animal's body weight from 200 g are referred to as <u>standard</u> (Std) response times for a 1.0-g sample size. Observed times are converted to standard response times as follows (1):

Std
$$t_r = 0bs t_r .(200 g/body wt., g)^{0.25}$$
.

Loss t calculates a theoretical Std t for the case in which sufficient weight of sample is placed in the furnace to produce a loss in sample weight of exactly 1.0 g. This conversion is accomplished as follows (1):

Loss
$$t_r = Std t_r \cdot \left[\frac{Sample wt. lost}{Sample wt.} \right]$$

2.8 PRELIMINARY TESTS

The state-of-the-art in combustion toxicology is such that one cannot predict at this time how the toxicity of the resultant gas mixture will vary with the conditions of the thermal degradation. For these tests, therefore, it was felt that a minimum of two temperatures should be used, and those temperatures should be ones that could be expected realistically to occur in actual fires. In addition, it was felt that one temperature should produce rapid thermal decomposition but not produce spontaneous flaming, and the second test temperature should produce flaming combustion, either spontaneous or induced by electrically heated wire -- but self-sustaining in either case.

Preliminary tests indicated that satisfactory decomposition could be attained for all six insulation materials at 550° C without incurring spontaneous ignition. Carbon monoxide production was measured at 550° C and was considered adequate to produce rat incapacitation within the 3-minute exposure period. At 750° C, decomposition of all materials was rapid enough to allow ignition with the hot-wire igniter. Therefore, 550° C was selected for the nonflaming mode and 750° C (with hot-wire ignition) was selected for the flaming mode.

3. RESULTS AND DISCUSSION

3.1 PRELIMINARY EXPERIMENTS

Experience with the previously-tested 14 insulation materials (2) indicated that a cross-linked polyolefin would ignite spontaneously at a temperature as low as 475°C. Since a material of similar composition was included in the six insulations being tested, small specimens of each of the six were pyrolyzed at 475°C to determine whether complete decomposition would occur without flaming. Most of the materials failed to decompose rapidly at this temperature. Visible smoke occurred late in the heating period and residues generally indicated incomplete decomposition.

The cross-linked polyolefin (#7-12-7-1) was retested at 550°C; no spontaneous ignition occurred, and at this temperature pyrolysis of all of the materials was rapid enough to produce an animal response (t_i) during the 30minute exposure period. All materials were tested therefore at 550°C for the nonflaming portion of this study.

Flaming combustion proved possible, either spontaneously or with hot-wire ignition, at 750°C for all materials; this temperature was utilized, therefore, for flaming mode combustions.

3.2 TOXICITY VERSUS THERMAL MODE

Five of the six materials proved more toxic (shorter t_i) in the flaming mode than they did nonflaming. The remaining material, silicone/polyolefin (#1-12-2-1) was more toxic in the 550°C nonflaming mode. A comparison of the effect of thermal protocol on the relative toxicities of each material, as measured by standard times-to-incapacitation, is presented in Table 3. The determination of statistically significant differences between modes of pyrolysis was made on the basis of Student's t-test.

	HEATING R	EGIMENS	STD t _i '	s (MEAN)	t-test(a vs. b)*
MATERIAL NO.	Б	b	a	b	<u>Result,(t(0.9755))</u>
	750544		20.0		
- 2-2-	/50F**	550NF	39.9	21.8	+
3-12-5-1	750F	550NF	8.1	15.4	+
6-12-12-1	750F	550NF	6.4	7.8	+
7-12-7-1	750F	550NF	6.7	16.7	+
8-14-8-1	750F	550NF	5.6	13.3	+
9-12-13-1	750F	550NF	7.1	11.2	+

TABLE 3. ANIMAL RESPONSE DIFFERENCES TO TWO HEATING REGIMENS

*(+) = different (t (0.975)); (-) = no difference (t (0.975)).

**750F = 750° C, flaming; 550NF = 550° C, nonflaming.

3.3 550°C NONFLAMING CONDITION

Nonflaming thermal degradation results are summarized in Table 4 for observed response times, in Table 5 for standard response times, and in Table 6 for response times normalized to an equivalent sample weight loss of 1.0 g (Loss t_r). The materials are listed within each table, from top to bottom, in order of increasing toxicity based on incapacitation time. The raw data collected during these tests appear in Appendix A, Table A-1.

The changes in position of materials from Tables 4 and 5 to Table 6 are reflections of the fractional part of each sample that was not thermally decomposed during its 10-minute heating regimen in the furnace. The largest change in rank position between standard and loss t_i 's was for the silicone/polyolefin material (#1-12-2-1) which dropped from first to fourth place, probably because only about 40 percent of the sample was vaporized, thereby producing a large change in the Loss- t_i value.

TABLE 4. OBSERVED RESPONSES TIMES, 550°C NONFLAMING CONDI	SES TIMES, 550°C NONFLAMING CONDITIC	BLE 4. OBSERVED RESPONSE
---	--------------------------------------	--------------------------

MATERIAL	N*	MEAN Obs t _i (Min)	SD	MEAN Obs t _d (Min)	SD)	MORT 30-Min	ALITY 3-Days
1-12-2-1 (Silicone/PO)	3	22.4	1.30	33.8**	6.27	1/3	3/3
7-12-7-1 (XLPO)	3	17.5	0.26	26.2***	4.46	2/3	3/3
3-12-5-1 (EPR/XLPO)	3	15.7	0.15	22.6	1.65	3/3	3/3
8-14-8-1 (EPR/Hypalon)	3	13.9	0.51	20.1	2.94	3/3	3/3
9-12-13-1 (EPDM/ Hypalon)	3	11.6	0.44	15.9	0.15	3/3	3/3
6-12-12-1 (Halar)	3	8.0	0.35	9.9	0.32	3/3	3/3

FIGURE 5. STANDARD RESPONSE TIMES, 550°C NONFLAMING CONDITION

ΜΛΤΕΡΙΛΙ	N1*	MEAN Std t (Min)	SD	MEAN	SD	MORTA 30 Min	LITY
	11.4						S-Days
1-12-2-1 (Silicone/PO)	3	21.8	1.59	32.9	5.94	1/3	3/3
7-12-7-1 (XLPO)	3	16.6	0.16	25.0	4.10	2/3	3/3
3-12-5-1 (EPR/XLPO)	3	15.4	0.10	22.1	1.52	3/3	3/3
8-14-8-1 (EPR/Hypalon)	3	13.3	0.68	19.4	3.16	3/3	3/3
9-12-13-1 (EPDM/							
Hypalon)	3	11.2	0.54	15.4	0.28	3/3	3/3
6-12-12-1 (Halar)	3	7.8	0.31	9.7	0.35	3/3	3/3

FIGURE 6. LOSS RESPONSE TIMES, 550°C NONFLAMING CONDITION

MATERIAL	N*	MEAN Loss t _i (Min)) SD	MEAN Loss t _d (Min)	SD	MOF 30-Mi	TALITY n 3-Days
		I					
7-12-7-1(XLPO)	3	14.1	0.13	21.1	3.47	2/3	3/3
8-14-8-1 (EPR/Hypalon)	3	9.8	0.50	14.2	2.32	3/3	3/3
3-12-5-1 (EPR/XLPO)	3	9.0	0.06	13.0	0.89	3/3	3/3
1-12-2-1 (Silicone/PO)	3	8.4	0.61	12.7	2.29	1/3	3/3
6-12-12-1 (Halar)	3	7.8	0.31	9.7	0.35	3/3	3/3
9-12-13-1 (EPDM/ Hypalon)	3	7.1	0.34	9.7	0.17	3/3	3/3
*Number of experimental **Observed deaths from s	an amp	imals expose le 1-12-2-1	d. were	at 30.9, 29.	5, and	41.0	minutes,

respectively. ***Observed deaths from sample 7-12-7-1 were at 31.3, 24.3, and 23.0 minutes,

respectively.

3.4 750°C FLAMING CONDITION

The results of tests conducted under flaming conditions are presented in Tables 7, 8, and 9. Raw data are in Appendix A, Table A-2. As at the lower temperature, the silicone/polyolefin insulation (#1-12-2-1) was the least toxic of the six materials at 750°C. An initial test with 1 g of the material failed to incapacitate any of the experimental animals during the 30-minute exposure period. A second test using 2 g produced a mean observed t_i of 21.3 minutes, from which the mean standard t_i (corrected to a 1-g sample size) of 39.9 minutes was calculated. Even with the double-sized fuel loading, none of the animals died during the 30-minute exposure or the 3-day post-exposure observation.

Halar (#6-12-12-1) was completely burned at 750° C with no measurable residue. It is interesting to note that although the observed, standard, and loss, mean t_i values for Halar are identical, the toxicity ranking moved from fifth place, based on observed and standard t_i's, to second place for Loss t_i. Thus the shift in Halar's relative toxicity ranking is due to the effect of the appreciable residue of noncombustible materials in the insulations with which it is compared.

3.5 RANKING OF MATERIALS BY RELATIVE TOXIC POTENTIAL

<u>Time-To-Incapacitation vs. Time-To-Death</u>: The rationale for the preference of t_i over t_d as a physiological endpoint for combustion toxicity studies is a compelling one for the following reasons: (1) It has been the general observation that many, if not most, potential victims in a developing fire situation either remove themselves from the hazardous environment or perish in it. In such situations, the onset of physical incapacitation and the corresponding loss of the ability to escape are tantamount to death. (2) In the evaluation of animal responses to the combustion products from hundreds of materials, a rather general observation has been the lack of any constant value for the t_d/t_i ratios among the various materials. For some atmospheres death occurs rather soon after incapacitation; for others incapacitation may occur as early as 5 minutes after t_o , with all animals surviving the total 30-minute exposure period (1). It is therefore obvious that, if incapacitation is equivalent to nonsurvival, the relative threat posed by different materials could be significantly misrepresented if the materials were ranked according to the t_d 's they produced.

TABLE 7. OBSERVED RESPONSE TIMES, 750°C FLAMING CONDITION

MATERIAL	N* Obs	MEAN 5 t _i (Min)	SD	MEAN Obs t _d (Min)	SD	MORTA 30-Min	LITY 3-Days
1-12-2-1 (Silicone/PO)	3	21.3**	0.35	NR***		0/3	0/3
3-12-5-1 (EPR/XLPO)	3	8.1	0.10	10.7	0.51	3/3	3/3
9-12-13-1 (EPDM/ Hypalon)	3	7.2	0.53	11.9	0.67	3/3	3/3
7-12-7-1 (XLPO)	3	6.7	0.38	9.7	0.49	3/3	3/3
6-12-12-1 (Halar)	3	6.4	0.17	8.4	0.81	3/3	3/3
8-14-8-1 (EPR/Hypalon)	3	5.8	0.50	8.9	1.30	3/3	3/3

*Number of experimental animals exposed.

**The 21.3 in response listed is for a 2-gram sample of material 1-12-2-1 only. A l-gram sample of this material decomposed under these conditions failed to incapacitate any of the rats during the 30-minute exposure period.

***NR = no response, i.e. no deaths within the 30-minute exposure period.

TABLE 8. STANDARD RESPONSE TIMES, 750°C FLAMING CONDITION

MATERIAL	N	MEAN Std t _i (Min)	SD	MEAN Std t _d (Min)	SD	MORT. 30-Min	ALITY 3-Days
1-12-2-1 (Silicone/PO)	3	39.9*	0.49	NR**		0/3	0/3
3-12-5-1 (EPR/XLPO)	3	8.1	0.25	10.7	0.62	3/3	3/3
9-12-13-1 (EPDM/ Hypalon)	3	7.1	0.43	11.8	0.82	3/3	3/3
7-12-7-1 (XLPO)	3	6.7	0.26	9.6	0.50	3/3	3/3
6-12-12-1 (Halar)	3	6.4	0.25	8.5	0.92	3/3	3/3
8-14-8-1 (EPR/Hypalon)	3	5.6	0.46	8.5	1.14	3/3	3/3

*The 39.9-min standard t_i was calculated from the observed response to a 2-gram sample of material 1-12-2-1. Rats exposed to gases from a 1-gram sample of the material were not incapacitated in the 30-min exposure period.

**NR = no response, i.e., no deaths within 30-minute exposure period.

MATERIAL	NI	MEAN Loss t _i (Min)	SD	MEAN Loss t _d (Min)	SD	MORT/ 30-Min	ALITY 3-Days
1-12-2-1 (Silicone/PO)	3	16.2*	0.20	NR		0/3	0/3
6-12-12-1 (Halar)	3	6.4	0.25	8.5	0.92	3/3	3/3
7-12-7-1 (XLPO)	3	5.8	0.23	8.3	0.43	3/3	3/3
3-12-5-1 (EPR/XLPO)	3	4.9	0.15	6.5	0.37	3/3	3/3
8-14-8-1 (EPR/Hypalon)	3	4.1	0.34	6.2	0.83	3/3	3/3
9-12-13-1 (EPDM/ Hypalon)	3	2.6	0.16	4.3	0.30	3/3	3/3

TABLE 9. LOSS RESPONSE TIMES, 750°C FLAMING CONDITION

*The mean loss t_i was calculated from the observed response to the gases from a 2-gram sample of material 1-12-2-1. Rats exposed to gases from a 1-gram sample were not incapacitated during the 30-minute period.

NR = no response, i.e., no deaths within the 30-minute exposure period.

Observed t_i vs. Normalized t_i : In the experimental measurement of inhalation toxicity, it is obvious that the quantity of toxic gas(es) taken into the lungs over a specified time interval is a function of the experimental subject's volumetric respiratory rate (VRR). Since it is well known that, for a given activity level, an animal's VRR is a function of its body mass (3), it follows that the magnitude of an inhalation dose acquired over a given interval of time will also be a function of its body mass.

In the case of those toxic gases that react stoichiometrically with some vital biological component(s), such as hemoglobin, cytochromes, enzymes, or any essential metabolite, one would expect to observe a quantitative relationship between the acquired dose of toxicant and the degree of the biological response to that dose. Gases such as carbon monoxide (CO) and hydrogen cyanide (HCN) are examples of toxic agents exhibiting this relationship, and our prediction is that hydrogen sulfide will also. We have previously shown (1) that, for CO and HCN, the effective dose required to elicit a given response is directly proportional to body mass, and the rate at which that dose is acquired by inhalation is inversely related to body mass raised to the 0.25 power -- Wt^{0.25}; therefore, two animals having different body weights would have respective response times (to identical atmospheres of CO and/or HCN) such that their ratio would equal the ratio of their respective body weights raised to the 0.25 power:

$$t_r/t_r' = \left[Body Wt/Body Wt' \right]^{-0.25}$$
.

One can take advantage of this relationship, under the proper circumstances of a toxicity that is primarily due to stoichiometrically reacting gases, to correct for the inability to have all experimental animals at a single body weight on the day of an exposure. This is the normalization that we have called Std t_r and it signifies that the t_r's for all animals have been mathematically converted to that t_r equivalent to a body mass of 200 g.

The authors have no hesitation concerning the use of this normalization in those cases for which the major toxic components of an atmosphere are one or more of the aforementioned gases. The validity of such an approach has been strengthened in the past by the observation that the precision of replicate measurements of t_i (as measured by relative standard deviations) increases significantly when Obs t_i is converted to Std t_i .

In the present study it was difficult to determine that normalization to a body weight of 200 g represented any decided improvement in precision, for the relative standard deviations (SD/mean) for Std t_i are less than for Obs t_i in only about one-half of the cases. This could mean that for these specialized materials there was less stoichiometry, between the quantity of toxic gases inhaled and the magnitude of the biological response, than had been the case for materials in general, and probably reflects their increased production of irritating gases.

For the present we still favor basing our final comparative evaluations on Std values, but we are including all of the data for nontransformed measurements (Obs t_r's) so that others may evaluate this decision (see Appendix A).

An additional normalization that the authors have utilized previously, as well as in the present report, is Loss t_r . The validation for this conversion also pertains only to experiments conducted with the stoichiometrically reacting gases. We have observed that, within experimental error, doubling the concentration of one of these gases doubled the biological response of the animal; that is, $(1/t_r)$ was doubled, or the t_r was halved. We further observed that when the quantity of a polymeric material placed in the furnace was doubled, the production of CO or HCN essentially doubled. Therefore, within reasonable limits, animal response was directly proportional to sample weight in those cases for which the major toxic products were CO, HCN, and/or hydrogen sulfide.

The rationale for reporting Loss t_r 's in the present report was the fact that some of the samples contain components that are thermally stable. Consequently, for some materials the atmospheres to which the animals were exposed represented the decomposition products from the entire gram of material placed in the furnace, while for other materials that were also loaded at the l-gram level, the decomposition products were evolved from something less than 1 gram.

For many readers, the Loss t_r values may be of little or no interest, but for the benefit of those who may have an interest in comparing relative toxicities for equal weights of material decomposed we have chosen to include them.

<u>Concept of Worst-Case Performance</u>: It has been our experience, with almost 200 materials, that no single mode of thermal degradation consistently yields a more toxic product mixture than any other mode. For this reason we support, at this time, the principle that the toxic rating by which one material

should be compared with another should be the most toxic response obtained for each material, regardless of which thermal decomposition mode produced that response -- that is, so long as the thermal conditions represent those to which a material could be reasonably expected to be exposed in a real fire situation.

Therefore, we have identified for each material in this study the shortest t_i produced by either of the thermal modes and designated this as the "worst-case" rating for that material. This process has been repeated for each of the three types of t_r 's presented (Obs, Std, and Loss). These selected worst-case values were then arranged in the order of decreasing t_i magnitude (increasing toxicity). The results are shown in Tables 10, 11 and 12 for Obs, Std, and Loss t_i , respectively. These tables also identify that thermal mode responsible for the worst-case performance.

As stated earlier, we would normally base our evaluation at this time on the "worst-case performance, Std t_i " (Table 11). This would be the case for this report also were it not for the fact that the material category of electrical insulation requires additional consideration. These considerations are discussed below.

Ranking of Electrical Insulation on the Basis of Potential Toxic Hazard per Unit Length of Conductor: It seems most logical to rank materials on the basis of those weights of each material that would be necessary to satisfy the same end-use requirement. For conductor insulation, this would be the quantity needed to cover a specified length of electrical conductor of a specified wire gauge. Therefore, the proper basis for comparison would be the weight of insulating material per unit length of equal-gauge conductor, e.g., grams of material per meter.

Once a measure of relative toxicity based on equal sample weights (e.g., Std t_i) has been accomplished, it is a simple arithmetic exercise to convert to relative toxicity based on equal lengths. (This conversion does assume that, for a given material, toxicity is proportional to sample weight.) Response times normalized in such fashion are designed t'_r . It is these respective t'_r values that would be utilized to compare the relative potential toxicities of alternate materials, and they would be calculated as follows:

$$r = \frac{t \cdot a \cdot b}{100},$$

t

RANK*	MATERIAL	THERMAL CONDITION**	N***	Obs t _i (Min)	SD^+
]	1-12-2-1 (Silicone/PO)	550NF	3	22.4	1.30
2	3-12-5-1 (EPR/XLPO)	750F	3	8.1	0.10
3	9-12-13-1 (EPDM/Hypalon)	750F	3	7.2	0.53
4	7-12-7-1 (XLPO)	750F	3	6.7	0.38
5	6-12-12-1 (Halar)	750F	3	6.4	0.17
6	8-14-8-1 (EPR/Hypalon)	750F	3	5.8	0.50

TABLE 10. MATERIAL RANK-ORDER BASED ON WORST-CASE PERFORMANCE FOR OBSERVED t MEAN

TABLE 11. MATERIAL RANK-ORDER BASED ON WORST-CASE PERFORMANCE FOR STANDARD t

RANK*	MATERIAL	THERMAL CONDITION**	N***	Std t _i (Min) ⁱ	SD^+
]	1-12-2-1 (Silicone/PO)	550NF	3	21.8	1.59
2	3-12-5-1 (EPR/XLPO)	750F	3	8.1	0.25
3	9-12-13-1 (EPDM/Hypalon)	750F	3	7.1	0.43
4	7-12-7-1 (XLPO)	750F	3	6.7	0.26
5	6-12-12-1 (Halar)	750F	3	6.4	0.25
6	8-14-8-1 (EPR/Hypalon)	750F	3	5.6	0.46

TABLE 12. MATERIAL RANK-ORDER ON WORST-CASE PERFORMANCE FOR LOSS t

RANK*	MATERIAL	THERMAL CONDITION**	N***	MEAN Loss t _i (Min)	SD ⁺
1	1-12-2-1 (Silicone/PO)	550NF	3	8.4	0.61
2	6-12-12-1 (Halar)	750F	3	6.4	0.25
3	7-12-7-1 (XLPO)	750F	3	5.8	0.23
4	3-12-5-1 (EPR/XLPO)	750F	3	4.9	0.15
5	8-12-8-1 (EPR/Hypalon)	750F	3	4.1	0.34
6	9-12-13-1 (EPDM/Hypalon)	750F	3	2.6	0.16

*Rank: 1 is least toxic.
**550NF = 550°C, nonflaming; 750F = 750°C, flaming.

*** N = Number of experimental animals exposed.

 † SD = Standard deviation.

where

 t'_{r} = calculated t_{r} for 1 meter of conductor, in min t_{r} = response time for 1 g of insulation, in min a = length of insulation per gram, in cm b = number of conductors per assembly 100 = cm/meter.

In the specific case where two or more materials were to be compared (for relative toxicity of thermal degracation products), one could summarize as follows:

- a. Ideally each insulation test specimen should be taken from wires of the same gauge, should be of equal weight (1 g), and should reflect the cross-sectional composition of the original system. The weight of insulation per unit length of wire should also be determined. With these data one can then compare materials on the basis of a response time calculated directly for the total weights of each material necessary to accomplish the same job.
- b. If the materials under consideration have not been tested under conditions specified in (a), but have been (or can be) tested as equalweight specimens from wires of different gauges, one <u>may be</u> able to calculate appropriately relative response times, under certain conditions. For example, if a material, samples from X-gauge, were to be used as a Y-gauge installation, one could calculate an appropriate Y-gauge t_r provided the insulation is either (i) homogeneous for both gauges, or (ii) heterogeneous but of constant cross-sectional composition in both the X- and Y-gauges.
- c. If conditions described for (b) are not met, then valid comparisons can be made <u>only</u> from tests made directly on each candidate material. If these tests have not been made, or the appropriate materials are not available for conducting such tests, then those materials simply cannot be evaluated for relative toxic potential.

For the six materials in this study the t_i -values based on worst-case performance are presented in column 4 of Table 13. Rank numbers are assigned only to the five materials that were supplied on 12 AWG conductors; the sixth

RANK-ORDER EVALUATIONS OF TOXICITY BASED ON A CALCULATED t (WORST-CASE PERFORMANCE) FOR EQUAL LENGTHS OF INSULATION FROM EQUAL-GAUGE WIRE ASSEMBLIES* TABLE 13.

CTIV	AWG	14	12	12	12	12	12
NO. OF	CUNDUCIONS FER ASSEMBLY	L	L	L	L	L	L
	SD ^{††}	0.50	9.3	4.2	1.3	1.7	0.54
	t _i (×100) [†]	6.1	127.7	105.4	33.5	28.5	17.5
WORST - CASE	NODE***	750F	550 NF	750F	750F	750F	750F
	MATERIAL	8-14-8-1 (EPR/Hypalon)	1-12-2-1 (Silicone/PO)	6-12-12-1 (Halar)	7-12-7-1 (XLPO)	9-12-13-1 (EPDM/Hypalon)	3-12-5-1 (EPR/XLPO)
	RANK**	*		2	m	4	IJ

 * Only those wire assemblies containing equal-gauge conductors are ranked as to relative toxocity.

**
 Rank = 1 is least toxic; relative rank is based on the calculated response time for that quantity of
 insulation from one meter of wire. All materials in this series were of the single conductor type. *** 550NF = 550°C, nonflaming; 750F - 750°C, flaming.

 $_{\uparrow\uparrow}^{T}$ Three animals were exposed per material in each thermal mode; see text for t $_{\dot{i}}$ calculation.

SD = Standard deviation.

material (#8-14-8-1, EPR/Hypalon) was supplied on a 14 AWG conductor and cannot be ranked logically with the others on the basis of t_i . Rank was based on the relative magnitude of t_i , which represents the predicted time-to-incapacitation (in minutes) for a 200-g rat exposed to the gases from the weight of insulation on 1 meter of wire thermally decomposed under the conditions in column 3 (Thermal Mode). Note that all table values of t_i have been multiplied by 100 for tabular convenience. Therefore, the t_i that one would predict from the quantity of XLPO (#7-12-7-1) found on 1 meter of 12 AWG wire would be 0.335 minute (0.335 x 100 = 33.5). For the 12 AWG wires, on an end-use basis, the silicone/polyolefin (#1-12-2-1) would seem to be the least-toxic choice of the five, and the EPR/XLPO (#3-12-5-1) would be the most toxic.

The change in rank order of relative toxicity that was observed for EPR/ Hypalon, when rank was based on conductors of equal length (Table 11 versus Table 13), is a significant and meaningful one. This material dropped from rank 2, which had resulted from testing equal <u>weights</u> of insulations, to rank 5 (of the 5 AWG-12 conductors) when comparison was based on equal <u>lengths</u> of insulations. The reason for this dramatic change is evident upon inspection of Table 1. We see that 1 meter of insulation (#3-12-5-1) weighs 46.1 g, which is the largest linear density of the five 12-gauge systems; therefore, this EPR/ XLPO has the heaviest insulation per unit length of any of the five -- more than 7.5-times the insulation weight of Halar, for example. It is this large quantity of insulation per unit length that elevates the real-world, end-use, relative toxic potential of EPR/XLPO from second-best, when compared by equal weights (Table 11), to that with the greatest potential hazard when comparison is based on equal lengths of insulation (Table 13).

A second example of significant change in rank order occurred with Halar (#6-12-12-1). In this case Halar went from rank 5 (of the 5 AWG-12 conductors), based on standard t_i, to rank 2 (second only to the least-toxic Silicone/PO) when ranked by toxicity for equal conductor length. Again the determining factor was the weight of insulation required for a given length of conductor. One gram of Halar insulates 16.39 cm of AWG-12 conductor, but an equal weight of XLPO (#7-12-7-1), its nearest competitor, will only insulate 5.03 cm of conductor. Thus over three-times the weight of XLPO is required to satisfy the same end-use requirement when compared to Halar; thereby negating the slightly lesser toxicity (per unit weight) of the XLPO. These examples serve to illustrate that

considerations other than relative toxicity for equal weights of material may be of paramount importance when a conductor is selected for a specified end use.

3.6 CAUTIONS AND LIMITATIONS

It is obvious that the discipline of combustion toxicology is yet an immature one, struggling even to establish itself as a descriptive science. And yet, because of the real need for solutions to potentially serious problems that face society -- and technology -- today, this neonatal area of research is being pressed for performance -- answers, predictions, correlations, etc. -that is at, or maybe beyond, the very limits of its capabilities.

The data reported herein were derived by a protocol that basically has been used for several years to evaluate approximately 200 polymeric materials and several discrete gases. The authors have little concern over the repeatability of the reported results, nor for the interpretations based on them, so far as their application to this one system is concerned. However, performance in this small-scale laboratory system is not, <u>per se</u>, one of the aforementioned serious problems facing society. There is, at the present time, little scientifically demonstrated evidence that the toxic behavior of real materials involved in real fires can be successfully predicted by <u>any</u> laboratory-scale model. There is even more disagreement than agreement among the results of various laboratories utilizing these protocols, as to the relative toxic potential of materials.

Some laboratories have adopted protocols that are significantly different from the CAMI approach for obtaining such relative values (4,5,6,7,8) and, despite a methodological precision in the reproduction of results that for some may approach that of the CAMI method, the relative toxicities assigned to the same materials by these various procedures may differ significantly, or even dramatically.

As an example, Anderson and Alarie (4) reported the relative evaluation of 17 polymeric materials. They utilized two separate protocols and reported that polytetrafluoroethylene (PTFE) was the most toxic of the 17 materials, was "... more than 100-times more toxic than Douglas Fir," and belonged in the category of "Super Toxic" materials. Previous evaluations of Douglas Fir by the CAMI protocol found it to have a Std t; of 5.3 minutes, while PTFE insulation had a

Std t_i of 6.7 minutes (2). The CAMI protocol therefore would rate PTFE as being equal to, or even less toxic than Douglas Fir, rather than <u>over 100 times</u> more toxic.

Hilado et al. (5) compared results from the USF*/NASA methodologies with those obtained with the FAA/CAMI protocol for the same materials; in none of seven separate temperature-profile variations of the USF/NASA method were the four test materials ranked in the same order as they were by the FAA/CAMI system. More significantly, all seven USF variations consistently ranked an ABS polymer "most toxic" while the CAMI method ranked it "next-to-the-least toxic."

Many such examples could be cited, and the inescapable conclusion is that one must combine caution with common sense in any attempt to relate such laboratory exercises to any environmental frame of reference other than that one from which the data originated.

The authors must therefore emphasize that the results reported in this study, and the interpretations based on those results, may not be directly applicable to thermal situations other than those utilized in the generation of the data. It is especially important to realize that the relative merit assigned to materials as a result of these tests could be entirely different from their relative toxicological merit based on behavior in a full-scale, uncontrolled fire.

In addition to caveats based on the potential nonrelevancy of the smallscale thermal environment, there is a final caution that is almost universally overlooked. The experimental animals utilized in these tests -- and in most, if not all, combustion toxicity testing -- are <u>rodents</u>. Although we feel the extrapolation from rodent to man can be a meaningful one in the case of CO, HCN, and hydrogen sulfide (when done properly), we are beginning to have serious reservations concerning the relevancy of the rodent as a human model for the irritant gases. And as most everyone is aware, who has ever smelled it, smoke from almost any fire is irritating to the respiratory tract. So, to the extent that a smoke contains irritant components, we could be seriously underestimating the toxic hazard of that smoke for humans.

*USF: University of San Francisco.

3.7 SUGGESTIONS FOR FUTURE RESEARCH

The previous discussion of cautions and limitations pertaining to the use of data such as those reported herein has suggested already the identity of problem areas that need further research. Serious and conscientious researchers, as well as regulatory officials, will continue to recommend only limited use of inhalation toxicity data until such time as those problems are resolved. In the opinion of the author, there are three such areas; the research needs for each of these will be discussed briefly.

<u>Thermal Decomposition</u>: It has been the experience of many laboratories conducting combustion-inhalation toxicity research that almost any change in the procedure used to thermally decompose a polymeric specimen will produce a change in the composition of the thermal degradation products (TDP) and, therefore, in the measured toxicity of such products for the subject animal species. Parameters known to influence these results include the following:

- (a) Rate at which thermal energy is transferred to the specimen. [This rate influences both the atmospheric concentration of TDP and the chemical composition of the products; these parameters directly influence inhalation toxicity assays, especially for the case of a composite (nonhomogeneous) bulk fuel specimen.]
- (b) Distribution of thermal energy transfer among the three types: radiative, convective, and conductive.
 [Many laboratory test procedures in use today transfer heat to the test specimen primarily by the conductive mode; in most real fires this transfer mode is the least significant of the three.]
- (c) Physical size and geometry of the specimen pieces. [Size of individual pieces influences rate of thermal decomposition for any specimen type; for composite specimens, it and the geometry influence the chemical composition of the TDP throughout the burn.]
- (d) Orientation of test specimen with respect to thermal sources(s).
 [Orientation is a factor primarily for composite specimens; it influences the temporal degradation sequence of individual components and, thus, the TDP composition as a function of time.]

(e) Ratio of the oxygen consumption rate to the rate at which oxygen can be replaced in the gaseous environment immediately surrounding the thermal decomposition process.

[This ratio influences toxicity by controlling the overall oxidation state of the final TDP. When materials are burned in air, in a real fire, this ratio is a function of the relative size of the convection cell that is renewing the oxygen supply at the base of the hot updraft. When, in the test situation, the thermal decomposition takes place in an enclosed space of such small volume (compared to the size of the specimen) that the rate of oxygen renewal is less than it would be in the real fire, then the TDP generated will be in a less-highly oxidized state. This means they will also exhibit a different toxicity rating than those produced in the real fire.]

There is an immediate need to design and conduct parametric studies that would examine critically the relative effect of changes in each of these areas on the composition and toxicity of TDP. The common basis for comparison should be the TDP produced from the same fuel material when burned under conditions that describe the specific type of "fire" for which that material is being tested. It is likely that not all the factors would have a <u>significant</u> impact on measured toxicity. Also, only two or three types of fires might have to be considered, for any given material, either because that material would not be used in ways that would expose it to totally different fires, or because its TDP did not change significantly with type of fire.

Until the question is settled--how closely the thermal test parameters must match the real fire model--there will continue to be some concern about the significance of toxicity test data.

Animal Model Relevancy. Rodents have always been the test animals of choice for most types of toxicity testing, and in a majority of those instances they have provided us with quite useful data. This was particularly true when the desired information related to maximum exposure levels that would not be detrimental to human health in any way.

In the area of current debate, concerning the measurement of relative toxicity of smokes, we are not concerned, however, with establishing <u>safe</u>

levels of smoke (or TDP). (If we were, smoke simply would not be authorized and all materials that could serve as potential fuels for an undesired fire would have to nonflammable!) Instead, we are attempting to design procedures by which the potential toxicity of smoke from one material can be measured relative to that of another material. Such relative toxic potential ratings could then be used as <u>one</u> of the components in an overall evaluation of relative fire hazard. Hopefully this information could then be used to select among materials so that the highly toxic smoke from any given fire situation could be reduced to the minimum commensurate with required engineering and economic factors. The modified environment would, however, still be a highly toxic one.

Using animals as models for humans requires a higher degree of correspondence between the two species when the objective is to measure changes in actual, expressed toxicity than when one is simply seeking a nontoxic exposure concentration--especially when in the latter case it is not unusual to add on safety factors of 2, or 10, or even 100. It would seem, therefore, that if rodents were to be used as human models for evaluating smoke toxicity, we should have established a mechanism for calculating a reliable human dose-response curve from rodent dose-response data. No one has accomplished this, to data, for all the major toxic components of smoke.

As a result of our own research, we feel confident about the correspondence between rodent and human dose-response relationships for the systemic toxic gases (such as CO, HCH, and hydrogen sulfide) and for the gases having an anesthesia-like effect (such as some hydrocarbons and ethers). We are concerned, however, that there could be a serious problem with the use of rodents in evaluating the effect on humans of irritant gas components of smoke.

For several irritant gases, the short-term (10 to 30 min) lethal concentrations for rodents have been found to be 100 or more times greater than what has been suggested as incapacitating concentrations for humans. Since all smokes contain irritant components, this could mean that the use of rodents would <u>underestimate</u> for humans the toxicity of all smokes, but not with equal bias. Those smokes with the higher relative irritant content would be rated erroneously as less toxic than those with a lower content.

The selection and experimental validation of an acceptable laboratory animal model for these evaluations should be given a high priority in the combustion toxicology research effort, as should the more accurate estimation of human tolerance limits.

Measured Toxicity vs toxic Hazard. Assuming that procedures now being used for measuring the potential smoke toxicity of a set of materials were reliable, some applications of such data are being made inappropriately. Toxicity "numbers" that come from tests of equal weights or equal surface areas of materials should not be compared directly to determine relative rank unless the materials in the end-use situation (where the real fire would occur) are also utilized in equal weights or areas.

Even the correction of measured toxicities for the relative quantities in the end-use configuration does not necessarily convert measured toxicity into potential toxic hazard. Since an important consideration is surviving a fire is not only the magnitude of the eventual smoke toxicity but also the rate at which that toxicity develops, this property of materials should also be taken into account in assessing relative toxic rank. (For example, it seems unrealistic to assign the same toxic hazard rank to two materials--even though they have the same measured toxicity per unit weight--if one flames and burns rapidly at 350 Centigrade while the other ignites only above 700 C and burns slowly!)

A part of the combustion toxicology research effort should, therefore, be directed toward devising a ranking relationship that would take into account additional material properties such as: decomposition temperature, ignition temperature, specific heat, thermal conductivity, and rate of heat release (for a defined thermal environment).



APPENDIX A

PRIMARY DATA, ALL TEST MODES

TABLE A-1. PRIMARY DATA FROM 550°C, NONFLAMING TESTS

MATERIAL	SAMPLE Wt (g)	SAMPLE Loss (g)	TIME TO VISIBLE SMOKE (Min)	MAX. SMOKE DENSITY (OD)	TIME TO SMOKE PEAK (Min)	MAX. CO (ppm)	TIME TO MAX. CO (Min)	t _i , Obs. (Min)	td, Obs (Min)
7-12-7-1 (XLPO)	1.00202	0.847	0.90	0.20	1.5	3892	8.3	17.6 17.2 17.7	31.3 24.3 23.0
3-12-5-1 EPR/XLPO	1.00186	0.589	1.51	0.27	3.9	4093	10.2	15.6 15.7 15.9	21.5 21.8 24.5
1-12-2-1 Silicone/PO	1.00212	0.386	0.56	0.21	2.9	2532	10.2	23.7 21.1 22.5	30.9 29.5 41.0
6-12-12-1 Halar)	1.00022	0.997	1.37	0.30	2.3	24472	٦2.٦	7.7 8.4 8.0	9.7 10.3 9.8
8-14-8-1 EPR/Hypalon	0.99965	0.734	0.66	0.51	1.9	5963	6.4	14.0 13.3 14.3	19.3 17.7 23.4
9-12-13-1 EPDM/Hypalon	0.99708	0.628	0.57	0.38	2.7	6603	12.1	12.1 11.3 11.4	15.8 15.9 16.1

TABLE A-2. PRIMARY DATA FROM 750°C, FLAMING TESTS

MATERIAL	SAMPLE Wt (g)	SAMPLE Loss (g)	TIME TO VISIBLE SMOKE (Min)	MAX. SMOKE DENSITY (OD)	TIME TO SMOKE PEAK (Min)	MAX. CO (ppm)	TIME TO MAX. CO (Min)	t _i , Obs. (Min)	t _d , Obs. (Min)
1-12-2-1 Silicone/PO	1.00083	0.385	0.37	0.14	0.7	1905	8.3	NN NN NN	NR NR *
3-12-5-1 EPR/XLPO	1.00078	0.608	none (until ignition)	0.25	1.4	6602	4.6	8.2 8.1 8.1	11.3 10.6 10.3
6-12-12-1 Halar	1.00037	1.000	0.46	0.38	0.6	10067	2.7	6.5 6.5 6.2	9.0 8.8 7.5
7-12-7-1 XLPO	0.99962	0.864	0.35	0.40	6.0	8623	4.6	7.0 6.9 6.3	10.3 9.5 9.4
8-14-8-1 EPR/Hypalon	1.00147	0.732	0.22	0.30	1.2	10952	4.6	ں بی تو بی تی تو م تی ت	10.2 7.6 8.9

MATERIAL	SAMPLE Wt (g)	SAMPLE Loss (g)	TIME TO VISIBLE SMOKE (Min)	MAX. SMOKE DENSITY (OD)	TIME TO SMOKE PEAK (Min)	MAX. CO (ppm)	TIME TO MAX. ()O (Min)	t _i , Obs (Min)	td, Obs (Min)
9-12-13-1 EPDM/Hypalon	0.99978	0.365	0.25	0.23	٦.2	8622	6.4	6.8 7.8 7.0	12.3 11.1 12.2
l-l2-2-l Silicone∕ Polyolefin**	1.99893	0.812	none (until ignition	0.14	1.2	2813	6.4	21.3 21.0 21.7	NR NR NR
*NR = no res **Silicone/Po 30 minutes.	ponse. lyolefin w	vas tested	at a 2-g	loading to ob	tain incapé	acitation	is less th	an	

TABLE A-2. PRIMARY DATA FROM 750°C, FLAMING TESTS (Continued)

APPENDIX B

TOXICITY RANK COMPARISONS WITH PREVIOUSLY TESTED INSULATIONS

The initial toxicity ranking of 14 wiring insulation materials, by the methods used in this study, has been previously reported (2). Each of the aforesaid materials was selected from 104 specimens tested by the Boeing Commercial Airplane Company, Seattle, Washington, for properties other than toxicity.

At the request of I. Litant, Ph.d., TSC Technical Monitor, data from the six insulations described in this report and from the 14 insulations previously tested by CAMI have been combined into a single potential toxicity rank-order for all 20 materials. This ranking, based on the standard t_i for equal weights of insulation decomposed under the "worst-case" condition for each, is presented in Table B-1.

A similar rank-order, based on the weights of each insulation necessary to satisfy the same end-use requirement, is shown in Table B-2. Ranking in this table applies only to wire assemblies containing equal gauge conductors and is based on the calculated animal response time to the gases produced from one meter of insulation from one conductor per assembly, when decomposed under its individual "worst-case" condition.

TABLE B-1. MATERIAL RANK-ORDER BASED ON WORST-CASE PERFORMANCE FOR STANDARD t

				MEAN	
RANK*	MATERIAL	THERMAL CONDITION**	N***	STD t, (Min) ⁱ	SD^+
1	A6-4X12-1 (Silicone/Mylar/ Glass Braid)	550NF	9	22.0 ⁺⁺	4.84
2	1-12-2-1 (Silicone/PO)	550NF	3	21.8	1.59
3	1-16-1 (Silicone/PO)	750F	9	17.9	1.58
4	3-12-5-1 (EPR/XLPO)	750F	3	8.1	0.25
5	A7-24X19-5 (PE/Al Shield)	750F	9	7.5	0.83
6	A1-14-1 (PVC)	750F	9	7.4	0.36
7	A5-00-3 (XLPE + Cu Armor)	750F	9	7.4	0.61
8	A7-00-2 (EPR/Neoprene)	750F	9	7.3	0.74
9	9-12-13-1 (EPDM/Hypalon)	750F	3	7.1	0.43
10	11-20-1 (Exane)	750F	9	7.0	0.37
11	A2-6/2X19-4 (PE/Cu Shield)	475NF	9	6.9	0.28
12	12-20-2 (Teflon)	650NF	9	6.7	1.70
13	7-12-7-1 (XLPO)	750F	3	6.7	0.26
14	A5-14-1 (EPR/Hypalon)	750F	9	6.6	0.44
15	6-12-12-1 (Halar)	750F	3	6.4	0.25
16	A3-7X14-2 (?/Cloth Tape/ Neoprene)†††	750F	9	6.0	0.41
17	8-14-8-1 (EPR/Hypalon)	750F	3	5.6	0.46
18	12-12-4 (Halar)	750NF	9	4.7	0.53
19	3-20-1 (Tefzel)	750F	9	4.5	1.48
20	13-16-1 (Kapton)	750F	9	4.5	0.61

*Rank 1 is least toxic.

**Numerical prefix indicates °C; F = flaming, NF = nonflaming.

*** N = Number of experimental animals exposed.

 $^{+}_{++}$ SD = Standard Deviation

Mean value is for 8 animals; one exposed animal was not incapacitated during the 30-minute exposure.
+++
? = Proprietary compound.

RANK**	MATERIAL	WORST-CASE THERMAL MODE***	t _i x a/100 PER ASSEMBLY, Min (x100)	sD [†] P	NO. OF CONDUCTORS PER ASSEMBLY	AMG	t _i x ab/100 PER CONDUCTOR, Min (x100)
- 0 m	3-20-1 (Tefzel) 12-20-2 (Teflon) 11-20-1 (Exane)	750F 650NF 750F	260 190 100	86 48 5.0		20 20 20	260 190 100
- 2	A2-6/2X19-4 (PE/Cu Shield) A7-24X19-5 (PE/A1 Shield)	475 NF 750F	4.7 1.1	0.20 0.12	12 24	19 19	56 27
- 0	13-16-1 (Kapton) 1-16-1 (Silicone/PO)	750F 750F	270 136	37 7.0		16 16	270 136
$\neg \circ$	Al-14-1 (PVC) A5-14-1 (EPR/Hypalon) A3-7714-2 (2/Cloth Tane/	750F 750F	180 38	6.0 2.3		14	180 38
0 4	Neoprene)††† 8-14-8-1 (EPR/Hypalon)	750F 750F	0.90 6.1	0.06 0.50	ν Γ	14 14	6.3 6.1
	1-12-2-1 (Silicone/PO) 6-12-12-1 (Halar)	550NF 750F	128 105	9.3 4.2		12	128 105
n	Ao-4X12-1 (STITCONE/Mylar/ Glass Braid)	550NF	18^{++}	4.0	4	12	72
4 G	12-12-4 (Halar) 7-12-7-1 (XLPO)	750NF 750F	57 34	7.0		22	57 34
6 7	9-12-13-1 (EPDM/Hypalon) 3-12-5-1 (EPR/XLPO)	750F 750F	29	1.7		12	29 18
- 2	A7-00-2 (EPR/Neoprene) A5-00-3 (XLPE + Cu Armor)	750F 750F	4.3 1.9	0.41 0.15		2/0 2/0	4.3 1.9
*0nly **Rank	wire assemblies containing eq l is least toxic; relative ra	ual-gauge con nk is based o	ductors are rank n the calculated	ked as to I respons	o relative to se time for t	xicity hat qu	'. lantity of
toxic *** Numer	<pre>: gases produced from one mete .ical prefix indicates °C; F =</pre>	r of insulati flaming, NF	on from one conc = nonflaming, i	ductor p∈ .e., 550N	er assembly (VF = 550°C, n	last o onflan	column). ning.
-							

Mean value is for 8 animals; one exposed animal did not incapacitate during the 30-minute exposure.

+++? = Proprietary compound.

 $^{\dagger}_{\uparrow\uparrow}$ SD = Standard deviation.

RANK-ORDER EVALUATIONS OF TOXICITY BASED ON A CALCULATED t'_1 (WORST CASE PERFORMANCE) FOR EQUAL LENGTHS OF INSULATION FROM EQUAL-GAUGE WIRE ASSEMBLIES* TABLE B-2.

B-3/B-4



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