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Reduction of Hydrogen Cyanide Concentrations and Acute Inhalation Toxicity from Flexible Polyurethane Foam Combustion Products by the Addition of Copper Compounds

Part IV. Effects of Combustion Conditions and Scaling on the Generation of Hydrogen Cyanide and Toxicity from Flexible Polyurethane Foam with and without Copper Compounds

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PART IV. EFFECTS OF COMBUSTION CONDITIONS AND SCALING ON THE GENERATION OF HYDROGEN CYANIDE AND TOXICITY FROM FLEXIBLE POLYURETHANE FOAM WITH AND WITHOUT COPPER COMPOUNDS[1]

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ABSTRACT

Two full-scale protocols (A & B) were tested to determine the efficacy of cuprous oxide (Cu_2O) in reducing the concentrations of hydrogen cyanide (HCN) from flexible polyurethane foams (FPU) when thermally decomposed under "realistic" room conditions. In each Protocol A test, a FPU cushion (untreated or treated with 0.1% Cu_2O) was cut in half, and the two halves were stacked on a load cell in a closed room. The ignition source was a hot wire placed between the two halves. Rats were exposed to the decomposition products to examine the toxicological effects of the foams with and without Cu_2O. Protocol B differed from Protocol A in that chairs were simulated by four FPU cushions attached to a steel frame; the treated FPU contained 1.0% Cu_2O; the cushions were covered with a cotton fabric; the chairs were ignited with cigarettes; and the burn room was open and connected to a corridor. In both protocols, the thermal decomposition progressed through nonflaming, smoldering and flaming phases and the concentrations of HCN and other gases were monitored. Foams used in the full-scale room burns were also examined under small-scale conditions (under flaming or a two-phase nonflaming/ramped heating mode) in the cup furnace smoke toxicity method. Both atmospheric and reduced O_2 conditions were studied. The small-scale tests showed an 87% reduction in the concentration of HCN and a 40 to 73% reduction in the toxicity of the thermal decomposition products when the Cu_2O-treated foams were tested. In the full-scale tests, the concentration of HCN was reduced 70% when the FPU contained 1.0% Cu_2O, but not when the foams contained 0.1% Cu_2O. Investigation into this discrepancy indicated that exposing the charred residues from the full-scale burn room tests to the ramped heating mode in the cup furnace smoke toxicity method would produce significant amounts of HCN (65-90 ppm) from the untreated foam chars and only 1-2 ppm from the 0.1% Cu_2O-treated foam chars indicating that the copper even at this low concentration was still active in reducing HCN generation. Some preliminary experiments comparing a melamine-treated and standard FPU foam (both without Cu_2O) in the two phase cup furnace smoke toxicity method showed 10 times more HCN generated by the melamine-treated FPU than the standard FPU and a 90% reduction of HCN from the melamine-treated FPU when it was treated with Cu_2O.

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Key words: acute toxicity; building technology; combustion products; copper; cup furnace smoke toxicity method; cuprous oxide; flexible polyurethane; hydrogen cyanide; inhalation; full-scale room tests; melamine.

1.0 INTRODUCTION

This laboratory previously showed that when flexible polyurethane foams (FPU) were thermally decomposed under small-scale conditions in the cup furnace smoke toxicity method apparatus via a two phase procedure (where a nonflaming phase is followed by ramped heating), higher concentrations of HCN were generated than if the FPU foams were decomposed under only nonflaming or flaming conditions [1][2]. This early study also showed higher concentrations of HCN were generated from FPU in full-scale room tests at the smoldering/flaming transition point. The two phase heating regime was chosen for examination since it simulated the fire scenario shown to cause the most fire deaths in the United States [2]. In this fire scenario, a cigarette is dropped on a piece of upholstered furniture containing FPU. The furniture smolders for some unspecified time (full-scale tests at NIST have shown that the smoldering stage can last as long as an hour) and ultimately bursts into flames. The fire victims (the majority of which die from smoke and toxic gas inhalation) are usually found outside the room of fire origin, an indication that the smoke had moved beyond the room of fire origin. This smoke movement will occur if the combustible materials in the room are flaming or have reached flashover conditions.

In previous studies, we found that FPU treated with copper dust, cupric oxide, cuprous oxide or copper sulfate, produced significantly less hydrogen cyanide (HCN) than untreated control foams when decomposed under the above mentioned small-scale laboratory conditions [3-5]. As little as 0.1% by weight of the copper compounds was sufficient to reduce the HCN generation by 80 to 90%.

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[2] Numbers in brackets refer to references listed at the end of this report.

The acute inhalation toxicity (as measured by lethality in Fischer 344 rats) produced from exposure to this smoke [3-5] was also reduced (presumably due to the decreased atmospheric concentrations of HCN). The copper compounds could be added to the foams during the formulation or as a post-treatment. The addition of 0.1% cuprous oxide (Cu_2O) (the most efficient of the compounds tested) did not change the flammability characteristics (ignitability, heat release rate, heat of combustion, CO/CO_2 ratios, rate of flame spread, or particulate formation) of the test foams [6].

Earlier work by Jellinek and coworkers showed that the concentrations of HCN generated from the thermal decomposition of a polyurethane at 300 and 400° C decreased when flowed through copper compounds [7,8]. In their studies, the polyurethane films were usually 15μm thick (50 mg). In some experiments, the metal powder was mixed with the polymer and, in others, copper metal films of 400 to 1000 Å were deposited on top of the polymer films. In most cases, the percent of copper was 10% or greater. The lowest concentration that they tested was a 2.6% copper film which inhibited the evolution of HCN by 66%. Their experiments indicated that copper acts as an oxidative catalyst which would decompose gaseous HCN into N_2, CO_2, H_2O and small amounts of nitrogen oxides. Our work differs from that of Jellinek in that we used much larger samples of FPU (including the work reported here on full-scale room burns of cushions and simulated chairs), much smaller concentraions of copper, and we examined the issue of toxicity.

From our earlier work [3-6] sponsored by the International Copper Association, Ltd. and The Society of the Plastics Industry, Inc., we concluded that:

- Hydrogen cyanide concentrations in the thermal decomposition products from a flexible polyurethane foam were significantly reduced when the foam was treated with copper or a number of different copper compounds and thermally decomposed via a two-phase heating system in the cup furnace smoke toxicity method.

- In particular, when cupric oxide (CuO) was used, the concentration of copper needed was only 0.08% by weight and when cuprous oxide (Cu_2O) was used, only 0.07% by weight was needed to significantly reduce the generation of HCN.

- Blood cyanide levels in Fischer 344 rats exposed to combustion products from the cupric oxide treated foams for 30 minutes were 1/2 to 1/4 those measured in the animals exposed to the smoke from the same amount of untreated foam.

- Fewer animal deaths occurred during the 30 minute exposures to the FPU treated with the copper and copper compounds compared to the untreated FPU, i.e., the LC_{50} (30 min) value of the treated foams was higher than the untreated foams.

- Post-exposure deaths were also reduced in the animals exposed to the combustion products from the copper and cuprous oxide-treated FPU foams. This reduction in post-exposures deaths was not apparent in the first year's work when most of the foam was treated with cupric oxide as a post-treatment. These delayed post-exposure deaths have <u>not</u> been observed in animals exposed to combustion products from flexible polyurethane foams decomposed in large-scale room fire tests. The cause of these post-exposure deaths is not known.

- The copper or copper compounds could be added to the foams during or after the foams were formulated and still be effective in reducing the toxicity and HCN yield under the specified small-scale test conditions.

- Flammability characteristics of the Cu_2O-treated and untreated foams were compared to assure that the positive effect on toxicity was not contradicted by negative effects on the flammability characteristics. The flammability characteristics examined were: 1. ignitability in three systems [the cup furnace smoke toxicity method, the Cone Calorimeter, and Lateral Ignition and Flame Spread Test (LIFT)], 2. heat release rates under small-scale (Cone Calorimeter) and medium-scale (furniture calorimeter) conditions, 3. heats of combustion under small-scale (Cone Calorimeter) and medium-scale (furniture calorimeter) conditions, 4. CO/CO_2 ratios under small-scale (Cone Calorimeter) and medium-scale (furniture calorimeter) conditions, 5. smoke obscuration (Cone Calorimeter), and 6. rate of flame spread (LIFT). No differences in flammability characteristics between the Cu_2O-treated (0.1%) and untreated FPU foam were observed.

In the present study, sponsored by the International Copper Association, Ltd. and The Society of the Plastics Industry, Inc., the objectives were to examine the generation of HCN and smoke toxicity of Cu_2O-treated and untreated FPU thermally decomposed under various oxidative, scaling and construction conditions as well as with two different concentrations of Cu_2O. Analyses of the toxic gas concentrations were conducted under 1. small-scale conditions in the cup furnace smoke toxicity method (flaming mode and nonflaming/ramped heating mode; the latter mode was also examined under reduced oxygen conditions), and 2. full-scale conditions in room burns (nonflaming/smoldering/-

flaming mode) under two experimental protocols. In Protocol A, foam cushions were cut in half and stacked on top of each other. A heated coil placed between the two halves started the nonflaming smoldering decomposition and an open flame started the flaming mode if the cushions did not undergo flaming spontaneously. In Protocol B, four cotton covered foam cushions were arranged on a steel frame to simulate a chair. Three cigarettes were placed on the seat cushion to initiate smoldering and ultimately flaming. In some of these chair tests, an external burner was added to try to simulate flashover conditions. Toxicity of the thermal decomposition products was examined by exposing Fischer 344 rats to the smoke from phase 2 (the ramped heating mode following the nonflaming mode) produced in the small-scale cup furnace smoke toxicity method and to smoke from the smoldering and flaming phases of some of the full-scale room burns. Elemental analyses were performed on the charred residues formed from some of the foams during the nonflaming modes in the cup furnace smoke toxicity method and following the nonflaming/smoldering/flaming modes in the full-scale burns. Some of the charred residues from the full-scale tests were exposed to the ramped heating mode in the cup furnace smoke toxicity method to determine if the Cu_2O would have any effect on the levels of any further HCN that might be generated. Some preliminary experiments with a melamine-treated FPU (with and without Cu_2O) were also conducted.

2.0 MATERIALS AND METHODS

2.1 MATERIALS

2.1.1 FLEXIBLE POLYURETHANE FOAMS (FPU)

Two batches of FPU foams were prepared by BASF Corporation[3] for these series of tests. Each batch consisted of Cu_2O treated foams and control foams without Cu_2O. The concentration of Cu_2O in batch 1 was 0.1% and that in batch 2 was 1.0%. The Cu_2O (M.W. 143.08) was obtained from American Chemet Corp., Deerfield, IL. These foams were continuously machine mixed on a pilot scale. The size of the laboratory samples from the first batch of foams (containing 0.1% Cu_2O) was approximately 102 cm (40 inches) wide by 366 cm (12 feet) long and 51 cm (20 inches) high. They were cut to 102 cm (40 inches) long by 102 cm (40 inches) wide by 10 cm (4 inches) high before being shipped to the National Institute of Standards and Technology (NIST). The second batch of foams arrived at NIST cut into squares 91.4 cm (36 inches) long by 91.4 cm (36 inches) wide by 10 cm (4 inches) high. BASF indicated that the presence of 0.1 or 1.0% by weight of cuprous oxide imparted a pinkish-tan color to the foam and resulted in faster creaming of the reaction. We found that all the copper-treated foams had a pale pink color. There was no evidence of scorching in these laboratory size buns. The formulations supplied by BASF are given in Table 1.

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[3] Certain commercial equipment, instruments, materials or companies are identified in this paper in order to adequately specify the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the equipment or material identified is necessarily the best available for the purpose.

To examine the effect of an increased loading of Cu_2O, in one of the full-scale room burns, additional Cu_2O was added at NIST as a post-treatment to the FPU already containing 0.1% Cu_2O. The additional Cu_2O was added by squeezing a Cu_2O-water slurry through the foam and drying the foam in an oven set at 75°C. The amount of Cu_2O added by this post-treatment was determined by the difference in weight of the foam before the addition and after the drying. In this case, the final concentration of Cu_2O was 1.9%.

Table 1. Formulations of the Untreated and Cu_2O-Treated FPU Foams Used in this Test Series

Ingredients	Batch 1		Batch 2	
	Untreated FPU (wt. %)	Cu_2O-Treated FPU (wt. %)	Untreated FPU (wt. %)	Cu_2O-Treated FPU (wt. %)
Polyoxypropylene polyol (3000 M.W.)	65.6	65.6	65.4	64.7
Water	2.3	2.3	2.3	2.3
Silicone surfactant	0.7	0.7	0.7	0.7
Amine catalyst	0.2	0.2	0.1	0.1
Tin catalyst	0.3	0.3	0.4	0.4
TDI (110 index)	30.9	30.9	30.8	30.5
Cu_2O	0	0.1	0	1.0
DMEA	NR	NR	0.4	0.4
Total (%)	100	100.1	100.1	100.1
Density (kg/m^3)	24.5	24.8	24.3	23.1

DMEA: Dimethylethanolamine
NR: Not reported by manufacturer
TDI: Toluene diisocyanate

2.1.2 MELAMINE-TREATED FLEXIBLE POLYURETHANE FOAM (Melamine-FPU)

In a prior study [9], a melamine-FPU (with a density of 50 kg/m^3) was found to produce 4 to 32 times more HCN than four other foams tested in the same study. The other tested foams were designated as "standard," "combustion modified high resiliency," "IMPAK rebonded fire retardant polyurethane," and "neoprene." All these foams were decomposed under flaming conditions in the cup furnace smoke toxicity method. In the present study, samples of this melamine-FPU foam were post-treated with Cu_2O by squeezing a Cu_2O-water slurry through the foam and drying the foam in an oven set at 75° C. The amount of Cu_2O added by this post-treatment was determined by the difference in weight of the foam before the addition and after the drying. Both the Cu_2O-treated and untreated melamine-FPU foams were examined in the two-phase thermal decomposition mode in the cup furnace smoke toxicity apparatus.

2.1.3 COTTON FABRIC

In the full-scale tests for Protocol B, the FPU cushions were covered with a Haitian cotton upholstery fabric with a thin latex back coating. This upholstery fabric was selected to ensure that the entire assembly would smolder when exposed to a burning cigarette. The weight of the Haitian cotton including the latex back coating was 0.66 kg/m^2.

2.1.4 CALIBRATION GASES

The calibration gases for the CO, CO_2, and HCN measurements were commercially supplied in specified concentrations in nitrogen. The concentration of HCN in the commercially supplied cylinders was routinely checked by silver nitrate ($AgNO_3$) titration [10], since it is known that the concentration of HCN stored under these conditions will decrease with time. For the NO_x measurements, the NO calibration gas in nitrogen was obtained from the Gas and Particulate Science Division, NIST.

2.1.5 ANIMALS

Fischer 344 male rats, weighing 200 to 300 grams, were obtained from Taconic Farms (Germantown, NY). Animal care and maintenance were performed in accordance with the procedures outlined in the National Institutes of Health's "Guide for the Care and Use of Laboratory Animals." Each rat was housed individually in suspended stainless steel cages and provided with food (Ralston Purina Rat Chow 5012) and water *ad libitum*. Twelve hours of fluorescent lighting per day were provided using an automatic timer. All animals (including the controls) were weighed daily from the day of arrival until the end of the post-exposure observation period. The rats were allowed to acclimate to laboratory conditions for at least seven days prior to experimentation.

2.2 METHODS

2.2.1 PHYSICAL PROPERTIES OF TREATED AND UNTREATED FPU

The tests for these physical properties were conducted at BASF according to ASTM D3574 [11]. The results are discussed in section 3.

2.2.1.1 Density

The density of the uncored foam was calculated from the mass and volume of the specimen and applies only to the immediate area of the specimen that was tested.

2.2.1.2 Tensile Strength

The tensile strength measures the applied tension which causes the foam to rupture. The tensile strength is equal to the breaking force divided by the original cross-sectional area of the specimen.

2.2.1.3 Elongation

This value indicates the percent elongation of the foam at the time of rupture as measured in the tensile strength test.

2.2.1.4 Tear Strength

This value indicates the ratio of the maximum force to the thickness of specimen needed to tear a rectangular block following a 40 mm cut in one side.

2.2.1.5 Resilience

The resilience test consists of dropping a steel ball on the foam and determining the percent height of the rebound.

2.2.1.6 Indentation Force Deflection Test (IFD)

The IFD test is a measurement of the force needed to produce 25% and 65% indentations in the foam. The force is applied with a flat circular indentor foot which is 323 cm^2 in area.

2.2.1.7 Support Factor

The support factor (also known as the sag factor, hardness ratio, modulus or comfort factor) is the ratio of the 65% indentation force deflection to the 25% indentation force deflection as measured in the IFD test and determined after one minute of rest.

2.2.1.8 Compression Set Test

Compression set tests consist of placing the foam between two flat plates which are parallel to each other and deflecting the specimen to either 50 or 90% of its thickness. The specimen is held in the apparatus for 22 hours at 70° C. After removal from the apparatus, the degree of compression is expressed as a percentage of the original thickness.

2.2.1.9 Air Flow

Air flow is a measure of the ease with which air passes through the cellular structure. The air flow value is the volume of air/sec at standard temperature and pressure (STP) required to maintain a constant pressure differential of 125 Pa across a flexible foam specimen.

2.2.2 SMALL-SCALE CUP FURNACE TESTS

2.2.2.1 Cup Furnace Smoke Toxicity Methodology

The cup furnace smoke toxicity method consists of a combustion system, the chemical analysis system, and the animal exposure system [12]. An illustration and schematic of the experimental arrangement are shown in Figures 1 and 2. The cup furnace smoke toxicity method apparatus is a closed system in which the individual material samples are decomposed in a quartz beaker set in a cup furnace

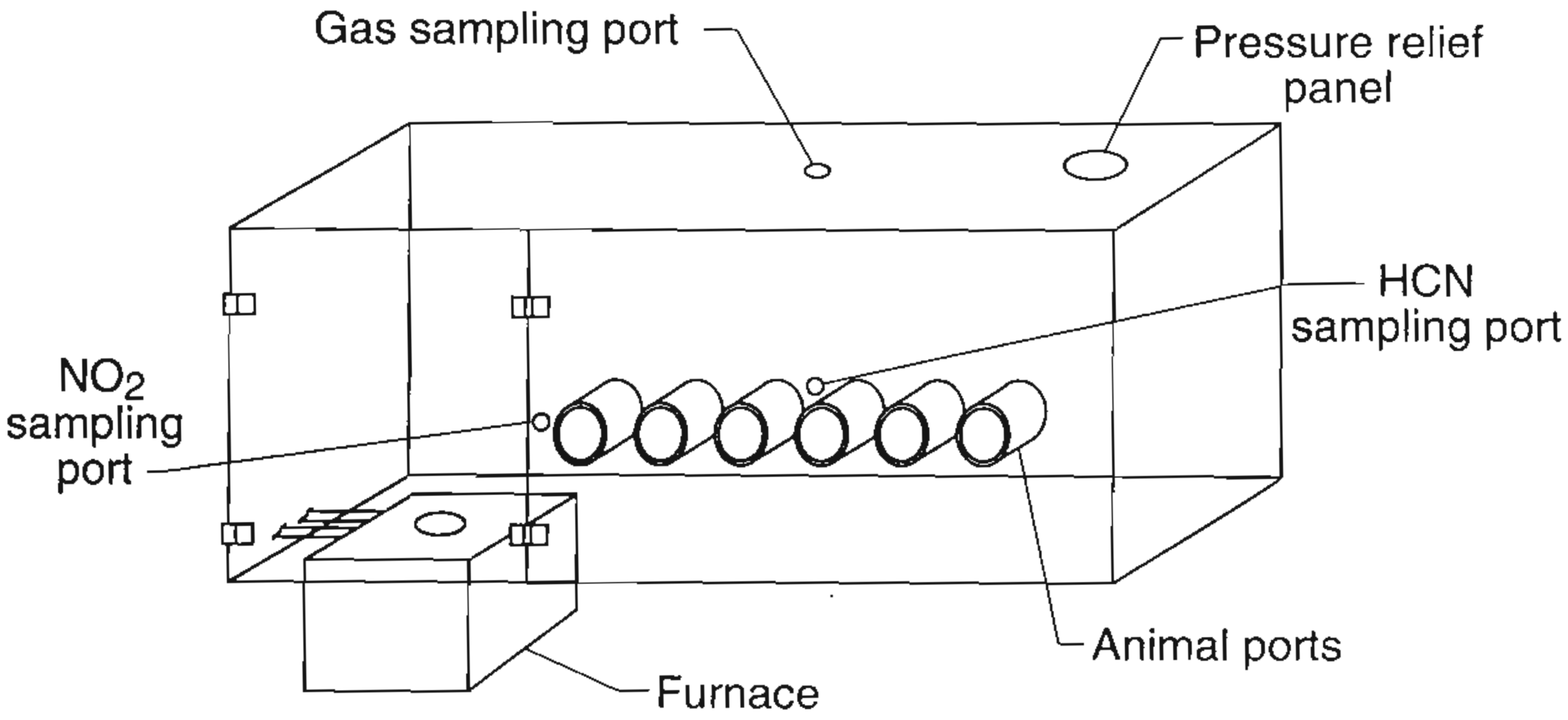

Figure 1. Cup furnace smoke toxicity animal exposure chamber and furnace

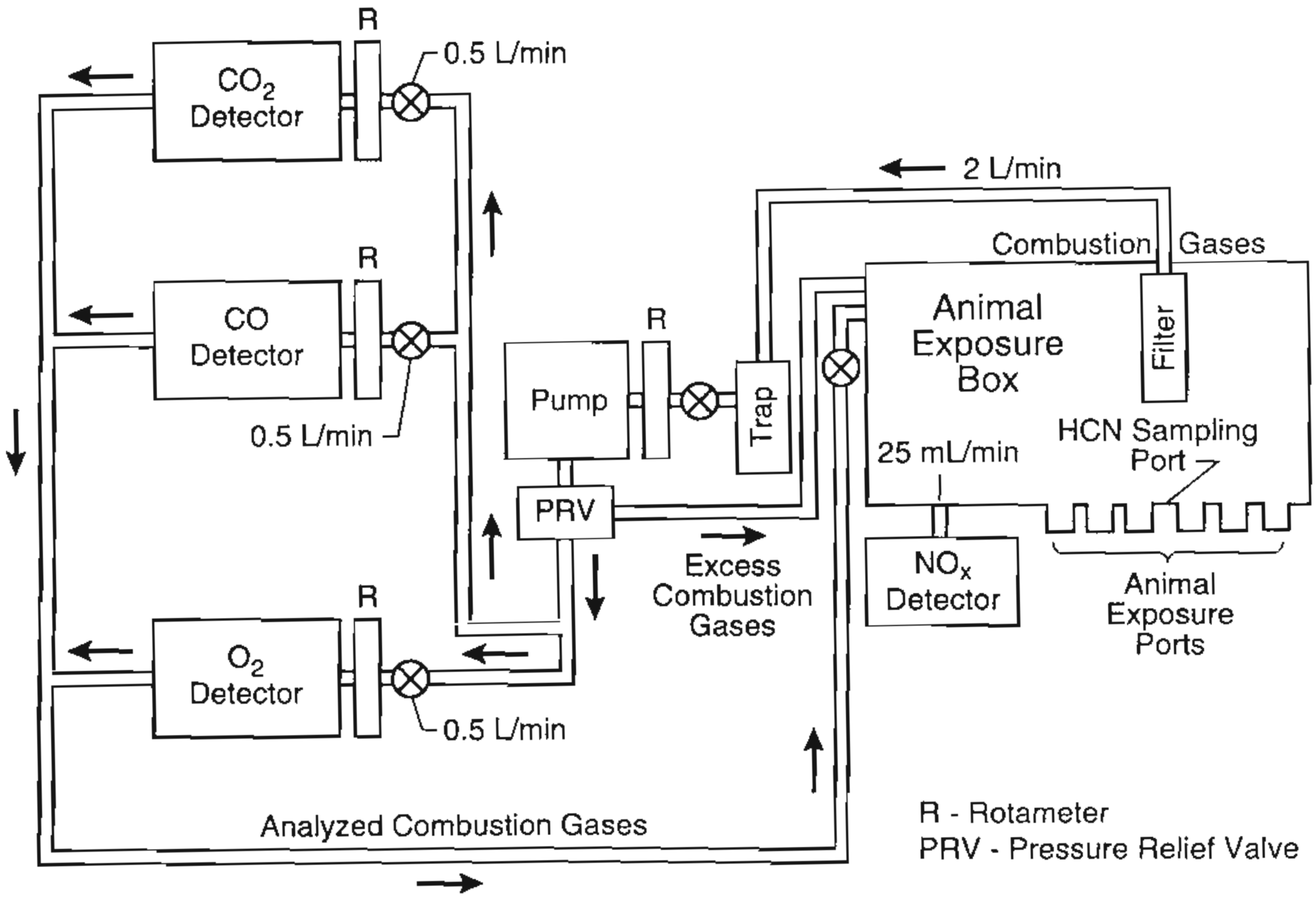

Figure 2. Schematic of cup furnace smoke toxicity apparatus and analytical instrumentation

located directly below the animal exposure chamber such that all the combustion products from the test material flow directly into the chamber. All the gases and smoke are kept in the 200 liter rectangular animal exposure chamber for the duration of the exposure. Those gases removed for chemical analysis are returned to the animal chamber except for the amount taken for HCN and NO_x analysis (see section 2.2.2.5 below). The samples were decomposed under the two phase thermal decomposition mode or under the flaming mode described in sections 2.2.2.2 and 2.2.2.4.

In each animal exposure experiment, six rats were placed in restrainers which were then inserted into the six portholes located along the front of the exposure chamber such that only the heads of the animals were exposed to the combustion atmospheres. The animals were observed to determine if death occurred either during the 30 minute exposures or the post-exposure observation period (at least 14 days). If the animals were still losing weight at the end of the 14 day observation period, they were kept and weighed daily until they showed signs of recovery (3 days of weight gain) or died. The percentage of animals dying in each experiment was plotted to produce a concentration-response curve from which LC_{50} values and their 95% confidence limits were calculated by the statistical method of Litchfield and Wilcoxon [13]. The LC_{50} in g/m^3 is defined here as the mass of material (including the Cu_2O) placed in the furnace divided by the exposure chamber volume which caused 50% of the animals to die during the 30 minute exposure only or during the exposure plus the post-exposure observation period.

2.2.2.2 Two-Phase Thermal Decomposition System

To assure that these newly prepared Cu_2O-treated and untreated FPU foams reacted in a similar fashion to those tested previously in our laboratory, the HCN generation and the acute inhalation toxicity of the combustion products of each of the two batches of FPU foams were assessed by a modified cup furnace smoke toxicity method. This method was modified to provide a two phase heating regime simulating the common fatal fire scenario in which a chair smolders for some time before flaming [1]. In this procedure, the material was first heated in a nonflaming mode for 30 minutes at approximately 25°C below the predetermined autoignition temperature of the control foam. If flaming occurred, the temperature of the nonflaming phase was reduced in subsequent experiments. A black char residue was formed during this first phase. In phase two, the temperature of the furnace was raised approximately 13°C/minute up to 800°C. In all cases in this series of experiments, there was not enough fuel left after phase one to allow flaming to occur during phase two. This two-phase mode is also referred to as the nonflaming/ramped heating mode.

For the FPU foams (with and without Cu_2O), the autoignition temperature was 400°C and the nonflaming temperature of phase one was 375°C. For the melamine-FPU foams, the autoignition temperature was initially found to be 475°C and the nonflaming temperature of phase one was 450°C. However, when two samples of the melamine-FPU foams treated with Cu_2O flamed at 450°C, the temperature of phase one was reduced to 420°C.

For those experiments with rats, the portholes were fitted with rubber stoppers during phase one. Insertion of the restrained animals caused the rubber stoppers to fall into the chamber and simultaneously exposed the animals to the chamber atmosphere. The animals were exposed to the test atmospheres for 30 minutes starting 5 minutes after the beginning of phase two. Since this is a closed system, the animals were exposed to the combustion products accumulated during phase one as well as the products generated during phase two.

2.2.2.3 Reduced Oxygen Experiments

A series of experiments was conducted at ambient and reduced oxygen concentrations with batch 1 foams (untreated and 0.1% Cu_2O treated). The steady-state O_2 concentrations in these experiments were 20%, 13% and 6%. To ensure the maintenance of the steady-state O_2 concentrations, the following experimental procedure was used. In each of these experiments, the entry of the exposure chamber was covered with a plastic bag, the O_2 concentration was reduced by the addition of nitrogen into the exposure chamber and the desired temperature of the furnace was obtained. Then, the sample which had previously been placed on the floor of the exposure chamber was dropped into the furnace using the plastic bag in a fashion similar to that of a glove box. The experiments were conducted in the two-phase thermal decomposition system described in section 2.2.2.2.

2.2.2.4 Flaming Experiments

Flaming mode experiments were conducted in the cup furnace smoke toxicity method apparatus using the Cu_2O-treated FPU and the untreated FPU foam to compare the generation of HCN in the flaming mode with the HCN generated from the two phase nonflaming/ramped heating mode. The furnace temperature was 425° C (i.e., 25° C above their autoignition temperatures). An electric spark was used to ensure immediate flaming. These tests were conducted for analytical measurements only, i.e., no animals were exposed. Flaming experiments with the untreated melamine-FPU in the cup furnace smoke toxicity method were done previously [9]. Cu_2O-treated melamine-FPU foam was not tested in the flaming mode.

2.2.2.5 Exposure Chamber Atmospheric Gas Measurements

Chemical analyses were conducted in all the experiments in order to determine the concentrations of HCN, CO, CO_2, and reduced O_2 that would be generated from different mass loadings of the

Cu_2O-treated or untreated FPU and melamine-FPU foams. In many of these experiments, NO_x (both NO_2 and NO) was also measured. Carbon monoxide and CO_2 were measured continuously by non-dispersive infrared analyzers and the obtained values are accurate to within 100 and 500 ppm, respectively. Oxygen concentrations were measured continuously with a paramagnetic analyzer. The concentrations of HCN were monitored by periodic sampling of the exposure chamber atmosphere (a 100 μL sample taken approximately every 3 minutes with a gas-tight syringe) and analyzed with a gas chromatograph (GC) equipped with a thermionic detector [14]. The HCN results are accurate to within 10%.

The concentration of NO_x was measured continuously by a chemiluminescent NO_x analyzer Model 14A (Thermo Electron Instruments, Hopkinton, MA). The analyzer is equipped with a molybdenum (Mo) converter (set at 375° C) which chemically reduces NO_2 to NO which then reacts with ozone. The reaction of NO with ozone produces electronically excited NO_2 which relaxes, emitting light that is detected by the instrument. In order to minimize the total gas volume removed during the animal exposure experiments, the chemiluminescent analyzer was modified so that the sample flow was reduced to about 25 mL/min. One should note that if a chemiluminescent analyzer with a stainless steel converter (at a high temperature, e.g., 800° C) is used, there will be interference from the HCN present in the combustion atmosphere. This interference was prevented with the use of the Mo converter. The amount of NO and NO_2 in the NO_x can be determined from the analyzer data, since two flow modes are available: in the first (NO) mode, a direct path of the sample gas to the reaction chamber is used, with only the NO producing a signal. In the second (NO_x) mode, the sample gas passes through the Mo converter and is changed to NO. Thus, in the NO_x mode, the instrument responds to the total oxides of nitrogen. The amount of NO_2 is estimated from the difference of the two signals. The calculated NO_x concentrations are accurate to 10% of the NO_x concentration.

The CO, CO_2, O_2 and NO_x data were recorded by an on-line computer every 15 seconds. In the tables, the average gas concentrations are obtained from the integrated areas under the instrument response curves calculated for the 30 minute animal exposure period divided by 30 minutes (i.e., ppm-min/30 min).

2.2.3 FULL-SCALE ROOM TESTS

2.2.3.1 Protocol A

2.2.3.1.1 Burn Room and Animal Exposure Chamber Configuration

The experimental arrangement, shown in Figure 3, consisted of a single compartment measuring 2.44 m wide by 2.44 m high by 3.66 m long connected to three animal exposure chambers by a stainless steel gas line. A door, which measured 1.02 m wide by 2.03 m high and which had a 25 mm undercut, provided access to the compartment. A pressure relief vent, measuring 0.75 m wide by 0.38 m high, was cut into the lower portion of the door. The burn room was lined with non-combustible materials. The walls and ceiling of the compartment were covered by two layers of 12.7 mm thick Marinite (which is an inorganic millboard containing calcium silicate). The floor substrate was a 102 mm thick slab of concrete covered with a single layer of 12.7 mm thick Marinite. The door was composed of a single sheet of 12.7 mm thick Marinite with the vent area covered by heavy duty aluminum foil. The door to the room was closed for all tests; in three out of the seven tests, the vent either ruptured (Test A3) or was left open (Tests A6 and A7) (details are provided in section 2.2.3.1.3).

2.2.3.1.2 Instrumentation

Table 2 lists all the instrumentation used in Protocol A and the location of the sampling points. Figure 3 shows the location of the instrumentation within the test compartment. Vertical lines of

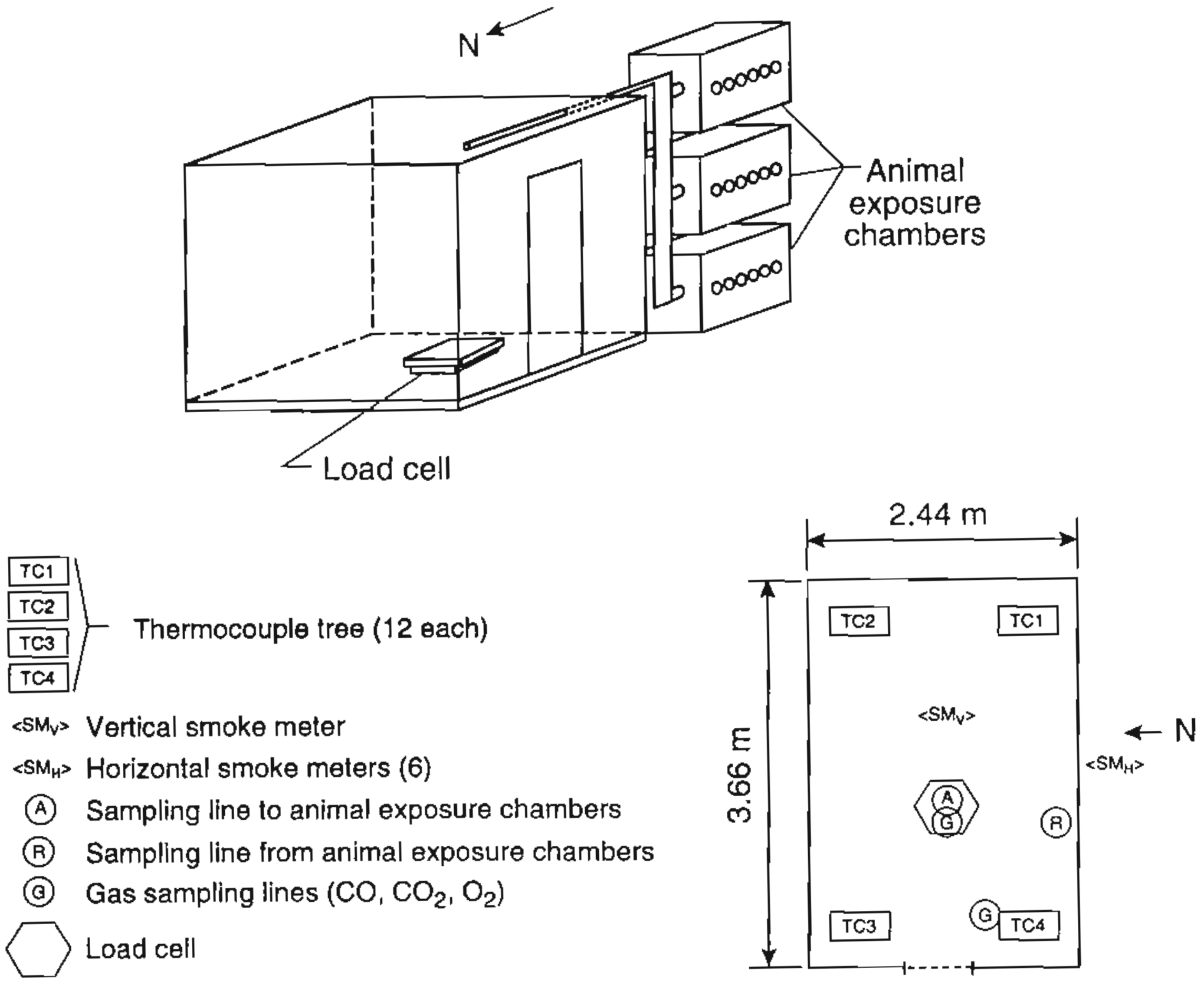

Figure 3. Floor plan and instrument locations for the large scale single compartment tests and animal exposure chamber arrangement and connection to the large scale test compartment

twelve thermocouples each, located in the four corners of the compartment, were used to determine the location within the compartment of the interface between the hot upper layer and cool lowerlayer. One vertical and six horizontal smoke meters were used to determine smoke particulate stratification within the compartment. A load cell which continuously monitored mass loss of the test foam was located near the center and 0.1 m above the burn room floor continuously monitored mass loss. Stainless steel gas probes (No. 1 and 2) for the continuous monitoring of CO, CO_2, and O_2 concentrations were located in the upper (center line 0.61 m from door opening, 0.15 m from the ceiling) and lower (center line 0.61 m from door opening, 0.3 m from the floor) portions of the compartment. In addition, another stainless steel gas line (No. 3), 55 mm in diameter, was located on the center line of the compartment 0.46 m from the doorway and 0.15 m from the ceiling and was used to transport gases from the burn room to the three animal exposure chambers which were connected in parallel. In other words, the burn room gases were continuously and simultaneously drawn through the three animal chambers by a blower motor. A bypass gas line from gas line No. 3 bypassed the animal exposure chambers and returned the gases back to the burn room near the ceiling. This bypass line was used to collect gas samples for HCN and NO_x from the burn room and also to collect the gases from the three animal chambers and return them to the burn room. A thermocouple in each of the animal exposure chambers monitored the temperature to which the animals were exposed.

Table 2. Location of Instrumentation

Instrument	Description	Notes
Gas Probes		
Ceiling	CO, CO_2, O_2 - 0.15 m from the ceiling (0.6 m from west and 1.22 m from north walls).	
Floor	CO, CO_2, O_2 - 0.3 m from floor (0.6 m from west and 1.22 m from north walls).	
By-pass Line	HCN and NO_x	
Animal Exposure Chamber	CO, CO_2, and O_2, port for HCN.	
Load Platform	1.23 m from north and 2.16 m from east walls (0.3 m height).	
Pressure Transducer	Across vent opening (0.1 m).	Tests A6 and A7, only
Smoke Meters		
Vertical	centerline of compartment (1.00 m from doorway).	
Horizontal	0.61, 0.91, 1.22, 1.52, 1.83, and 2.29 m (0.86 m from doorway).	
Thermocouple	Animal Exposure Chambers - 3 Thermocouples, one for each exposure chamber.	
Thermocouple Trees		
NE Corner	0.15, 0.66, 0.81, 0.97, 1.12, 1.27, 1.42, 1.57, 1.72,1.88, 2.03, 2.15 m	
SE Corner	0.15, 0.66, 0.81, 0.97, 1.12, 1.27, 1.42, 1.57, 1.72,1.88, 2.03, 2.15 m	
NW Corner	0.15, 0.66, 0.81, 0.97, 1.12, 1.27, 1.42, 1.57, 1.72,1.88, 2.03, 2.15 m	
SW Corner	0.15, 0.66, 0.81, 0.97, 1.12, 1.27, 1.42, 1.57, 1.72,1.88, 2.03, 2.15 m	
Door Vent	0.05, 0.13, 0.25, and 0.36 m	Tests A6 and A7, only

Carbon monoxide, CO_2, and O_2 were continuously monitored from the upper and lower layers in the burn room and from each of the three animal exposure chambers. Nitrogen oxides in the burn room were continuously monitored from the bypass line. Periodic gas samples for HCN in the burn room were taken from the bypass line in both impingers for subsequent ion chromatographic (IC) analysis and evacuated gas sampling bulbs for subsequent GC analysis. Evacuated gas sampling bulbs were also used to monitor the HCN in the animal exposure chambers.

The gas sampling and analytical techniques for HCN, CO, CO_2, O_2 and NO_x in the burn room and animal exposure chambers of the full-scale tests were the same as those previously described for the small-scale tests. To monitor the HCN in the burn room with the evacuated bulb gas sampling technique, samples were taken from the bypass line a few minutes before flaming ignition and about once every minute during the flaming period. A glass wool filter was used in the line to avoid clogging. To monitor the HCN in the animal exposure chambers, two evacuated gas sampling bulbs were filled from each of the three chambers during the 30 minute animal exposure period. Since the animal exposure chambers were closed prior to the insertion of the animals, the concentrations in these chambers should have stayed constant. Two samples were considered sufficient to assure that the concentrations had not changed.

For IC analysis of HCN, a commercially available ion chromatograph (Waters Model ILC-1 Ion/Liquid Chromatograph) equipped with a Waters 460 Electrochemical Detector was used. The electrochemical detector was used with an Ag working electrode and an Ag/AgCℓ reference electrode. An anion column (ICPAK-A HR) was preceded by an Anion Guard-Pak Precolumn Module (both of which are commercially available from Waters). Chromatograms were recorded on a Spectra-Physics Model SP 4270 Integrator. Stock solutions of CN^-, nominally 1000 ppm, were prepared by dissolving 0.2503 g of KCN in 100 mL of the eluent mentioned below. Calibration solutions of 0.01 to 0.05 ppm for CN^- were prepared by serial dilution of the stock solutions with the eluent. The eluent for the ion chromatograph was 95% 5 mM KOH/5% acetonitrile at a flow of 1.0 mL/min. The sample loop had a volume of 100 µL. Unknowns were diluted 1:10 or 1:100 before injection onto the column. Samples and standards were loaded into the loop using a 1 mL syringe and a 0.45 µm syringe filter.

The sampling of the HCN for IC analysis was conducted by bubbling a portion of the gaseous combustion products from the bypass line through tared 125 or 250 mL glass impingers containing approximately 125 mL of 95% 5mM KOH/5% acetonitrile. Sampling started when the foam in the burn room underwent flaming ignition, at which time, gases were bubbled through an impinger for 300 sec unless the filter plugged. If plugging occurred, the time was noted and a clean impinger assembly was started. To maximize the collection efficiency and prevent soot from being carried into other components of the system, a 45 mm diameter PTFE filter (0.45 µm nominal porosity) was connected in series behind the glass impinger. The PTFE filter with soot particles was added to the impinger solution before an aliquot was removed for analysis. The flow through the impinger was maintained at approximately 800 mL/min with a mass flow controller. The actual volume of gas collected in the impingers was monitored with a dry gas meter (1.0 L/revolution) and used in calculating the average HCN concentration. The impingers were weighed to 0.01 g accuracy after collection and the resulting solution weight was used in the calculation for average HCN concentration. Two impingers were connected in parallel with appropriate shutoff valves to allow flow through one impinger while the other, containing dissolved combustion gases, was replaced with a new impinger. The undissolved combustion products were vented to an exhaust hood. A diagram of the collection system is shown in Figure 4.

2.2.3.1.3 Full-Scale Room Burn Experimental Test Plan (Protocol A)

Table 3 summarizes the test conditions used in Protocol A. Seven tests were conducted - four without Cu_2O (tests no. A1-A4) and three with Cu_2O (tests no. A5-A7). In each test, one block of foam was cut in half such that each half measured 0.5 m wide by 1.0 m long by 0.1 m thick. The foam blocks were stacked to form a 0.2 m thick polyurethane foam structure and placed on a load cell to monitor mass loss during the tests. To simulate a nonflaming/smoldering/flaming fire scenario, a specially designed electric heater[4] was placed between the two foam blocks. This heater system was used to initiate nonflaming combustion. The degree of charring indicated that at some point the nonflaming combustion started an internal smoldering. Approximately one hour after initiation of nonflaming combustion, a small propane gas diffusion burner flame was applied to the charred material to produce flaming combustion if flaming did not occur spontaneously. The burner was equipped with a remotely actuated ignitor producing approximately a 120 mm long flame. The flame was applied to the charred surface long enough to insure flaming ignition of the test sample. In two of the 7 tests [A3 (untreated FPU) and A5 (0.1% Cu_2O-treated)], the foams self-ignited after about 60 minutes. In test A3, the pressure relief vent in the door ruptured shortly after flaming ignition. Two of the tests (A6 and A7) with Cu_2O-treated FPU were conducted with the vent open to examine the effect of increased ventilation. Test A7 was conducted with a foam to which 1.8% Cu_2O was added

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[4] The electric heater assembly was made by evenly winding 2.33 m of # 28 nichrome wire around two 3 mm diameter ceramic rods for a total electrical resistance of 34.5 ohms. By trial and error, it was found that an applied voltage of 65-70 VAC would provide sufficient thermal energy to cause the foams to smolder without forcing them into flaming combustion.

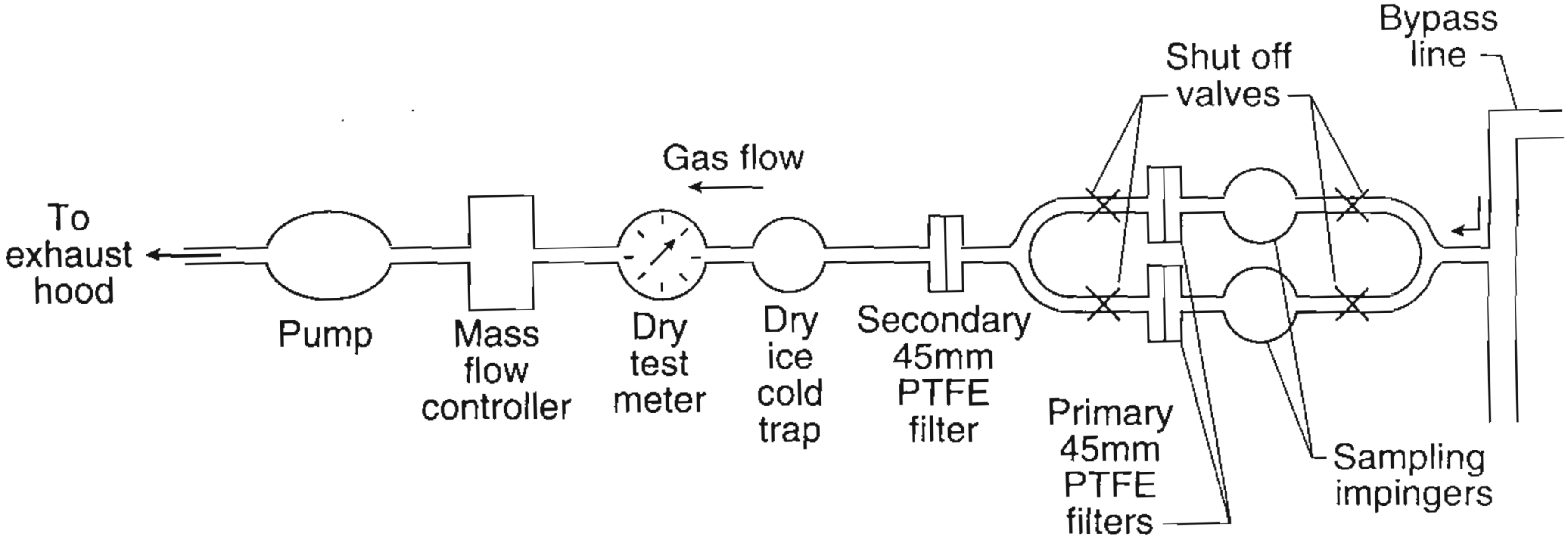

Figure 4. Combustion product collection system for large-scale tests

as a post-treatment so the final level of Cu_2O was 1.9%; the post-treatment was performed as described in section 2.1.1.

Two analytical tests without animals were conducted to characterize the burning properties of the Cu_2O treated FPU and the untreated foams. Five tests were conducted with animals. Each animal exposure chamber was equipped with an intake and an exhaust shut-off port. These ports were opened at the beginning of each test and the combustion gases from the burn room were allowed to continuously circulate between the exposure chambers and the burn room. At predetermined CO concentrations, individual animal chambers were closed. Six animals in restrainers were inserted into portholes in the front of the chambers such that only their heads were exposed to the combustion atmospheres. The animals remained in the exposure chambers for 30 minutes. Since each chamber was closed at a different time, three different smoke concentrations from each test, could be presented to the animals. Treatment of the animals prior to and following each exposure was the same as that for the small-scale cup furnace smoke toxicity method studies described in sections 2.1.6, 2.2.2.1. and 2.2.2.2.

Table 3. Test Conditions in the Full-Scale Room Toxicity Tests for Protocol A

Test No.	Cu_2O (%)	Animals Exposed	Flaming Ignition	Door Vent	Sample Weight (kg)	Smolder Time (s)	Comments
A1	0	No	Manual	Closed	2.40	4490	NO_x not analyzed
A2	0	Yes	Manual	Closed	2.40	4440	
A3	0	Yes	Self-ignition	Closed open[a]	2.38	4260	
A4	0	Yes	Manual	Closed	2.38	3780	
A5	0.1	No	Self-ignition	Closed	2.40	3890	
A6	0.1	Yes	Manual	Open	2.40	3180	
A7	1.9	Yes	Manual	Open	2.46	3080	Power outage

a. Vent ruptured shortly after flaming ignition.

2.2.3.2 Protocol B

2.2.3.2.1 Test Arrangement and Instrumentation

The tests were conducted in a collinear burn room/corridor/target room arrangement, as shown in Figure 5. The walls and ceiling of the compartments were covered by two layers of 12.7 mm thick Marinite. The floor substrate was a 102 mm thick slab of concrete covered with a single layer of 12.7 mm thick Marinite. The burn room and target room each measured 3.66 m long by 2.44 m wide by 2.44 m high. The corridor measured 4.57 m long by 2.44 m wide by 2.44 m high. The two interconnecting doorways and the exit doorway were 2.03 m high by 0.76 m wide.

In order to monitor mass loss continuously, each mockup chair assembly was located approximately 0.1 m above the burn room floor on a load platform that was in the center of the burn room.

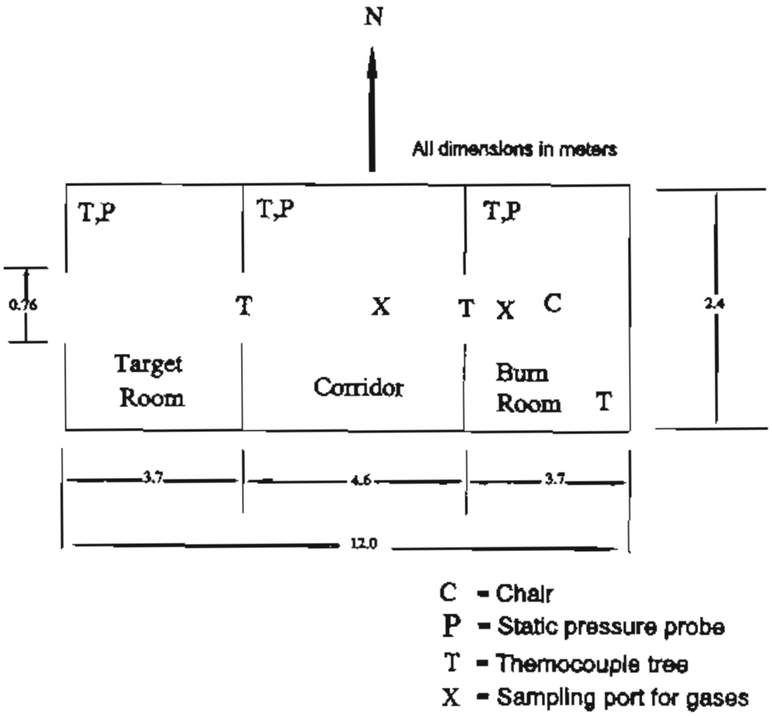

Figure 5. Schematic representation of room arrangement and instrumentation for Protocol B.

Table 4 lists all the instrumentation used in these experiments and the location of the sampling points. Figure 5 shows the location of the instrumentation within the test compartments. Thermocouple trees consisting of vertical lines of twelve thermocouples were located in opposite corners of the burn room and the far corners of the corridor and target room and were used to determine the location within the compartment of the interface between the hot upper layer and cool lower layer and determine the average temperatures of each layer. Thermocouple trees were also located in the vertical centerline of each doorway opening. In conjunction with a pressure transducer, these thermocouple trees were used to determine total flow into and out of each compartment [15].

The main exhaust hood was also instrumented to provide data on temperature, flow, smoke obscuration, and gas analysis of CO, CO_2, and O_2. These data were used to determine heat release rate (by oxygen consumption calorimetry), yields of CO, CO_2, and the specific extinction coefficient.

A gas sampling line was provided to draw a small fraction of the total gas flow to a convenient location for the determination of HCN and NO_x as well as CO, CO_2, and O_2. For the first two tests, the sampling line was a 55 mm diameter stainless steel tube. For the remaining four tests, the sampling line was a 52 mm diameter pyrex tube. The location of the sampling tube was either in the corridor on the center line of the compartment 0.46 m from the doorway and 0.15 m from the ceiling or in the burn room above the center line of the burn room doorway (0.15m from doorway and 0.15 m from ceiling). The sampling tube was used to transport gases from the corridor or burn room to gas sampling stations. Carbon monoxide, CO_2, NO_x, and O_2 were continuously monitored. Periodic gas samples for HCN were taken from the sampling line in evacuated gas sampling bulbs for subsequent GC analysis.

Table 4. Location of Instrumentation in Three Compartment Fire Tests (Protocol B)

Location	Instrument	Description	Notes
Burn Room	Load Platform	Centered in compartment	
	Pressure Transducer	Across doorway opening, 0.09 m from floor	
	Sampling Port	Above doorway opening 0.15 m from ceiling; CO_2, CO, and HCN	Tests B5 & B6 only
	Thermocouple	Centered over chair assembly 25 mm below ceiling	
	Thermocouple Trees		
	SE Corner	12 - TC's; 0.15, 0.67, 0.825, 0.987, 1.12, 1.28, 1.43, 1.58, 1.72, 1.88, 2.02, 2.14 m	
	NW Corner	12 - TC's; 0.15, 0.67, 0.825, 0.987, 1.12, 1.28, 1.43, 1.58, 1.72, 1.88, 2.02, 2.14 m	
	Doorway	11 - TC's; 0.15, 0.65, 0.81, 0.97, 1.11, 1.24, 1.40, 1.55, 1.705, 1.855, 2.02 m	
Corridor	Thermocouple Tree		
	NW Corner	12 - TC's; 0.15, 0.66, 0.81, 0.97, 1.12, 1.27, 1.42, 1.57, 1.72, 1.88, 2.03, 2.15 m	
	Sampling Port	Center line of compartment; 0.46 m from burn room door, 0.15 m from ceiling; CO_2, CO, and HCN	Tests B1-B4, only
Target Room	Thermocouple Tree		
	NW Corner	9 - TC's; 0.25, 0.66, 1.07, 1.47, 1.885, 2.2, 2.3, 2.365, 2.4 m	
Exhaust Hood	Gas Analyzers	Centerline of exhaust hood; CO_2, CO, and, O_2	
	Smoke Meter	single beam obscuration meter	
	Static Pressure Probes	9 - equally distributed along cross sectional area of exhaust hood	
	Thermocouples	10 - equally distributed along cross sectional area of exhaust hood	

2.2.3.2.2 Full-Scale Room Burn Experimental Test Plan (Protocol B)

Three sets of experiments were conducted. Each set consisted of two tests: one chair assembly made with the cotton cover fabric and untreated flexible polyurethane foam and one chair assembly made with cotton cover fabric and Cu_2O-treated FPU. The test conditions are described in Table 5. During the first set of tests, an auxiliary burner was used to irradiate the charred remains of the chair assembly after the flaming combustion ended. This was done to determine if the charred residue would release additional HCN. These two tests also used the stainless steel sampling tube. Tests B3 to B6 used the pyrex sampling tube and differed only in the location of the sampling tube. The type of sampling tube material used was changed from stainless steel to pyrex after the first two tests to determine if the metal had any effect on HCN loss in the sampling lines.

Table 5. Test Conditions in the Full-Scale Room Tests (Protocol B)

Test No.	Cu_2O (%)	Sampling Position	Sampling Tube	Sample Weight (kg)	Smolder Time (s)	Flaming Ignition	Auxiliary Gas Burner (kW)
B1	0	Corridor	Stainless Steel	7.24	3670	Spontaneous	200
B2	1.0	Corridor	Stainless Steel	7.10	1350	Spontaneous	550
B3	0	Corridor	Pyrex	7.36	2200	Spontaneous	0
B4	1.0	Corridor	Pyrex	7.18	1990	Spontaneous	0
B5	0	Burn Room	Pyrex	7.28	3560	Spontaneous	0
B6	1.0	Burn Room	Pyrex	7.14	1820	Spontaneous	0

Smoldering was initiated by simultaneously placing a total of three lit cigarettes on the seat cushion, one cigarette at each of the crevices between the seat cushion and the sides and one at the crevice between the seat and the back cushion. Three cigarettes were used to maximize the amount of char present prior to the transition to flaming combustion. Each chair assembly went into flaming combustion without the need to use a flaming ignition source. For tests B1 and B2, an auxiliary natural gas burner was located at the center of the back wall. The surface of the burner was at the same height as the top of the seat cushion. The burner was used to try to create a flashover condition and to determine if additional HCN would be released by the charred residue if the room went to flashover after the seat assembly stopped flaming. This burner was not used in the remaining four tests.

2.2.4 ANALYSIS OF CHARRED RESIDUES

2.2.4.1 Elemental Analysis

Cuprous oxide treated and untreated FPU foams (which had not been heated) and charred residues from the small-scale tests (taken following phase 1 from the cup furnace smoke toxicity procedure) and Protocol A full-scale tests (following the nonflaming/smoldering/flaming tests) were subjected to elemental chemical analysis. The charred residues used for chemical analysis from the cup furnace smoke toxicity method were generated in the cup furnace by decomposing approximately 4 g of the untreated FPU samples and Cu_2O-treated FPU foams (equivalent to a concentration of 20 g/m^3) in the nonflaming mode at 375° C for 30 minutes. In the full-scale tests from Protocol A, the charred residues were taken from the remains of the foams after the nonflaming/smoldering/flaming portions of the tests. The elemental analysis of both the charred residues and foams were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee.

2.2.4.2 Ramped Heating of Charred Residues in the Small-Scale Cup Furnace

Some charred residues of Cu_2O-treated and untreated FPU foams remaining after the nonflaming/smoldering/flaming experiments in the full-scale room burns were exposed to the phase two ramped heating mode of the cup furnace smoke toxicity method to see whether additional amounts of HCN could be generated and whether the presence of Cu_2O had any effect. In the Protocol A procedure, about 0.3 g of the charred residue (which is approximately equal to the amount of charred residue remaining after 6 g of FPU were thermally decomposed at 375° C for 30 minutes) were ramped heated from 375° C to 800° C. In Protocol B, the chars from the full-scale tests were separated by flake size to distinguish between the char from the cotton fabric and that from the FPU. Hydrogen cyanide concentrations were measured by GC (see section 2.2.2.5) during phase 2 for 30 minutes starting 5 minutes after the start of the ramped heating.

2.2.5 N-GAS MODEL PREDICTION

An empirical mathematical model (called the N-Gas model) based on studies of the toxicological interactions of up to six gases - CO, CO_2, HCN, reduced O_2, $HC\ell$ and HBr - has been developed at NIST to predict the toxic potency of materials and to determine if an unusual toxicological response will occur [16-20]. The following equation used in this series of experiments was empirically derived to predict the death of 50% of the animals either within the 30 minute exposures or during the post-exposure period. An N-Gas value of ≈ 1 predicts that approximately 50% of the animals should die.

$$\frac{m\,[CO]}{[CO_2]-b} + \frac{[HCN]}{LC_{50}HCN} + \frac{21-[O_2]}{21-LC_{50}O_2} + \frac{[HBr]}{LC_{50}HBr} + \frac{[HCl]}{LC_{50}HCl} \approx 1 \qquad (1)$$

Since the FPU used in these studies did not produce $HC\ell$ or HBr upon thermal decomposition, these two factors were not used in these studies for the determination of the N-Gas value. For this study, the following formula was used:

$$\frac{m\,[CO]}{[CO_2]-b} + \frac{[HCN]}{LC_{50}HCN} + \frac{21-[O_2]}{21-LC_{50}O_2} = 1.1\ (0.9\ -\ 1.3) \qquad (2)$$

where the numbers in the brackets indicate the actual time-weighted average concentration of the gases in ppm (CO, CO_2, HCN) or percent (O_2). The numbers in the parentheses are the 95% confidence limits of the N-Gas value. If the deaths are due to the toxic interactions of these gases, no deaths would be expected if the N-Gas value was below 0.9 and all the animals would be expected to die if the N-Gas value was above 1.3. The LC_{50} value of HCN is 200 ppm for 30 min exposures or 150 ppm for 30 min exposures plus 24 hour post-exposure deaths; the LC_{50} value for O_2 is 5.4%. The terms m and b equal -18 and 122000, respectively, if the CO_2 concentrations are 5% or less or 23 and -38,600, respectively if the CO_2 concentrations are above 5%.

3.0 RESULTS AND DISCUSSION

The main purpose of the studies presented in this report was to validate with full-scale room burns prior small-scale findings that the presence of low levels of Cu_2O (0.1% to 1.0% by weight) in FPU foams would significantly reduce the HCN generated during the thermal decomposition of the foams. The small-scale tests indicated a 80 to 90% reduction in the HCN generation. In addition, we also were interested in determining if the presence of the Cu_2O affected the physical properties of the foams and finally, since Protocol A was conducted in a closed room and the reduction in HCN generation was not observed, we also examined the effect of reduced oxygen on the reaction of Cu_2O and HCN.

3.1 PHYSICAL PROPERTIES OF Cu_2O-TREATED AND UNTREATED FPU

The physical properties of the 1.0% Cu_2O-treated and untreated FPU from batch 2 were examined by BASF in accordance with the experimental procedures described in ASTM D3574 [11]. The results of these tests (Table 6) indicate no significant differences between the Cu_2O-treated and the untreated foams. If there were no significant differences at the 1% Cu_2O level, one would not expect to see significant differences at the 0.1% level. According to T. Smeincinski, who made the foams at BASF, slight differences in the physical properties would probably be eliminated through optimization of the proper catalysis levels in the formulation.

Table 6. Physical Properties of the Untreated and 1.0% Cu_2O-Treated FPU Foams in Batch 2[a]

Physical Property[b]	Untreated FPU		1.0% Cu_2O-Treated FPU	
	SI units	(U.S. customary units)	SI units	(U.S. customary units)
Density kg/m^3 (lb/ft^3)	24.6	(1.52)	23.3	(1.44)
Tensile strength kPa (lb/in^2)	119	(17.3)	120	(17.4)
Elongation %	157	(157)	153	(153)
Tear strength N/m (lb/in)	440	(2.5)	370	(2.1)
Resilience %	39	(39)	35	(35)
IFD N/323 cm^2 (lb/50 in^2)				
25% Deflection	199	(44.7)	210	(47.3)
65% Deflection	402	(90.5)	421	(94.7)
Support factor	2.02	(2.02)	2.00	(2.00)
Compression sets %				
50%	9.6	(9.6)	7.6	(7.6)
90%	14.4	(14.4)	24.4	(24.4)
Air flow dm^3/sec (ft^3/min)	0.47	(1.0)	0.23	(0.5)

(a) The tests for these physical properties were conducted at BASF according to ASTM D3574.
(b) The description of each of these tests can be found in Section 2.2.1.

3.2 SMALL-SCALE TESTS

The two phase combustion mode (nonflaming/ramped heating) of the cup furnace smoke toxicity method was used to verify that the results with the batch 1 and batch 2 FPU prepared for this study would agree with the results that had been obtained previously [3-5]. The current FPU foams differed from those used before only in that larger pieces of foam were continuously machine mixed on a pilot scale, whereas previously, the foams had been hand-mixed by the same supplier. The Cu_2O was added during the formulation. In our first year's study, copper or copper compounds had been added to a flexible polyurethane foam as a post-treatment in our laboratory.

In addition, we examined the difference in HCN generation from a Melamine-treated FPU foam and a standard FPU foam and examined the effect of the addition of Cu_2O to the Melamine-treated FPU foam. This type of foam is one of two FPU foams now allowed in furniture in Great Britain. Finally, we examined the Cu_2O-treated foams and the untreated foams under small-scale flaming conditions.

3.2.1 Cup Furnace Smoke Toxicity Method

3.2.1.1 Two Phase Combustion Mode - FPU Foams

The 30 minute nonflaming phase was conducted at 25°C below the material's autoignition temperature which was determined as 400°C. During the 35 minute ramped heating phase, the temperature of the furnace was increased approximately 13°C/min until 800°C was obtained. In the tests with animals, the rats were exposed to the combustion products for 30 minutes starting 5 minutes after the beginning of the ramped heating which was the period when most of the HCN was generated. The dotted curves in Figure 6 shows the generation of HCN from the decomposition of 22 g/m^3 of untreated FPU and 20 g/m^3 of 0.1% Cu_2O-treated FPU during the two phases. Similar to our previous studies, the untreated FPU produced significantly more HCN during the ramped heating phase than the Cu_2O-treated FPU, i.e., the maximum HCN from the untreated foam was 200 ppm; whereas, that from the Cu_2O-treated FPU was 30 ppm - an 85% reduction. A significant reduction of HCN in the presence of 0.1% Cu_2O was noted at all mass loadings of FPU tested (Figure 7). The chemical and toxicological results for the untreated FPU and the 0.1% Cu_2O-treated foams are presented in Tables 7 and 8, respectively. These tables plus Figure 7 show that the average HCN concentration following the thermal decomposition of the untreated foams ranged from 70 (at a mass loading of 12.5 g/m^3) to 150 ppm (26 g/m^3). The maximum HCN concentrations ranged from 100 ppm (12.5 g/m^3) to 220 ppm (26 g/m^3). In the combustion atmospheres of the 0.1% Cu_2O foams, the average HCN concentration ranged from 10 ppm (at a mass loading of 18 g/m^3) to 35 ppm (37 g/m^3) and the maximum HCN concentrations ranged from 15 (22 g/m^3) to 45 ppm (37 g/m^3). The 30 minute LC_{50} values went from 26.6 (untreated) to 38.0 g/m^3 (treated) and the 30 minute and 14 day LC_{50} values went from 15.0 (untreated) to 25.5 g/m^3 (treated). These results indicate a 43 to 70% reduction in toxicity. An increase in LC_{50} value indicates lower toxicity since it means that more of the material is needed to cause the same effect.

Two small-scale cup furnace analytical tests (no animals) were conducted with the Batch 2 foams (untreated and 1.0% Cu_2O-treated) to check that these foams also produced HCN reduction results similar to those seen in previous tests with lower levels of Cu_2O. In these two experiments, the mass loading was 30 g/m^3 for both the untreated and treated foams. The average and maximum HCN concentrations for the untreated foam were 155 and 225 ppm, respectively; whereas, the average and maximum HCN concentrations for the 1.0% Cu_2O-treated foam were 25 and 30 ppm, respectively. This constitutes an 84% (in the case of the average concentration) and 87% (in the case of the maximum concentration) reduction in HCN generation. These data are depicted in Figure 8 and Table 9. Although no animals were exposed in these experiments, the N-Gas values shown in Table 9 indicate that this loading of untreated FPU would have generated a lethal level of gases, while the atmosphere would not have been lethal if the foam were treated with the Cu_2O.

Tables 10 and 11 show that the toxicological and HCN results, respectively, from this series of tests agree very well with those obtained previously. The toxicological results in Table 10 indicate that in the current series of experiments, the 0.1% Cu_2O-treated foams showed a decrease in toxicity of 41% (based on deaths during the 30 minute exposures) and 73% (based on deaths during the 30 minute exposures plus 14 day post-exposure observation period). HCN yields shown in Table 11 indicate a 7.9 fold decrease in HCN for the 0.1% Cu_2O treated foams and a 7.5 fold decrease for the 1.0% Cu_2O treated foams in the current series of tests. A 10 fold decrease was observed in the 1988 tests. The decrease appears to correlate with the form of copper and its percentage in the foam.

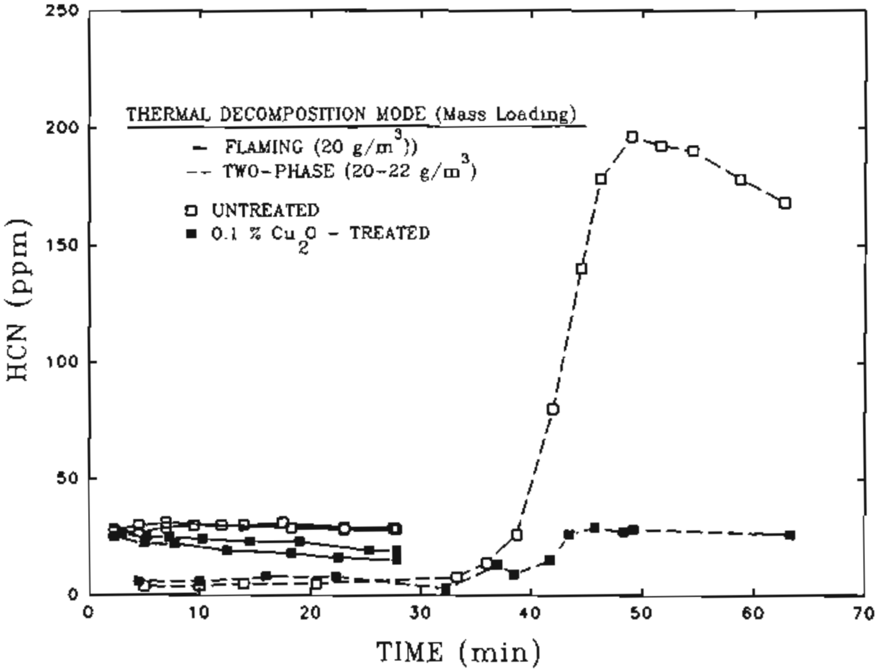

Figure 6. HCN generation from untreated and 0.1% Cu_2O-treated flexible polyurethane foam decomposed in the flaming mode or the two-phase ramped heating mode.

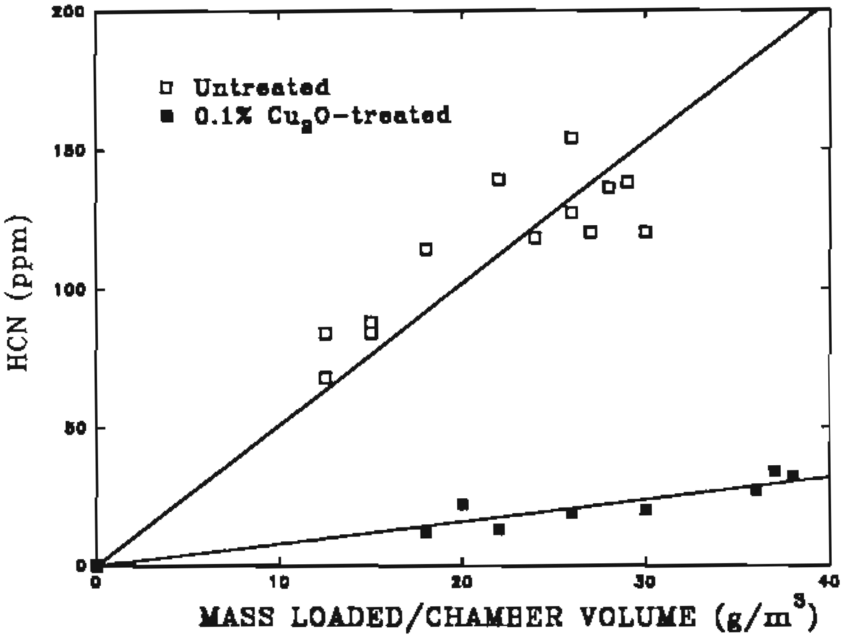

Figure 7. HCN generation from different mass loadings of untreated and 0.1% Cu_2O-treated flexible polyurethane foam decomposed in the two-phase ramped heating mode.

Table 7. Results from Flexible Polyurethane Foam (Batch 1), Without Cu_2O, Decomposed Via the Small-Scale Two Phase Toxicity Protocol

Mass/chamber vol.		Average Gas Concentrations[a]					Max[b] HCN (ppm)	N-Gas Value[c]		# died/# tested[d]		Day of Death[e]	LC_{50} (g/m^3)	
Loaded (g/m^3)	Consumed (g/m^3)	CO (ppm)	CO_2 (ppm)	O_2 (%)	HCN (ppm)	NO_x (ppm)		WE	WE & PE	WE	WE & PE		30 min.	30 min. & 14 days
12.5	12.5	1060	4430	20.3	70	NM	100	0.55	0.66	0/6	0/6	-		
12.5	12.5	1060	4380	20.3	85	NM	120	0.63	0.77	0/6	3/6	0,10,11		
15.0	15.0	1170	5020	20.2	85	NM	120	0.66	0.80	0/6	0/6	-		
15.0	15.0	1240	5310	20.2	90	NM	120	0.69	0.83	0/6	3/6	2,7,8		
18.0	18.0	1670	5870	20.1	110	NM	150	0.89	1.08	0/6	6/6	0,4,4,4,9,24		
22.0	21.9	1940	5890	20.0	140	NM	200	1.07	1.30	1/6	5/6	2,2,11,14	26.6	15.0
24.0	24.0	2060	6060	20.0	120	NM	200	0.98	1.18	1/6	5/6	5,12,13,14,	(24.4 - 29.1)[f]	(12.2 - 18.4)[f]
26.0	26.0	2300	3820	20.2	150	NM	220	1.17	1.43	A	A	A		
26.0	26.0	2480	4360	20.1	NM	NM	NM	NM	NM	A	A	A		
26.0	25.9	2410	5780	20.2	130	NM	180	1.07	1.28	3/5	5/5	2,17		
27.0	27.0	2250	6170	20.0	120	0-3	190	1.02	1.22	1/6	3/6	15,20		
28.0	28.0	2420	6590	19.9	140	0-1	210	1.03	1.36	3/6	5/6	1,1		
29.0	28.9	2570	6390	19.1	140	NM	200	1.10	1.45	5/6	6/6	1		
30.0	30.0	2860	6700	19.9	120	0-1	180	1.13	1.33	6/6	6/6	-		

a. Average gas concentration during 30 minute animal exposure.
b. Maximum HCN concentration during 30 minute animal exposure.
c. N-Gas value determined by equation (2) in Materials and Methods section.
d. Number of animals that died within exposure (WE) or within plus post-exposure (WE & PE)/Number of animals tested.
e. Days the animals died during post-exposure period.
f. 95% confidence limits of the LC_{50}.
NM. Not measured.
A. Analytical test without animals.

Table 8. Results from Flexible Polyurethane Foam (Batch 1), with 0.1% Cu_2O, Decomposed via the Small-Scale Two Phase Toxicity Protocol

Mass/chamber vol.		Average Gas Concentrations[a]					Max[b] HCN (ppm)	N-Gas prediction[c]		# died/# tested[d]		Day of Death[e]	LC_{50} (g/m^3)	
Loaded (g/m^3)	Consumed (g/m^3)	CO (ppm)	CO_2 (ppm)	O_2 (%)	HCN (ppm)	$NO_x/NO_2/NO$ (ppm)		WE	WE & PE	WE	WE & PE		30 min	30 min & 14 days
18.0	18.0	1700	6350	20.2	10	3/ND/ND	20	0.38	0.40	0/6	1/6	8	38.0 (31.1 - 46.4)[f]	25.5 (21.7 - 30.0)[f]
20.0	19.8	1790	6330	20.0	20	NM	30	0.46	0.49	0/6	1/6	16		
22.0	21.9	1670	5910	20.1	15	5/3/2	15	0.39	0.41	0/6	3/6	15,20,22		
24.0	23.9	1750	5920	20.1	NM	7/3/4	NM	NM	NM	0/6	3/6	10,10,13		
26.0	25.9	2060	6090	20.1	20	6/4/2	20	0.48	0.51	2/6	2/6	-		
30.0	29.9	2740	8400	19.7	20	17/9/8	25	0.63	0.66	2/5	4/5	15,17		
36.0	35.9	3210	9650	19.5	25	27/13/14	35	0.76	0.80	2/6	6/6	3,3,14,18		
37.0	36.9	3420	9650	19.5	35	33/10/23	45	0.83	0.88	1/6	6/6	11,14,14, 18,38		
38.0	38.0	3930	10500	19.4	30	28/13/15	40	0.91	0.96	5/6	6/6	18		

For legend, see Table 7.
ND. Not detected.

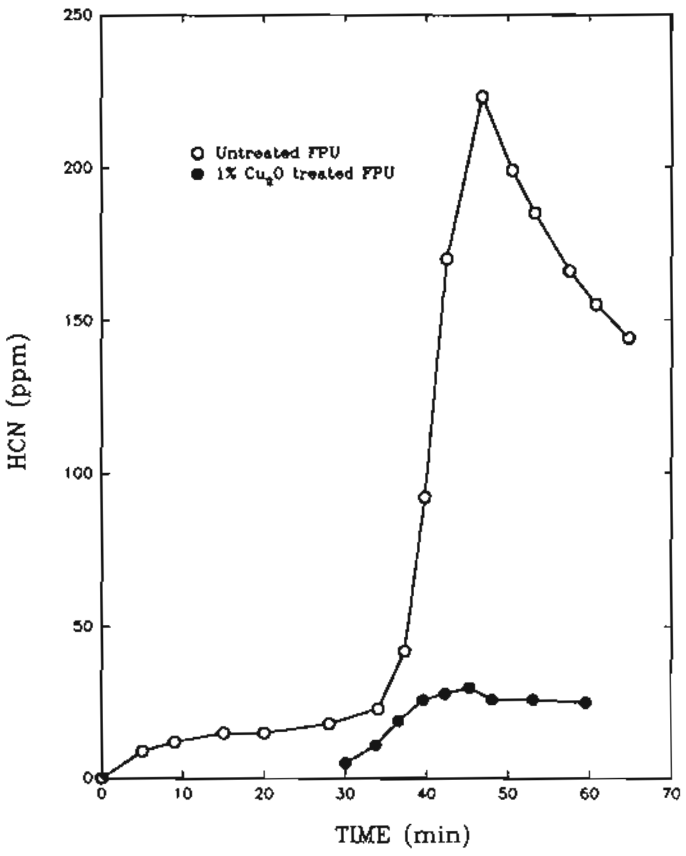

Figure 8. HCN generation from untreated and 1% Cu_2O-treated flexible polyurethane foam decomposed in the two-phase ramped heating mode.

Table 9. Chemical Results from Flexible Polyurethane Foam With and without 1.0% Cu_2O Decomposed via the Small-Scale Two-Phase Toxicity Protocol

Mass/chamber volume		Average Gas Concentrations[a]					Max[b] HCN (ppm)	N-Gas Prediction[c]	
Loaded (g/m^3)	Consumed (g/m^3)	CO (ppm)	CO_2 (ppm)	O_2 (%)	HCN (ppm)	NO_x (ppm)		WE	WE & PE
UNTREATED FPU									
30.0	30.0	2636	7396	20.2	156	ND	223	1.25	1.51
1.0% Cu_2O-TREATED FPU									
30.0	29.8	2353	7152	19.8	25	13	30	0.58	0.62

a. Average gas concentration during the 30 minute ramped heating phase that the animals would normally be exposed.
b. Maximum HCN concentration during the 30 minute ramped beating phase.
c. N-Gas value determined by equation (2).
ND: Not detected.
WE: Within exposure
WE & PE: Within exposure plus post-exposure observation period.

Table 10. Comparison of LC_{50} Results in the Small-Scale Toxicity Tests

Test Series	Untreated Foams LC_{50} (g/m^3)		Copper or Copper compounds	Treated Foams LC_{50} (g/m^3)	
	Within Exposure	Within plus Post-exposure		Within Exposure	Within plus Post-exposure
1990[a]	27 (24-29)[d]	15 (12-18)	0.1% Cu_2O	38 (31-46)	26 (22-30)
1988[b]	27 (24-30)	23 (11-45)	varied	43 (41-45)	23 (15-35)
1989[c]	27 (25-28)	18 (16-20)	0.0072% Cu	26 (25-27)	20 (19-21)
			0.072% Cu	35 (32-38)	18 (13-24)
			0.0072% Cu_2O	31 (29-33)	25 (22-28)
			0.072% Cu_2O	36 (35-37)	28 (24-31)

a. Data from current test series.
b. Data from test series conducted in 1988; see reference 3.
c. Data from test series conducted in 1989; see reference 4.
d. Numbers in parentheses are the 95% confidence limits of the LC_{50} value.

Table 11. Comparison of HCN Yields in the Small-Scale Toxicity Tests

Test Series	Untreated Foams Avg. HCN Yields[a] ± S.D. (g/g x 10^{-3})	Copper or Copper Compounds	Treated Foams Avg. HCN Yields[a] ± S.D. (g/g x 10^{-3})
1991[b]	8.2 (n=1)	1.0% Cu_2O	1.1 (n=1)
1990[b]	8.7 ± 1.0 (n=13)	0.1% Cu_2O	1.1 ± 0.2 (n=8)
1988[c]	8.0 ± 2.0 (n=12)	varied	0.8 ± 0.3 (n=25)
1989[d]	8.0 ± 3.4 (n=11)	0.0072% Cu	5.2 ± 1.1 (n=8)
		0.072% Cu	2.5 ± 0.4 (n=11)
		0.0072% Cu_2O	2.7 ± 0.6 (n=11)
		0.072% Cu_2O	1.4 ± 0.4 (n=13)

a. Yields based on maximum HCN determined in each test. The number of tests that were used to compute the average is n.
b. Data from current test series.
c. Data from test series conducted in 1988; see reference 3.
d. Data from test series conducted in 1989; see reference 4.

3.2.1.2 Is the Nitrogen from HCN Being Converted to NO_x When FPU is Treated With Cu_2O

In the small-scale testing, 3 ppm NO_x was the maximum concentration observed when the untreated foams were thermally decomposed according to the two phase thermal decomposition mode in the cup furnace. However, a range of 3 to 33 ppm of NO_x was observed when the 0.1% Cu_2O-treated foam was decomposed (Tables 7 & 8) and 13 ppm NO_x was found when 30 g/m^3 of the 1.0% Cu_2O-treated foam was ramped heated (Table 9). Figure 9 shows the HCN and NO_x results when a mass loading of 30 g/m^3 untreated or 0.1% Cu_2O-treated FPU was thermally decomposed. The maximum HCN from the untreated foam was 184 ppm; whereas, the maximum HCN from the 0.1% Cu_2O treated foam was 27 ppm. The 0.1% Cu_2O treated foam also produced a maximum of 21 ppm NO_x of which about half was NO_2 and half was NO. Therefore, in the presence of 1.0% or 0.1% Cu_2O, approximately 11% of the HCN normally produced in the absence of copper is generated and about 6% of the nitrogen shows up as NO_x (Table 12).

Table 12. HCN and NO_x from Untreated and Treated FPU and Percent HCN and NO_x Generated After Treatment with 0.1% or 1.0% Cu_2O Compared to the HCN from the Untreated Foams Decomposed in the Cup Furnace Toxicity Apparatus.

Mass loaded (g/m^3)	Untreated FPU			0.1% Cu_2O-treated FPU			1.0% Cu_2O-treated FPU			HCN (treated FPU) / HCN (Untreated FPU)		NO_x (treated FPU) / HCN (untreated FPU)
	HCN Av. (ppm)	HCN Max. (ppm)	NO_x Av. (ppm)	HCN Av. (ppm)	HCN Max. (ppm)	NO_x Av. (ppm)	HCN Av. (ppm)	HCN Max. (ppm)	NO_x Av. (ppm)	Average (%)	Maximum (%)	Average (%)
18	110	150	NM	10	20	3	-	-	-	9	13	3
22	140	200	NM	15	15	5	-	-	-	11	7	4
24	120	200	NM	NM	NM	7	-	-	-	-	-	6
26	150	220	NM	20	20	6	-	-	-	14	9	4
26	130	180	NM	20	20	6	-	-	-	15	11	5
30	120	180	0-1	20	25	17	-	-	-	17	14	14
30	156	223	0	-	-	-	25	30	13	16	13	8

Av. Average HCN or NO_2 calculated during the 30 minutes of Phase Two of the two phase thermal decomposition mode.
Max. Maximum HCN value observed during the 30 minutes of Phase Two of the two phase thermal decomposition mode.
-. No data.
NM: Not measured.

3.2.1.3 Two Phase Combustion Mode - Melamine-Foams

The melamine-foam with and without Cu_2O was decomposed via the two phase combustion mode in the cup furnace smoke toxicity method apparatus. In the ramped heating phase (phase 2), the untreated melamine-foam (20 g/m^3) produced approximately 6 times more HCN (approximately 1200 ppm) than an equal amount of standard FPU foam (approximately 200 ppm) (Fig. 10). The presence of Cu_2O reduced the HCN from the melamine foam by 90 percent (Fig. 11 and Table 13).

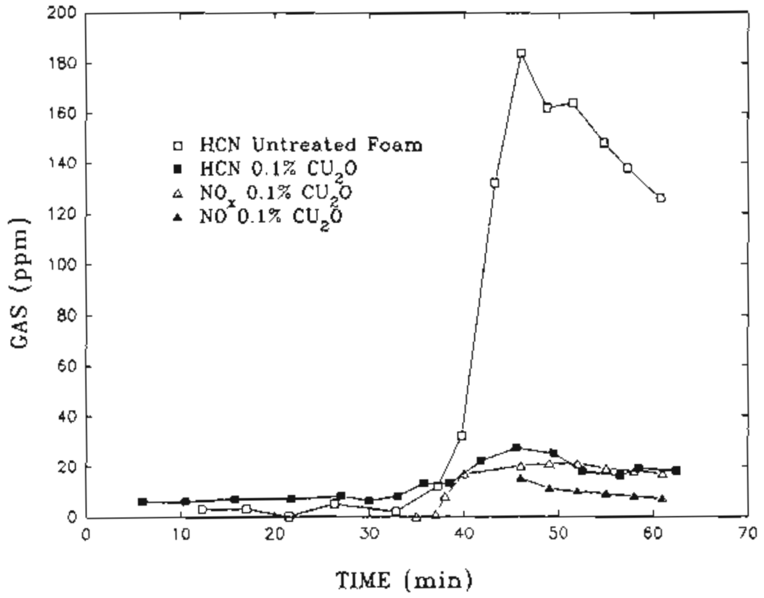

Figure 9. Generation of HCN, NO_x, or NO from 0.1% Cu_2O-treated flexible polyurethane foam compared to HCN from untreated foam. No NO_x or NO was found in the untreated foam.

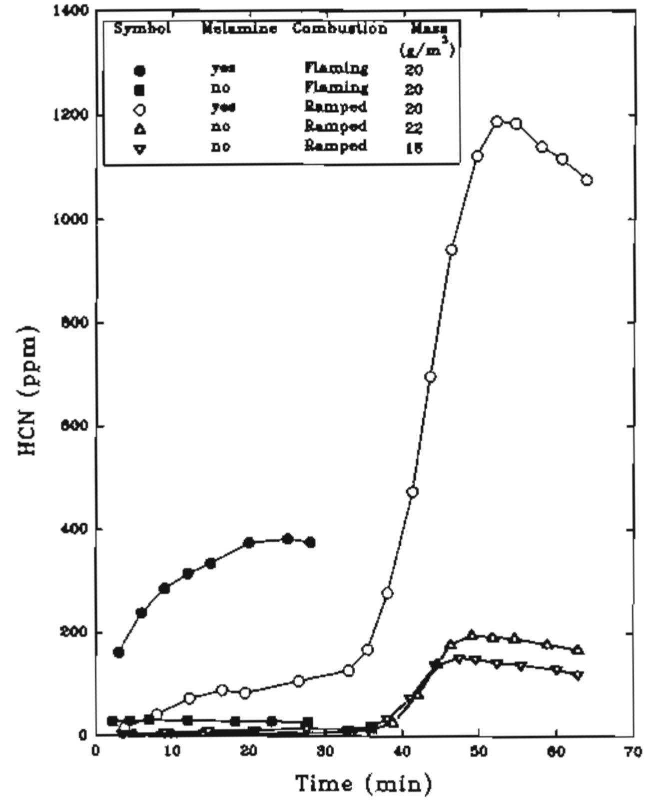

Figure 10. Generation of HCN from untreated or melamine-treated flexible polyurethane foam decomposed in the flaming or two-phase ramped heating mode.

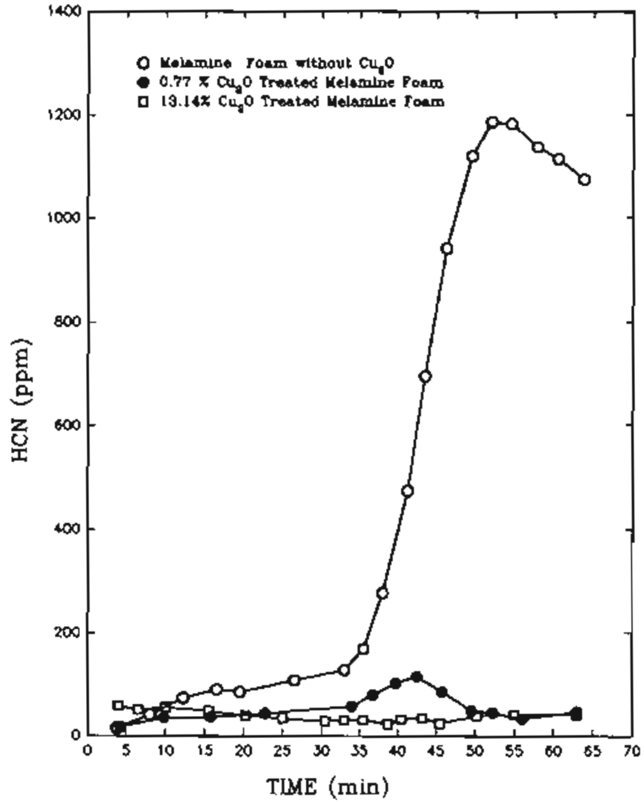

Figure 11. Generation of HCN from melamine-treated flexible polyurethane foam with and without the addition of Cu_2O. Foams were decomposed via the two-phase ramped heating mode.

Table 13. Hydrogen Cyanide Generation from FPU With and Without Melamine and Cu_2O

Melamine Treatment	Mass Loading (g/m^3)	Mass Consumed (g/m^3)	Cu_2O (%)	HCN Average (ppm)	HCN Maximum (ppm)
+	20.0	19.7	0	870	1187
-	18.0	18.0	0	110	152
-	22.0	21.9	0	140	196
+	20.0	19.8	0.77	65	120
+	20.0	19.4	13.14	35	40
-	20.0	19.8	0.1	20	30
-	18.0	18.0	0.1	10	20
-	22.0	21.9	0.1	15	15
-	30.0	29.8	1.0	25	30

+: Melamine treated
-: No melamine present

3.2.1.4 Flaming Mode - FPU Foams and Melamine Foams

The two FPU foams (untreated and 0.1% Cu_2O-treated) were thermally decomposed in the flaming mode (425° C) to determine the concentrations of HCN. Two experiments at 20 g/m^3 were conducted for each foam. Under flaming conditions, the untreated foam produced much less HCN than when decomposed in the two phase thermal mode, and still less when treated with Cu_2O (Fig. 6).

Under flaming conditions, the untreated melamine foam generated more HCN than the untreated FPU foam, but less than under the two-phase combustion conditions (Fig. 10). The Cu_2O-treated melamine foam was not tested under flaming conditions.

3.2.1.5 Reduced Oxygen Experiments

The production of HCN from the untreated and 0.1% Cu_2O treated FPU foams was examined under different O_2 concentrations to determine if full-scale HCN generation from the foams in a closed room would be affected by the lower O_2 concentrations expected under such closed room conditions. If Jellinek's hypothesis were correct, namely, that copper reduced HCN generation via a catalytic oxidation reaction [7,8], then it was possible that under lower O_2 concentrations, the copper would be less effective and more HCN would be generated.

Small-scale experiments with and without 0.1% Cu_2O were conducted at three O_2 concentrations: approximately ambient (20%), 12.5% (the lowest concentration observed in the closed room full-scale tests, Protocol A) and 6% (Fig. 12). The untreated FPU and the 0.1% Cu_2O-treated FPU were decomposed according to the two-phase ramped heating method described in the Methods and Materials section. Table 14 indicates that the average concentration of HCN was 74% less when the 0.1% Cu_2O was present and the oxygen concentrations were approximately ambient (20%). Reducing the O_2 concentration to approximately 12.5% did not change the average or maximum HCN concentrations in the absence or presence of the Cu_2O. At 12.5% O_2, the percent reduction of HCN was 79%. When the O_2 concentration was lowered to approximately 6%, the HCN level was lower in both the untreated foam and the Cu_2O-treated foam. At 6% O_2, the reduction in HCN was 82% in the treated foam as compared to the untreated foam. These results indicated that the Cu_2O effect on reduction of HCN would still be effective at O_2 concentrations as low as 6% and Cu_2O as low as 0.1%.

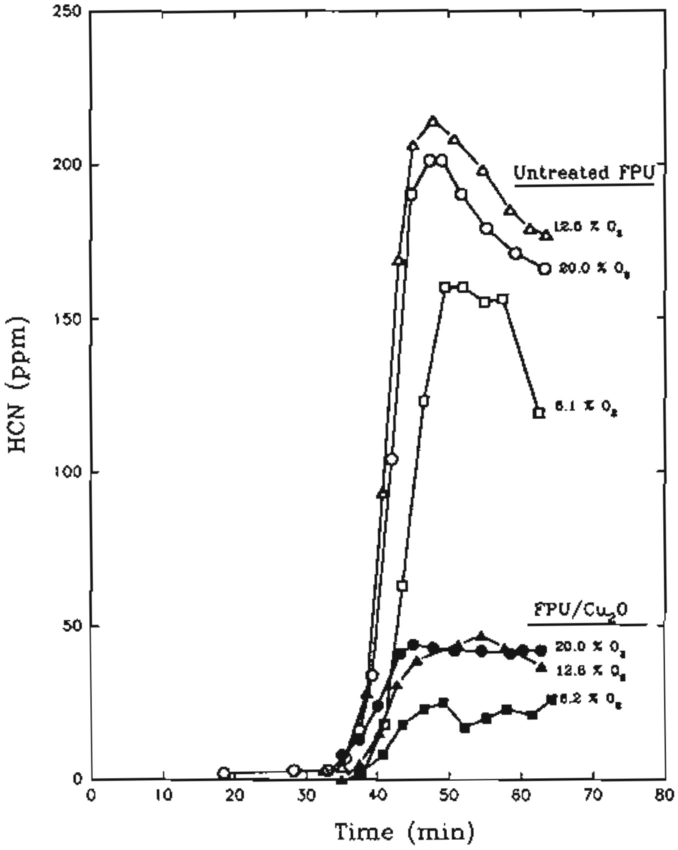

Figure 12. Effect of reduced oxygen concentrations on the generation of HCN from flexible polyurethane foam with and without 0.1% Cu_2O. Foams were decomposed via the two-phase ramped heating mode.

Table 14. Effect of Various Oxygen Concentrations on Flexible Polyurethane Foam, With and without 0.1% Cu_2O, Decomposed via the Small-Scale Two-Phase Toxicity Protocol

Mass/chamber vol.		Average Gas Concentrations[a]					Max[b] HCN (ppm)	Low O_2 Conc (%)	N-Gas prediction[c]	
Loaded (g/m^3)	Consumed (g/m^3)	CO (ppm)	CO_2 (ppm)	O_2 (%)	HCN (ppm)	NO_x (ppm)			WE	WE & PE
UNTREATED FPU										
30.0	30.0	2830	4930	20.0	140	ND	200	19.8	1.21	1.44
30.0	30.0	2400	4070	12.5	160	ND	210	12.3	1.72	1.99
30.0	30.0	1930	3050	6.1	100	NM	160	6.0	1.75	1.92
0.1% Cu_2O-TREATED FPU										
30.0	29.9	2970	5620	20.0	36	ND	44	19.7	0.71	0.77
30.0	30.0	2500	5000	12.8	34	ND	47	12.7	1.09	1.15
30.0	29.9	1800	3770	6.2	18	NM	25	5.9	1.32	1.35

a. Average gas concentration during the 30 minute phase two time that animals would normally be exposed.
b. Maximum HCN concentration during the 30 minute phase two time.
c. Lowest O_2 concentration during the 30 minute phase two time.
d. N-Gas value determined by equation (2).
ND: Not detected.
NM: Not measured.

3.3 FULL-SCALE ROOM BURNS

3.3.1 PROTOCOL A

Seven full-scale room burns were conducted in a closed room. The experimental research plan is described in detail in section 2.2.3.1.3. Briefly, tests A1 through A4 used the untreated foams and tests A5 and A6 used the 0.1% Cu_2O-treated foams. In test A7, the 0.1% Cu_2O-treated foam was post-treated with additional Cu_2O to make the final concentration 1.9%. In each test, the foam block was cut in half and one half was stacked on top of the other. The smoldering was started with a heated coil placed between the two halves. In two tests, the foams self-ignited at approximately 60 minutes. In the other cases, flaming was initiated with a small propane gas diffusion burner after smoldering about one hour. In test A3, the pressure relief vent in the door of the room ruptured shortly after flaming. Tests A6 and A7 were conducted with the vent open to determine the effect of increased ventilation.

3.3.1.1 Compartment Temperatures

Figures 13 to 18 show the upper and lower compartment gas temperatures (the values plotted are the average values obtained from the thermocouples located in the upper and those located in the lower layer). The interface height between the hot upper gases and cooler lower gases for tests A1 - A6 was approximately 0.3 m from the floor of the compartment and did not appreciably change from test to test regardless of whether the vent was open or closed. Since the load cell was located 0.1 m above the floor and the stacked cushions were 0.2 m high, the interface was approximately at the top of the cushion prior to any collapse.

Table 15 summarizes the upper and lower compartment temperatures at the time of flaming ignition and the upper and lower compartment peak temperatures. Peak upper compartment temperatures ranged from 210°C to 280°C. The peak lower compartment temperature ranged from 80°C to 130°C. Test A3 had the highest lower compartment temperature, but this may have been due to the fact that the vent cover panel in the door of the closed room ruptured shortly after flaming ignition of the foam block. Test A6, which was run with the vent open, did not show a significantly different temperature profile than that of the other tests. In agreement with previous studies on flammability characteristics of untreated and Cu_2O-treated FPU [6], the presence of 0.1% Cu_2O did not affect the temperatures at the time of flaming ignition nor the peak upper and lower layer temperatures.

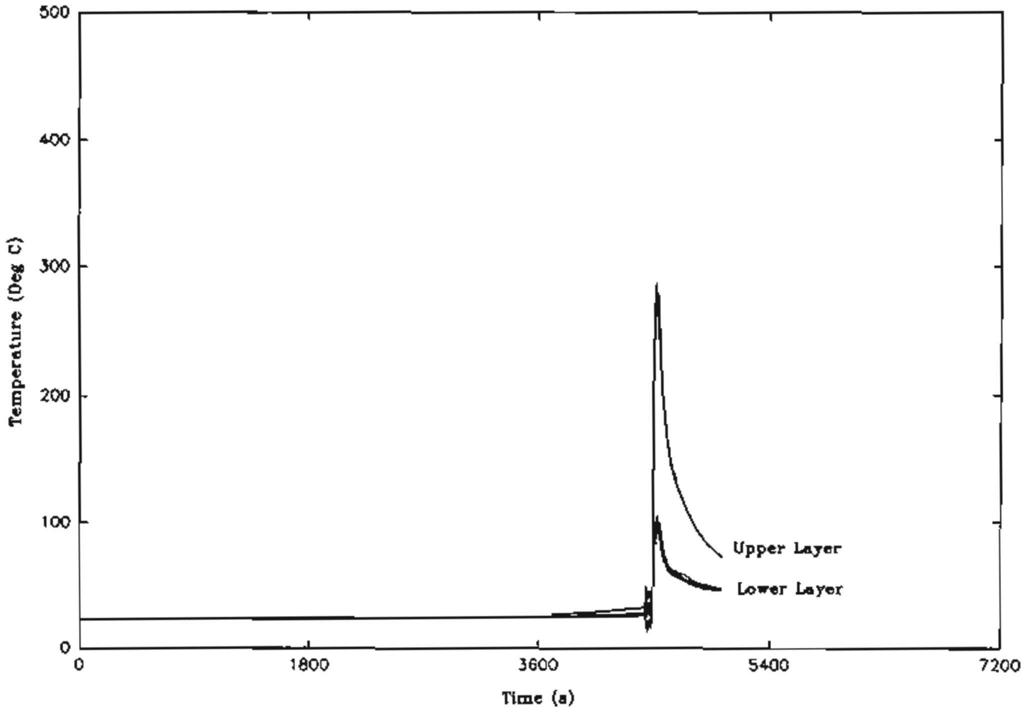

Figure 13. Gas temperatures in the upper and lower portions of the burn room for test A1.

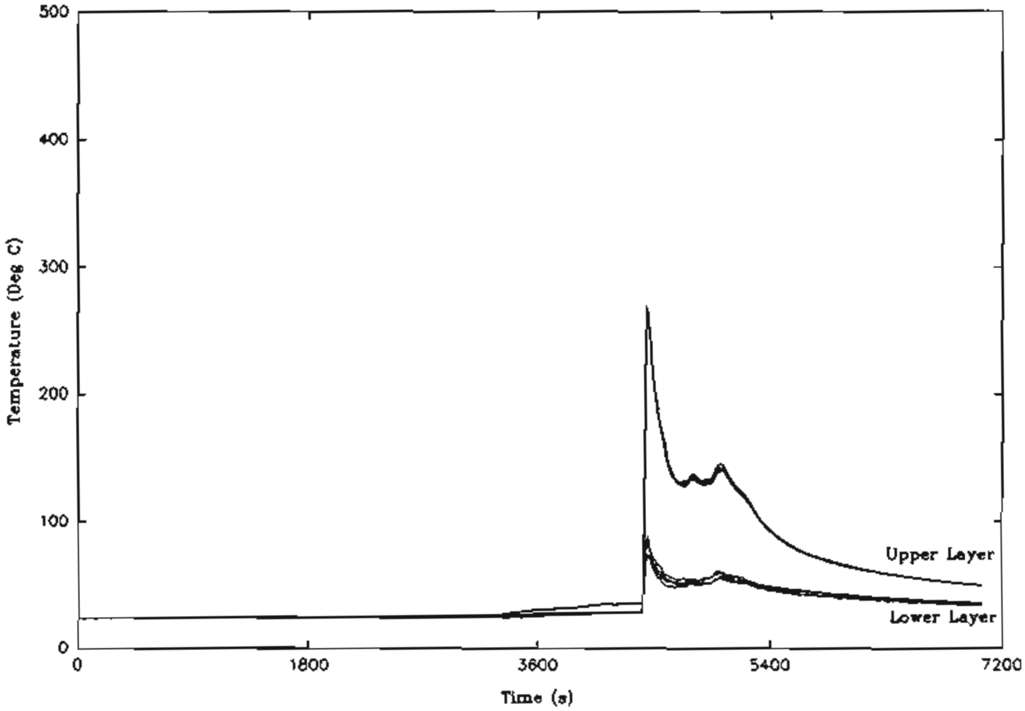

Figure 14. Gas temperatures in the upper and lower portions of the burn room for test A2.

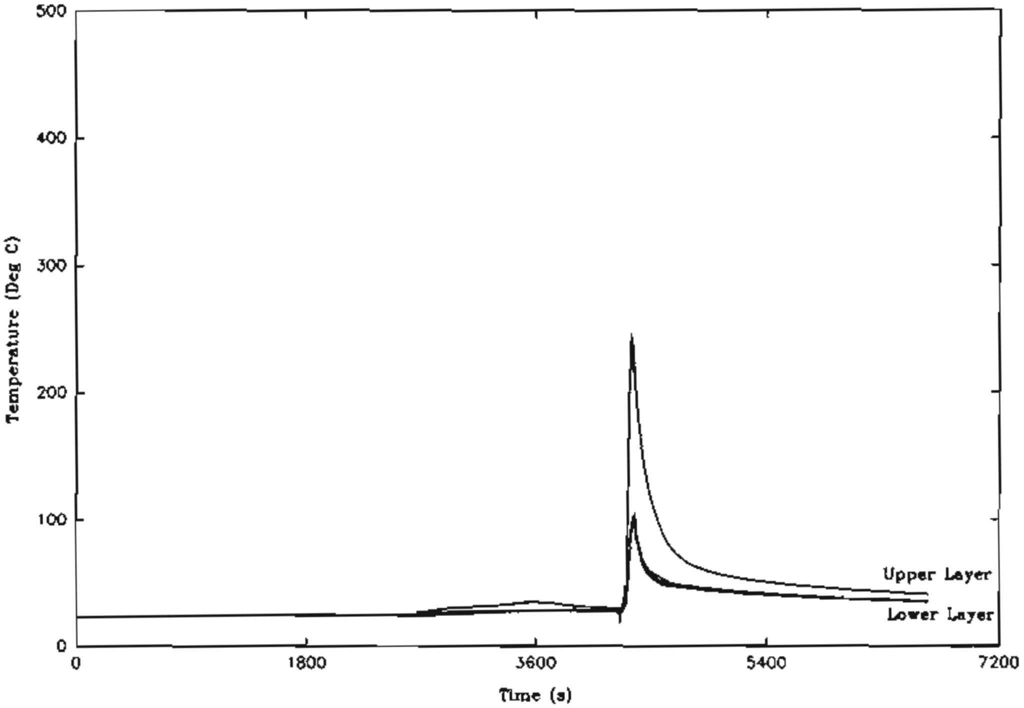

Figure 15. Gas temperatures in the upper and lower portions of the burn room for test A3.

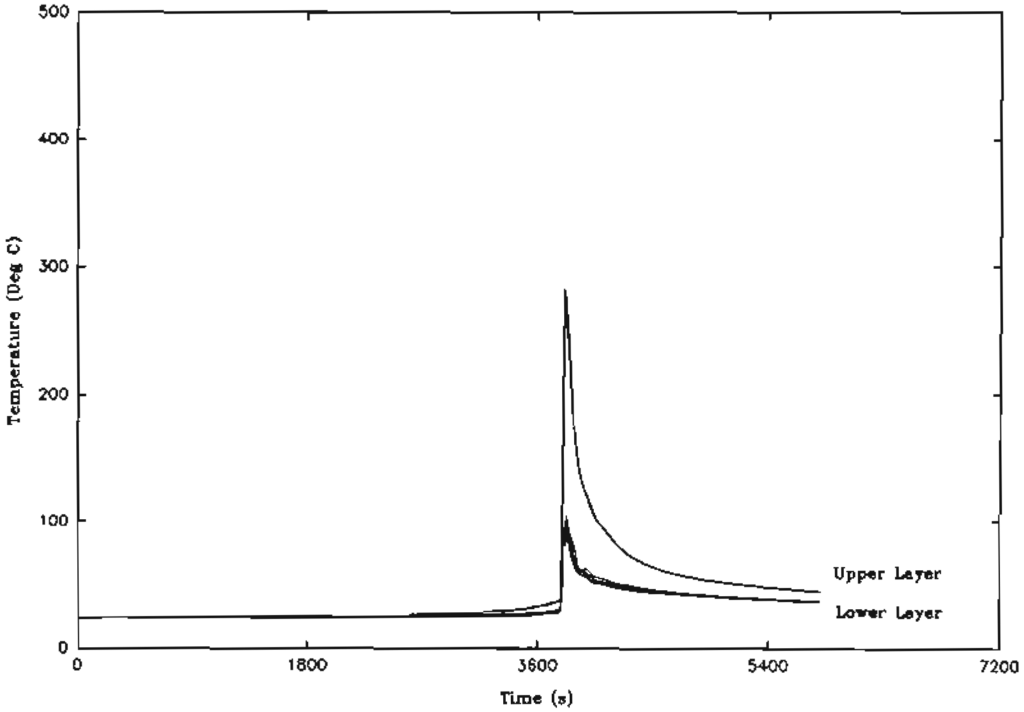

Figure 16. Gas temperatures in the upper and lower portions of the burn room for test A4.

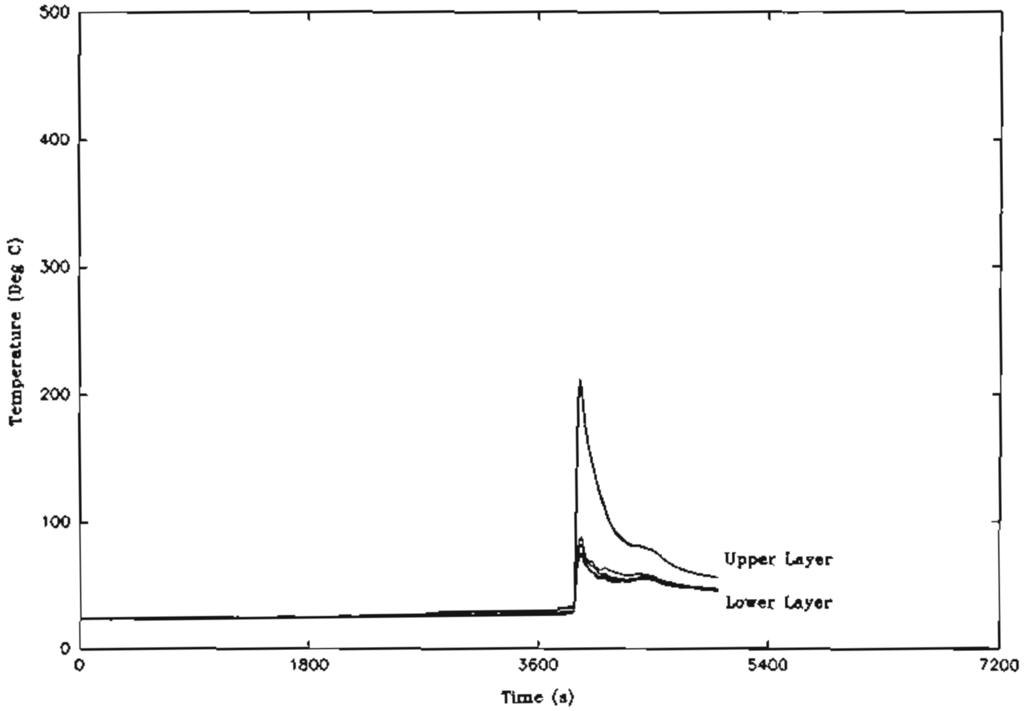

Figure 17. Gas temperatures in the upper and lower portions of the burn room for test A5.

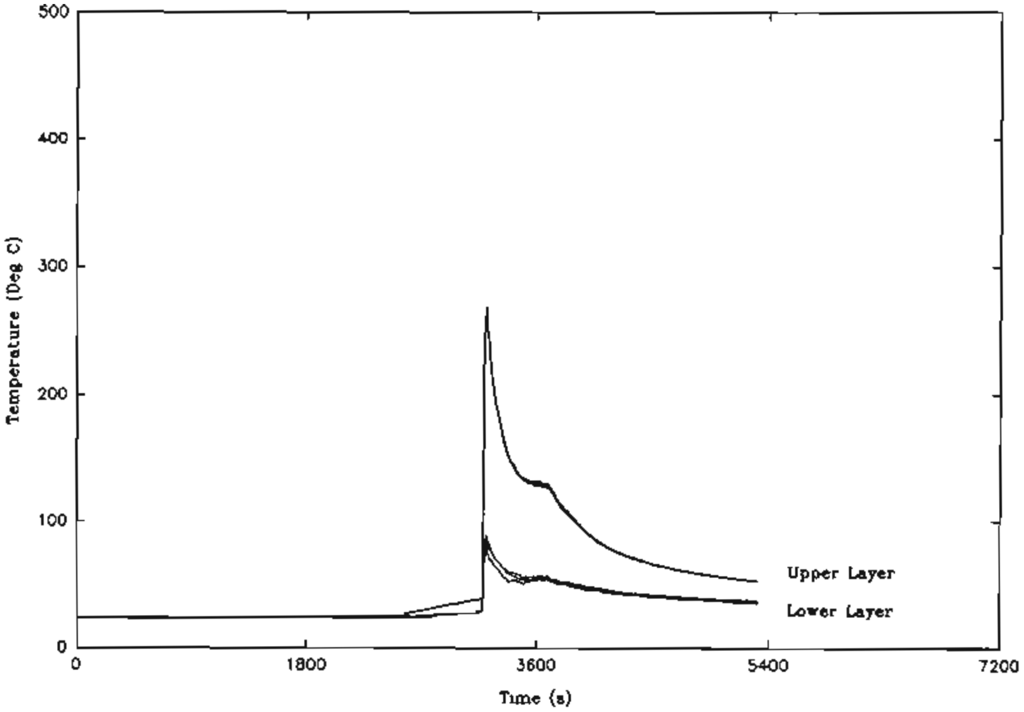

Figure 18. Gas temperatures in the upper and lower portions of the burn room for test A6.

3.3.1.2 Mass Loss

For full-scale tests A1 to A6, Table 16 lists the mass loss during smoldering combustion, flaming combustion and percent of the initial mass of material consumed. This table also provides the average mass loss rates during each phase of combustion. The average mass loss rate data was determined by taking the slope of the mass loss data over the period represented by a steady mass loss. Therefore, the initial long period of non-measurable weight loss was not included in the computations. It is assumed that this period represents combustion driven by the heating coil and not self-sustained (or smoldering) combustion. Figures 19 and 20 show the time dependence of the mass loss data during tests A1 to A6. For all the closed vent tests, only about 60% of the total amount of material available for combustion burned. This was independent of the presence of Cu_2O - compare test A5 (0.1% Cu_2O present) to tests A1 to A4 (no Cu_2O). Comparing tests A5 and A6 (Figure 20) shows the effect of the opened vent. The open vent test (test A6) consumed 96% of the material available as compared to the 62% for the closed vent test (test A5) of the same material. While the actual mass loss rates during each phase of combustion varied from test to test, the presence of 0.1% Cu_2O did not appear to have any effect on the decomposition rate during either smoldering or flaming combustion. These results agree with our flammability studies which indicated that the presence of copper did not affect the flammability characteristics of the foams [6]. For tests A1 to A4, the average smoldering mass loss rate was 0.6 g/s $\pm$ a standard deviation of 0.2 g/s and the average flaming mass loss rate was 3.0 g/s $\pm$ 1.6 g/s. A comparison of these smoldering or flaming values with those of tests A5 and A6, the Cu_2O-treated foam, where the average smoldering mass loss rate was 0.5 and the flaming mass loss rate was 1.8 g/s, indicate that neither the smoldering or flaming values are significantly different.

Table 15. Upper and Lower Compartment Temperatures (Protocol A)

Test Number	Cu_2O (%)	Temperature at Time of Flaming Ignition (°C)		Peak Temperature (°C)	
		Upper Layer	Lower Layer	Upper Layer	Lower Layer
A1	0	50	30	260	100
A2	0	40	30	260	80
A3	0	50	40	240	130
A4	0	40	30	280	80
A5	0.1	40	30	210	80
A6	0.1	40	30	270	90

Table 16. Mass Loss Data for the Full-Scale Tests (Protocol A)

Test No.	Cu_2O (%)	Vent	Mass Loss (kg)		Total Consumed (%)	Average Mass Loss Rate (g/s)	
			Smoldering	Flaming		Smoldering	Flaming
A1	0	C	0.46	0.97	60	0.6	3.2
A2	0	C	0.48	0.79	53	0.3	1.1
A3	0	R	0.62	0.70	56	0.6	2.7
A4	0	C	1.07	0.54	68	0.8	5.0
A5	0.1	C	0.41	1.08	62	0.2	1.8
A6	0.1	O	0.97	1.40	96	0.7	1.7

C: closed
R: Ruptured
O: Open

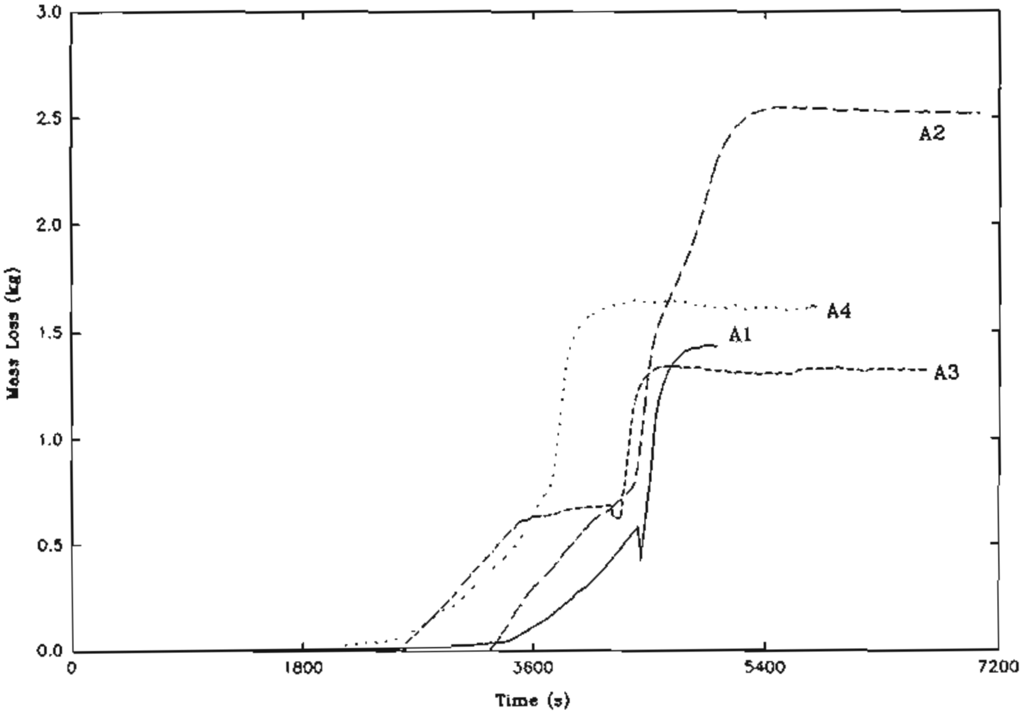

Figure 19. Comparison of mass loss for untreated foams in tests A1, A2, A3, and A4.

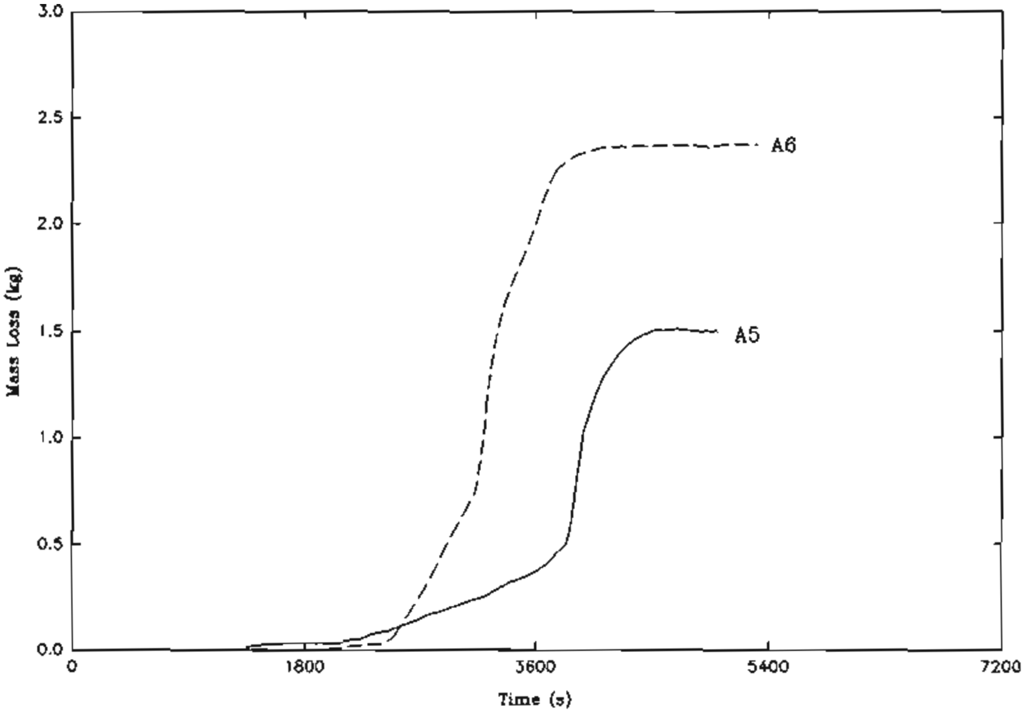

Figure 20. Comparison of mass loss for 0.1% Cu_2O-treated foams in tests A5 and A6.

3.3.1.3 Specific Gaseous Species - CO, CO_2, and O_2

Figures 21 to 25 show the CO, CO_2, and O_2 concentrations in the upper and lower part of the burn room for each of the experiments, A1-A5. The CO analyzer in the upper part of the compartment developed a background oscillation that varied about the actual gas concentration. Therefore, while the signal appears noisy, it does reflect an accurate representation of the "real" data. The data show a small difference between upper and lower compartment gas concentrations. These tests exhibit a certain degree of combustion product homogeneity and indicate that perhaps two distinct layers may not have existed. Table 17 shows the yields of CO and CO_2 for each phase of combustion (i.e., smoldering and flaming). In general, pre-flaming yields for CO varied from 0.08 to 0.28 and flaming yields ranged from 0.04 to 0.19. The CO_2 yields showed a dramatic difference between pre-flaming (varied from 0.28 to 0.66) and flaming (varied from 0.93 to 2.50) conditions. Due to instrument failure and a power outage, there is only one set of data (A5) for the Cu_2O-treated foams. Comparison of the CO and the CO_2 data from test A5 (0.1% Cu_2O) with the results from the tests with the untreated FPU foams showed that the yields did not appear to be significantly different.

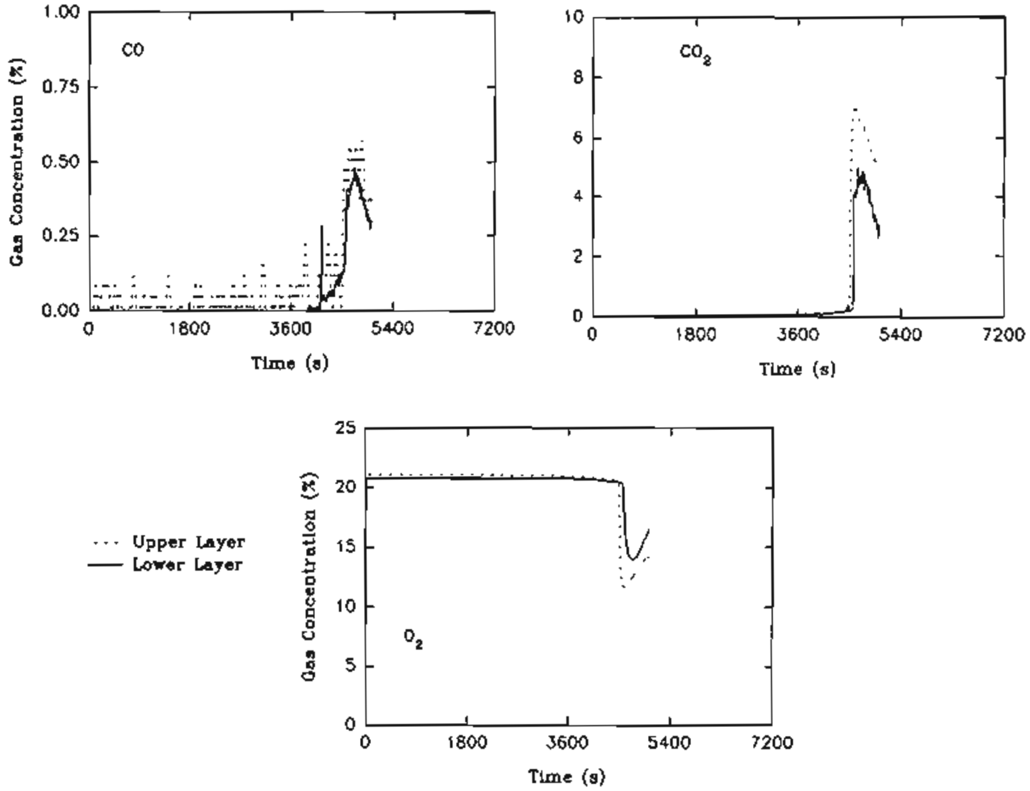

Figure 21. Gas concentrations of CO, CO_2, and O_2 in the upper and lower layers of the burn room for test A1.

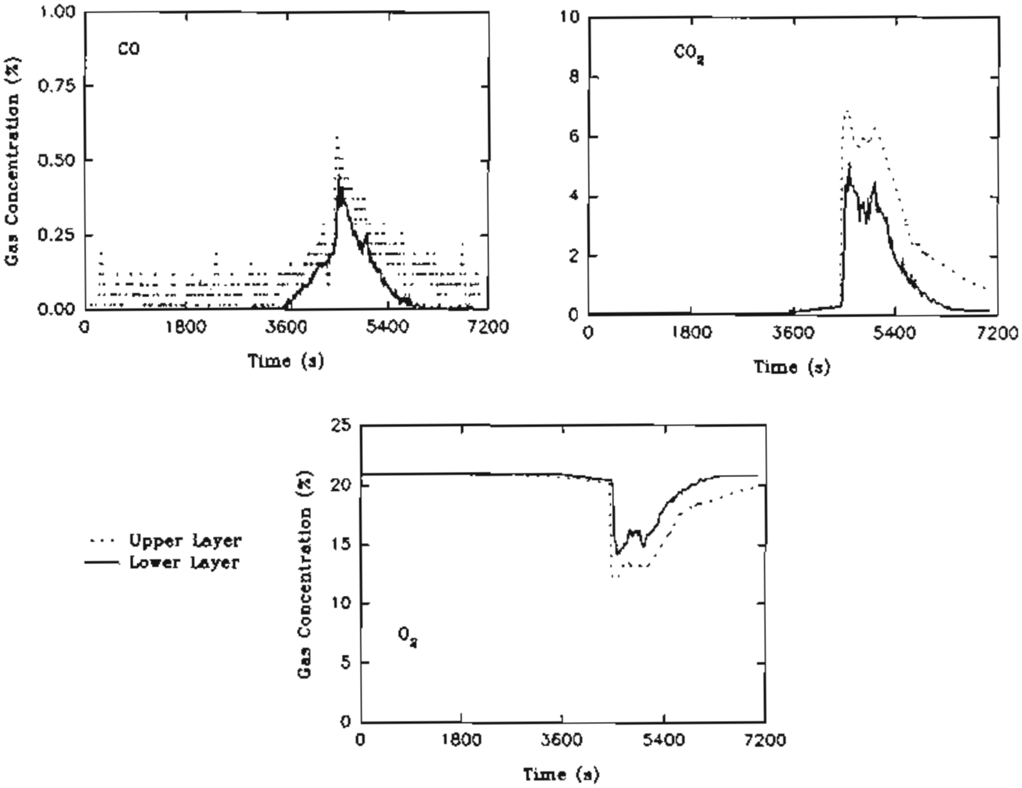

Figure 22. Gas concentrations of CO, CO_2, and O_2 in the upper and lower layers of the burn room for test A2.

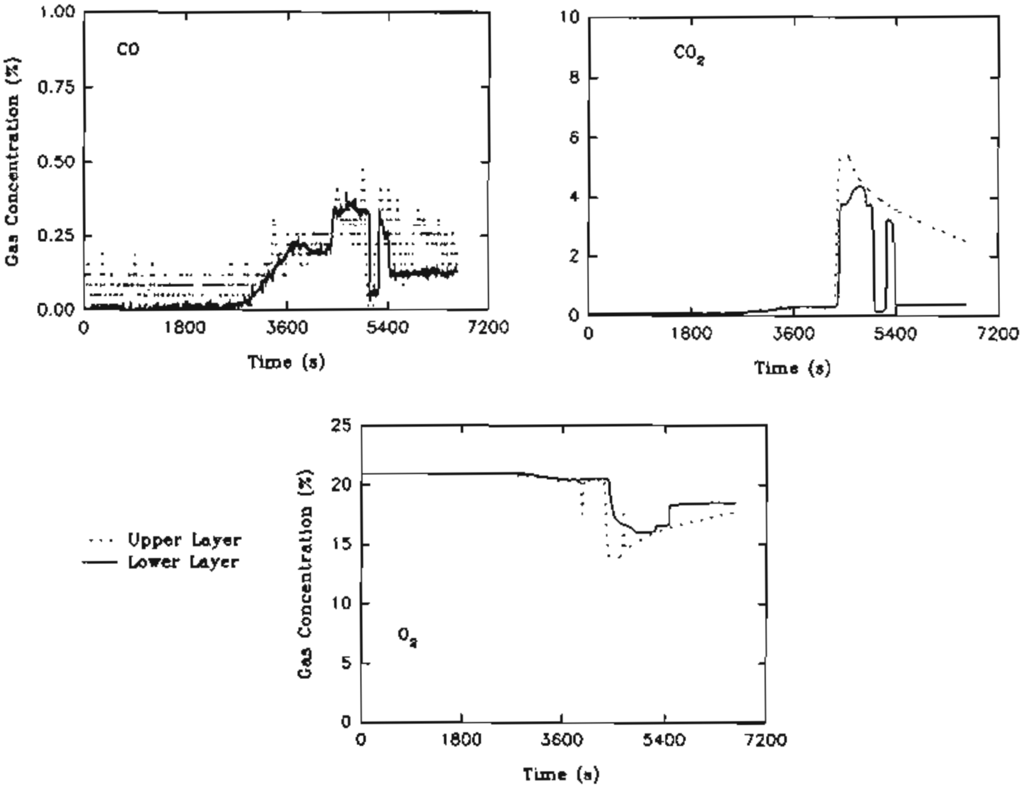

Figure 23. Gas concentrations of CO, CO_2, and O_2 in the upper and lower layers of the burn room for test A3.

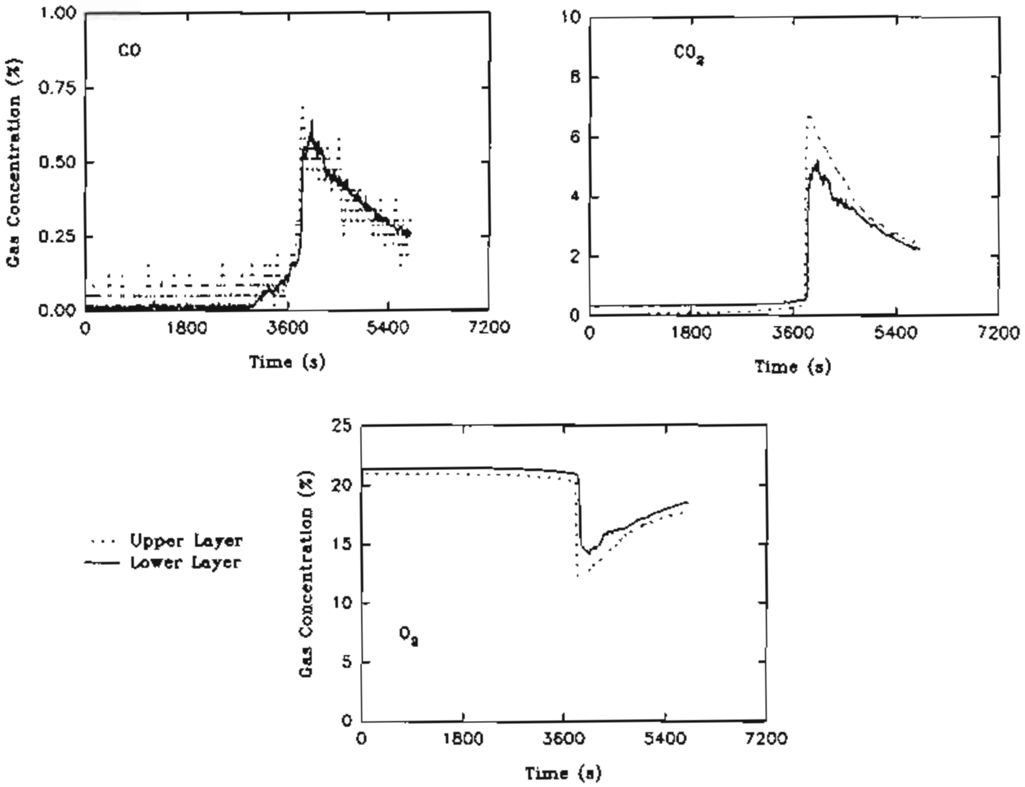

Figure 24. Gas concentrations of CO, CO$_2$, and O$_2$ in the upper and lower layers of the burn room for test A4.

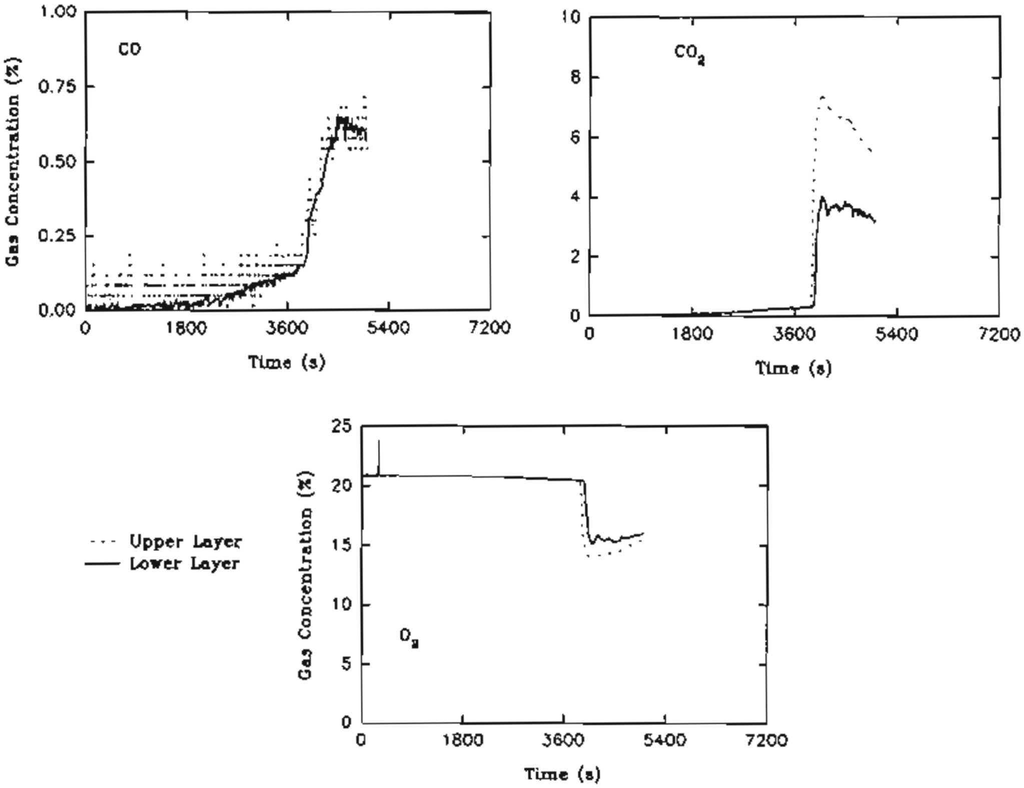

Figure 25. Gas concentrations of CO, CO$_2$, and O$_2$ in the upper and lower layers of the burn room for test A5.

Table 18 provides the chemical and toxicological results from the three animal exposure chambers that were connected to each of the full-scale room burns of the untreated and 0.1% Cu_2O-treated FPU that were decomposed under Protocol A. The experimental plan was to expose the rats to the smoke generated by the smoldering immediately prior to flaming and then to the smoke immediately following flaming. The times that flaming occurred and the times that the bottom, middle, and top animal exposure chambers were closed are given in Table 18. Experiments A1 and A5 were to collect analytical chemical data only and no rats were exposed. Unfortunately, there was a power outage during the test in which the FPU that received the additional post-treatment of Cu_2O (Test A7 with 1.9% Cu_2O) and much of the data from that test was lost. In the other tests, the rats were placed into the chambers shortly after they were closed. Since each chamber is a closed system, the concentrations in each chamber should remain stable for the 30 minute animal exposure period. The deaths of the animals are directly related to the concentrations of the gases and their toxicological interactions as depicted by the N-Gas Model. The results show good N-Gas agreement; in other words, if the N-Gas value is above 1.0, deaths of the animals occurred. The main questions, however, are whether the 0.1% Cu_2O-treated FPU generated less HCN and was less toxic. If one assumes that the concentrations of CO will increase proportionately as more material is thermally decomposed and the amount of HCN will also increase unless there is some interference (e.g., the Cu_2O prevents the formation of HCN), then one can normalize the HCN values to the CO values to see if there is any significant difference in the presence of Cu_2O. The results in Table 19 indicate that in Protocol A (only 0.1% Cu_2O in the FPU and the smoldering was initiated with a heated coil between two stacked cushions) no significant difference in the levels of HCN generated between the untreated and treated foams was observed.

Table 17. Gas Yields and HCN Concentrations from Untreated and 0.1% Cu_2O-Treated Flexible Polyurethane Foam Thermally Decomposed in the Full-Scale Burn Room Tests

Test No.	Cu_2O (%)	Type	Ignition Time (s)	Pre-Flaming Yields (kg/kg x 10^{-3})		Flaming Yields (kg/kg x 10^{-3})			Max. HCN & Time Measured				Minimum O_2 & Time Measured	
				CO	CO_2	CO	CO_2	HCN[a]	HCN[a] (ppm)	Time (s)	HCN[b]	Time (s)	O_2 (%)	Time (s)
A1	0	Analytical	4490	130	420	140	1950	2.1	130	4650	-[c]	-[c]	13.9	4760
A2	0	Animal	4440	250	570	70	1770	7.1	120	4260	120	4440-4740	14.1	4600
A3[d]	0	Animal	4260	270	660	40	930	2.0	90	4430	100	4500-4800	16.0	4980
A4	0	Animal	3780	80	280	190	2500	4.1	120	3930	200	3810-4080	14.0	4030
A5	0.1	Analytical	3890	280	300	90	2100	2.5	110	4260	140	4070-4370	15.2	4500
A6[e]	0.1	Animal	3180	-[f]	-[f]	-[f]	-[f]	6.6	190	3250	230	3200-3390	13.0	3400
A7[e]	1.9	Animal	3080	PO	PO	PO	PO	PO	130	3780	150	3600-3900	PO	PO

a. Measured by gas chromatography
b. Measured by ion chromatography
c. No data, line clogged.
d. Pressure relief vent ruptured after flaming.
e. Pressure relief vent open during test.
PO. Power outage; computer data lost
f. No data, instrument failure.

Table 18. Chemical and Toxicological Results from Animal Exposure Chambers Filled During Full-Scale Room Burns of Untreated and 0.1% Cu_2O-treated Flexible Polyurethane Foam (Protocol A)

Test No.	Cu_2O (%)	Animal Exposure Chamber	Time of Flaming (s)	Time Chamber Closed (s)	Avg. Temp[a] (°C)	Average Gas Concentrations[b]				N-Gas Value[c]	No. Died[d] / No. Tested
						CO (ppm)	CO_2 (%)	HCN (ppm)	O_2 (%)		
A2[e]	0	Bottom		3930	24	200	1.1	ND	20.4	0.07	0/6
		Middle[f]	4420	4650	27	-[f]	-[f]	55	-[f]	-[f]	2/6
		Top		5040	30	2800	3.4	70	15.0	1.33	6/6
A3	0	Bottom		3830	24	400	0.8	15	20.4	0.51	0/6
		Middle	4250	4420	25	2100	1.9	25	18.4	0.66	0/6
		Top		4680	26	2300	2.2	30	16.1	0.89	0/6
A4	0	Bottom		3770	24	300	1.3	20	20.1	0.21	0/6
		Middle	3800	3900	25	3100	2.7	60	17.3	1.13	1/6
		Top		4080	27	3900	5.1	110	16.1	1.86	6/6
A6[g]	0.1	Bottom		3090	24	300	1.2	10	20.2	0.14	0/6
		Middle	3170	3240	25	2600	1.9	40	18.1	0.84	0/6
		Top		3330	25	3700	4.4	80	15.2	1.65	6/6
A7[g]	1.9	Bottom		3080	-[h]	-[h]	-[h]	5	-[h]	-[h]	0/6
		Middle	3080	3245	-	-	-	55	-	-	0/6
		Top		3390	-	-	-	65	-	-	6/6

a. Average temperature in animal exposure chambers during 30 minute exposures.

b. Average gas concentrations in animal exposure chambers during 30 minute exposures.

c. N-Gas value calculated as described in Materials and Methods section.

d. Number of animals that died during the exposure/Number of animals tested in each chamber. There were no post-exposure deaths.

e. Pressure relief vent ruptured during test.

f. Leak between exposure chamber and analyzers.

g. Pressure relief vent open.

h. Power failure; data lost.

ND. Not detected.

Table 19. Ratio of HCN to CO in Animal Exposure Chambers in Protocol A

Test No.	Cu_2O (%)	Animal Exposure Chamber	$\frac{HCN}{CO}$	$\frac{HCN}{CO}$ Mean ± Standard Deviation
A2	0	Bottom Middle Top	ND ND 0.03	0.03 ± 0.02
A3	0	Bottom Middle Top	0.04 0.01 0.01	
A4	0	Bottom Middle Top	0.07 0.02 0.03	
A6	0.1	Bottom Middle Top	0.03 0.02 0.02	0.02 ± 0.01

ND: No data

3.3.2 PROTOCOL B

A total of six tests were performed. Three tests were conducted with the control untreated foam chair assembly and three tests were conducted with the 1.0% Cu_2O-treated foam chair assembly. The experimental plan for these tests are described in Section 2.2.3.2.2. and Table 5. The ignition procedure was the same for each test. For tests B1 and B2, the auxiliary burner was used after the end of flaming of the chair assembly.

3.3.2.1 Burn Room Fire Conditions

Figures 26 through 31 show the heat release rate, mass loss, and upper layer gas temperature in the burn room as a function of time for each of the six tests. These data are summarized in Table 20.

Table 20. Summary of Fire Conditions in the Burn Room (Protocol B)

Test #	Cu_2O (%)	Weight Loss at Flaming Ignition (%)	Average Mass Loss Rate		Peak Heat Release Rate (kW)	Burn Room Upper Layer Temperature (°C)
			Smoldering (g/s)	Flaming (g/s)		
B1	0	34	0.9	31.0	460	450
B2	1.0	9	1.2	26.8	850	460
B3	0	15	1.5	19.2	804	430
B4	1.0	11	0.8	23.5	1055	390
B5	0	27	1.0	28.2	720	466
B6	1.0	10	0.7	21.9	718	391

Table 20 shows that for four out of six tests the peak heat release ranged from 700 to 850 kW regardless of the presence of Cu_2O. Test B1 (untreated foam) seems to be low compared to the other untreated foam chairs and test B4 (1.0% Cu_2O) appears to be high compared to the other treated foams. Figures 26 and 27 show the results for tests B1 and B2. Both of these figures show two peak heat release rates for each test. The first peak was caused by the chair assembly, while the second peak was the output from the auxiliary burner. It can be seen from the data that the 1% Cu_2O-treated foam chair assembly had nearly twice the peak heat release rate than the non-copper treated foam chair assembly. This, however, was most likely due to the fact that the untreated foam smoldered longer in this test than in any of the other untreated or treated foam tests and test B2 smoldered the shortest time compared to any of the other treated or untreated foams. It may be that we are comparing two experiments which were outliers. Figures 28 to 31 show comparable data for the other four tests.

The time to flaming and the weight loss at flaming are summarized in Table 21 for each test. In general, the untreated foam appeared to smolder for longer periods of time, over 2000 s, than the 1.0% Cu_2O-treated foams, from 1350 s to 1990 s, consuming more material and probably generating more char before bursting into flaming combustion. A t-test was conducted to compare the mean smoldering time of the untreated foam chairs to that of the treated foams. An observed test statistic above 2.776 indicates a statistical significant difference at the 5% level. The 5% level of significance indicates that there is a 5% chance that a test statistic greater than this cutoff will occur when, in fact, the true mean smoldering time is the same for both the treated and untreated chairs. Usually, either the 5% or 1% levels of significance are used, and we have greater faith in rejecting the null hypothesis (i.e., all six measurements of smoldering time come from a normal distribution with the same mean and variance) if it is rejected at the 1% level (here, it is not). However, in this case, the test statistic does fall slightly above the 5% significance level cutoff; the observed test statistic was 2.79. This type of borderline result indicates that more experiments would need to be done to resolve this issue.

There are various definitions for flashover. Some use compartment size and ventilation conditions to calculate a heat release rate that would be indicative of flashover. Others use an upper layer gas temperature limit to define flashover. In a compartment of this size and with the specified door opening, flashover conditions would be expected to produce an energy release rate of about 1200 kW. Table 20 shows that the highest heat release rate value was 1050 kW. This is considerably less than would be expected for flashover. Using an upper layer gas temperature criterion of 500° C or 600° C, Table 20 also shows that flashover was not achieved by either criterion.

Table 21. Chair Assembly Weight Loss at Flaming Ignition

Test #	Cu_2O (%)	Time to Flaming (s)	Weight Loss at Flaming (kg)
B1	0	3670	2.5
B2	1.0	1350	0.7
B3	0	2200	1.1
B4	1.0	1990	0.8
B5	0	3560	2.0
B6	1.0	1820	0.7

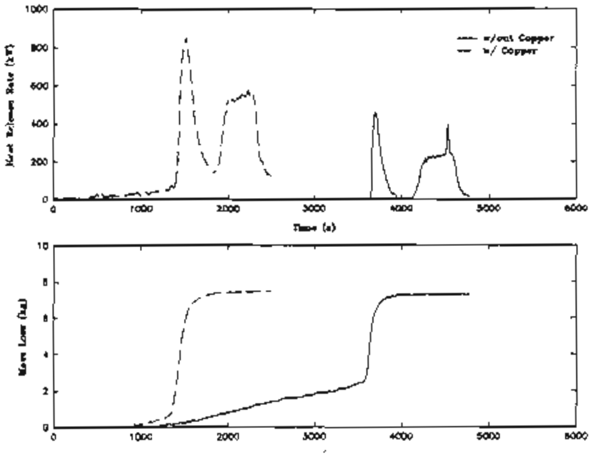

Figure 26. Heat release rate and mass loss data for tests B1 and B2.

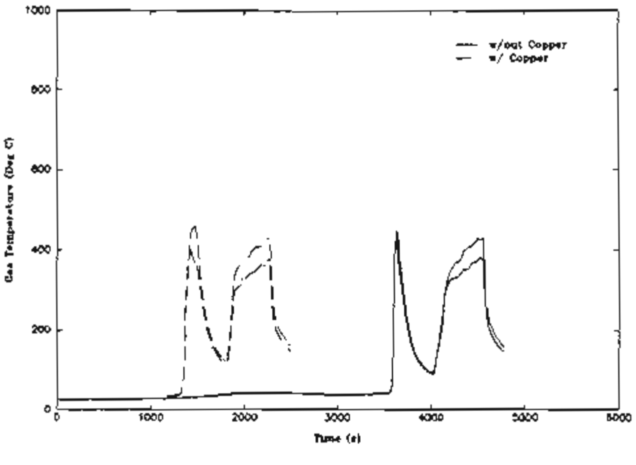

Figure 27. Burn room upper layer gas temperature (SE and NW corners) for tests B1 and B2.

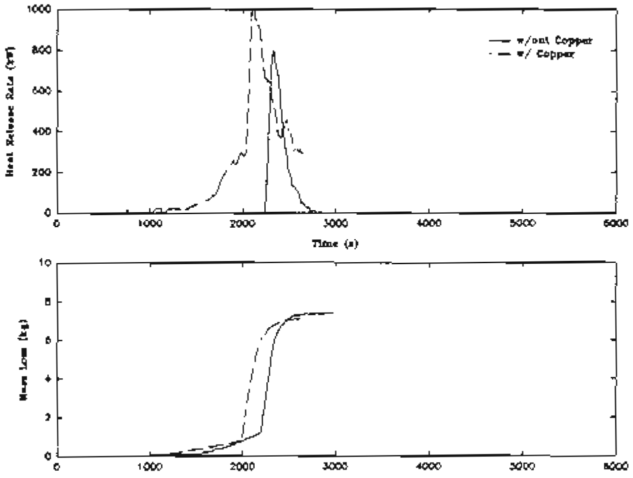

Figure 28. Heat release rate and mass loss data for tests B3 and B4.

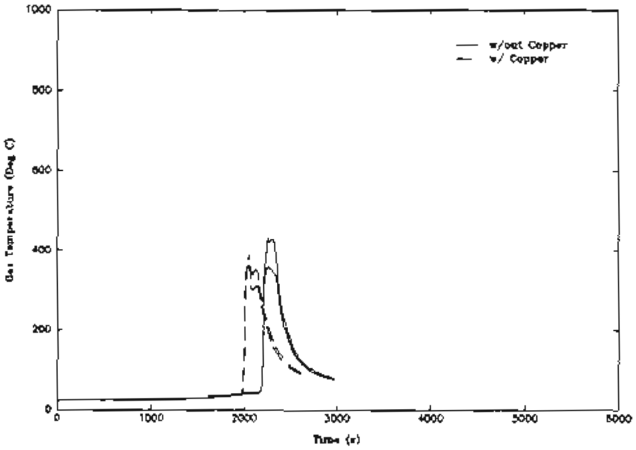

Figure 29. Burn room upper layer gas temperature (SE and NW corners) for tests B3 and B4.

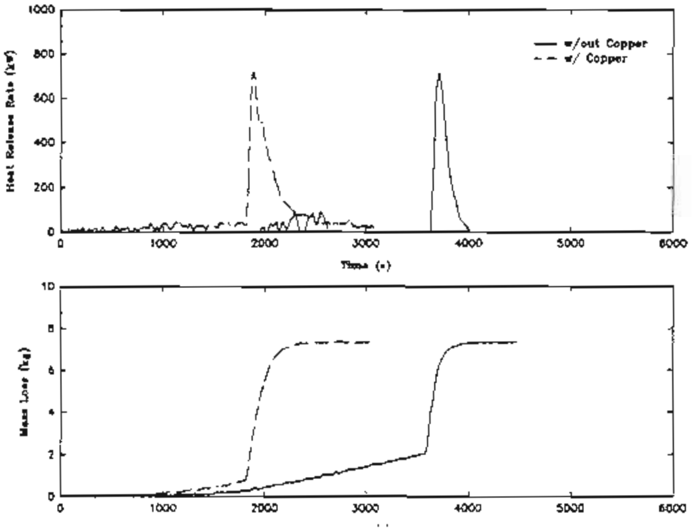

Figure 30. Heat release rate and mass loss data for tests B5 and B6.

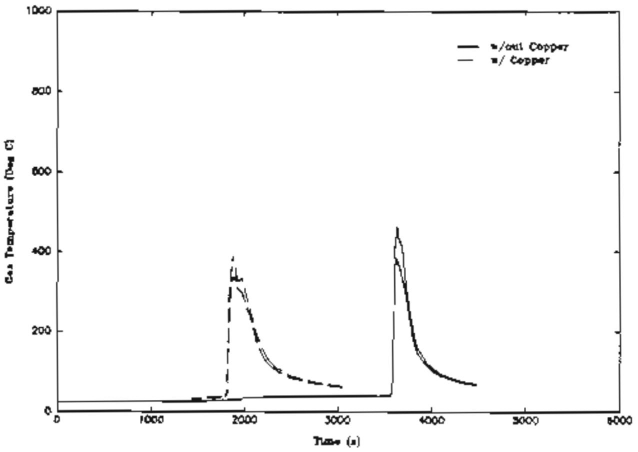

Figure 31. Burn room upper layer gas temperature (SE and NW corners) for tests B5 and B6

3.3.2.2 Yields of Gas Species - CO, CO_2, HCN - and Maximum Values of NO, NO_x and HCN

Since gas analyzers were installed in the exhaust stack to monitor CO_2 and CO, yields of these gases were calculated in a straightforward manner. HCN, however, was only monitored in the sampling port located either in the corridor or the burn room, depending on the test. HCN was therefore determined by a method previously described by Babrauskas, et al. [21]. In this method, the HCN yield is estimated based on the measurements of CO_2 and HCN in the sampling port. The HCN yield is computed as

$$f_{HCN} = \frac{27}{44}\,\frac{[HCN]_{port}}{[CO_2]_{port}}\,f_{CO_{2\,stack}} \tag{3}$$

where $f_{CO2\ stack}$ is the yield of CO_2 as measured in the exhaust stack, and the constants 27 and 44 represent the molecular weights of HCN and CO_2, respectively.

Because of sample port gas analyzer failures in the first two tests, a second, indirect, method was developed to compute the HCN yield. In this alternative method, it was assumed that the sampling port was drawing compartment gases at a constant rate, namely, the flow as measured at the start of the test. In actuality, this air flow could not have been constant throughout the test. However, while this approximation introduces a small uncertainty in the real air flow (about 25%) in the sampling port, its effect on HCN yield is on the order of the ratio of mass flow in the sampling port to the mass flow out the burn room door. The yield of HCN was determined by assuming the mass fraction of HCN in the door is the same as the mass fraction of HCN in the sampling port (eq. 5). This was divided by the chair assembly mass loss during comparable sampling intervals.

The total mass flow out of the burn room door was determined from thermocouple and pressure instrumentation located in the burn room doorway. These data elements were combined to produce a mass flow value based on an algorithm defined in RAPID [15]. The chair assembly mass loss rate was measured by the load platform. The mass flow of HCN at the sampling point was determined at the peak HCN concentration using the following relationship

$$\dot{m}_{HCN,port} = \frac{27}{29}\,[HCN]_{port}\,\rho_0 \frac{(T_{amb})}{(T_g)}\,V_{port} \tag{4}$$

where $\dot{m}$ is the mass flow rate, T is the temperature, amb stands for ambient, g is the gas, ρ_0 is the density of air at T_{amb}, V is the gas flow velocity in the sampling port, and the constants 27 and 29 represent the molecular weights of HCN and air, respectively.

The mass flow of HCN out the door was computed by

$$\dot{m}_{HCN,door} = \dot{m}_{total,door}\,\frac{\dot{m}_{HCN,port}}{\dot{m}_{total,port}} \tag{5}$$

The yield of HCN, f_{HCN}, was then determined by

$$f_{HCN} = \frac{\dot{m}_{HCN,door}}{\dot{m}_{sample}} \tag{6}$$

For comparative purposes, the HCN yields for all six tests were calculated in this manner. The average HCN yield of the untreated foam chair assemblies was found to be 0.007 by eq.(3) and 0.005 by eq.(6). The average HCN yield of the Cu_2O-treated foam chair assemblies was 0.002 by eq.(3) and 0.003 by eq.(6) These data showed similar trends and the same order of magnitude.

Table 22 lists the yield data for CO_2, CO, and HCN. In order to maintain consistency with previously published results eq.(6) was only used for tests B1 and B2. Eq.(3) was used in calculating the HCN yields for tests B3 through B6.

Since flashover appears not to have been achieved in any of these tests, CO yields would be expected to be below the 0.2 [21] value observed under flashover conditions. The data in Table 22 clearly shows that the CO yield is well below flashover expected values. This is consistent with the heat release rate and upper layer temperature criteria for flashover.

A comparison of CO_2 and CO yields for 1.0% Cu_2O-treated and untreated chair assemblies shows that the average CO_2 yield decreases in the presence of copper, while the average CO yield appears to increase from 0.003 to 0.006; however, comparison of the mean and standard deviations of the CO values for the two foams indicated that the values fell within one standard deviation of the mean.

The significant difference was, of course, that the HCN yield decreased from 0.007 without the Cu_2O treatment to 0.002 in the presence of Cu_2O.

Table 22. Comparison of Yield Values for CO_2, CO, and HCN (Protocol B)

Gas Species	Untreated Foam Assemblies		Cu_2O-Treated Foam Assemblies	
	Tests B1, B3, B5	Mean ± standard deviation	Tests B2, B4, B6	Mean ± standard deviation
CO_2	1.63 1.78 1.50	1.64 ± 0.14	0.96 0.60 0.74	0.77 ± 0.18
CO	0.003 0.002 0.005	0.003 ± 0.002	0.002 0.004 0.011	0.006 ± 0.005
HCN	0.006[a] 0.006[b] 0.008[b]	0.007 ± 0.001	0.003[a] 0.001[b] 0.003[b]	0.002 ± 0.001

a) computed by eq.(6)
b) computed by eq.(3)

The question arose as to whether the HCN was being converted to NO_x. In the small-scale work, it appeared that little or no NO_x was generated from the untreated foams and about 10% of the nitrogen that would have become HCN is produced as NO_x when the foams are Cu_2O-treated. In the full-scale tests, some NO_x was observed in all the experiments (where NO_x was measured) regardless of whether the foams were treated with Cu_2O or not. In Protocol A, the maximum NO_x concentration was 35 ppm for the untreated foams and ranged from 40 to 85 ppm for the treated foams. In Protocol B, the maximum NO_x ranged from 20 (untreated) to 110 ppm (treated), and the peak of NO_x always came after the peak of HCN (Table 23). With the exception of experiment B5, it seemed that the Cu_2O-treated foams generated more NO_x than the untreated foams.

To answer the question of whether the HCN was being converted to NO_x in the full-scale tests, Table 23 shows that the untreated foams (tests # B1, B3, and B5) in Protocol B generated an average HCN of 160 ppm and an average NO_x of 57 ppm. The average NO_x in the treated foams (tests # B2, B4, and B6) was 93 ppm. To determine the NO_x converted from HCN, substract the NO_x (57 ppm) already formed by the untreated foams from the total total NO_x generated in the treated foams (93 ppm) to find the new NO_x (36 ppm) generated in the treated foams. Thus, an additional amount of 36 ppm of NO_x is generated in the treated foams or, stated in another way, 23% of the HCN is converted to NO_x.

Table 23. Comparison of Peak NO, NO_x, and HCN Concentrations

Test	Cu_2O (%)	Peak NO_x (ppm)	Peak NO (ppm)	Peak NO_x Time (s)	Peak HCN (ppm)	Peak HCN Time (s)
A1	0	No NO_x Measurements			130	4650
A2	0	Instrument Failure			120	4260
A3	0	35	30	4637	90	4425
A4	0	35	35	4316	120	3930
A5	0.1	40	40	4796	110	4260
A6	0.1	85	75	3951	190	3250
A7	0.1	Power Outage			130	3780
B1	0	20	NM	3776	190	3660
B2	1.0	60	NM	1576	75	1440
B3	0	40	NM	2457	140	2240
B4	1.0	110	NM	2196	95	2055
B5	0	110	NM	3776	150	3630
B6	1.0	110	NM	2016	70	1875

NM. Not measured

3.4 EXAMINATION OF CHARRED RESIDUES

3.4.1 ELEMENTAL ANALYSIS

Elemental analyses were conducted on the foams with and without 0.1% Cu_2O that were used in this study and a typical flexible polyurethane foam designated GM-21 [22] that had been used in many previous studies at NIST. These analyses were performed on the foams prior to any heating, on the charred residues after phase 1 of the two phase heating regime in the cup furnace (there were no residues left after phase 2), and on the charred residues following the full-scale tests in which the foams had undergone both smoldering and flaming. The purpose was to try to determine why the full-scale tests of the 0.1% Cu_2O-treated FPU foams under Protocol A were not showing the same reduction in HCN generation as seen in the small-scale tests.

These elemental analyses indicated that the charred residues from the cup furnace smoke toxicity method (following the nonflaming, but prior to the ramped heating) and the charred residues from the full scale burn room tests of the 0.1% Cu_2O-FPU (following the nonflaming/smoldering/flaming mode) had approximately the same nitrogen fraction (Table 24). This nitrogen fraction was about 2.5 times that found in the virgin foam. In addition, the copper content following phase 1 heating of the 0.1% Cu_2O-treated foams was concentrated approximately 8 times over that initially found in the 0.1% treated foams. Our prior small-scale work showed that the highest concentrations of HCN were generated when the chars formed during phase 1 were ramped heated in phase 2 [1]. The fact that the nitrogen fraction of the charred residues from the full-scale room burns following both smoldering and flaming had the same nitrogen content as the phase 1 charred residues suggested the possibility that the copper effect was not being observed in the full-scale room burns in Protocol A because the foams and chars were not being sufficiently heated. One of the reasons for including the auxiliary burner in Protocol B was to try to increase the temperatures to which the chars would be exposed. In section 3.3.2.1, the room temperature results indicate that flashover conditions were not obtained even with the auxiliary burner. In a real fire which reaches flashover, the temperatures would be significantly higher. Since we were unable to achieve flashover temperatures in our limited number of full-scale room burns, we ramped heated the charred residues from the full-scale tests using the small-scale apparatus. The results from these ramped heating tests are described in Section 3.4.2.

Table 24. Elemental Analysis of Flexible Polyurethane Foams and Chars

Foam/ char	Cu_2O (%)	Test	Treatment	C (%)	H (%)	N (%)	O_2 (%)	Cu (%)
Foam	0	None	None	62.4	9.03	5.63	21.7	0
Foam	0.1	None	None	62.1	9.00	5.61	24.3	0.06
GM-21 Foam	0	None	None	61.2	8.70	4.21	NM	NM
Char	0	Cup	Phase 1	59.9	3.51	13.1	19.2	0.05
GM-21 Char	0	Cup	Phase 1	60.4	2.84	12.1	NM	NM
GM-21 Char	0	Cup	Phase 1	63.7	3.22	11.1	NM	NM
Char	0.1	Cup	Phase 1	57.2	3.24	14.3	21.0	0.84
Char	0	FS-A3	NF/F	64.4	1.82	13.6	15.6	0
Char	0.1	FS-A5	NF/F	66.4	2.46	14.9	14.0	0.39

FS: Full-scale
NM: Not measured

3.4.2 RAMPED HEATING OF CHARRED RESIDUES

The full-scale charred residues were ramped heated in the small-scale apparatus to see: 1. if additional HCN would be generated and 2. if the presence of the copper would affect this generation of HCN. Table 25 indicates that the charred residues of the untreated FPU foams from the full-scale room burns were still capable of generating significant quantities of HCN if heated sufficiently. The charred residues from Protocol A that did not have any copper generated an average of 65 to 85 ppm of HCN and a maximum of 90 to 120 ppm of HCN. The charred residues from Protocol B that had no copper also generated average levels of 30 to 75 ppm of HCN and maximum amounts of 45 to 110 ppm HCN. The presence of Cu_2O in the charred residues essentially eliminated all of the HCN that would have been produced in its absence. In chars from both protocols, the highest level of HCN observed was 3 ppm when copper was present in the foams prior to heating.

It is still not entirely clear why in the first series of tests (Protocol A), the Cu_2O was less effective than in the second series of tests (Protocol B). It may have been the low level of Cu_2O (0.1% vs. 1.0%) or the Protocol B scenario may have been more realistic (cotton covered FPU chairs ignited by cigarettes vs. two stacked cushions ignited by a heated coil placed between the two cushions) or it may have been that the charred residues were not sufficiently heated. More research is needed to determine which if any of these reasons is the correct one. What is clear is that when these charred residues were ramped heated in the cup furnace, the presence of the copper significantly reduced the HCN generation.

Table 25. Generation of HCN from Ramped Heating of Charred Residues from Full-Scale Room Burns[a]

Full-Scale Charred Residue	Treatment	Cu_2O (%)	Nitrogen in char (%)	Char Weight (g)	Average HCN (ppm)	Maximum HCN (ppm)
FS-A3	NF/Smoldering/Flaming	0	13.57	0.29	65	90
FS-A4		0	NM	0.30	85	120
FS-A5		0.1	14.87	0.30	1	2
FS-A6		0.1	NM	0.29	1	1
FS-A7		1.9	NM	0.32	< 1	< 1
FS-B1[b]	NF/Smoldering/Flaming	0	NM	0.60	75	110
FS-B3		0	NM	0.61	30	45
FS-B2		1.0	NM	0.60	1	1
FS-B4		1.0	NM	0.61	0	0
FS-B6		1.0	NM	0.59	3	3

a. Untreated and Cu_2O-treated flexible polyurethane foams were thermally decomposed in full-scale room burns. The charred residues were then ramped heated (375 - 800° C) in the cup furnace of the cup furnace smoke toxicity method and the HCN concentrations were measured for 30 minutes starting 5 minutes after beginning of ramped heating.

b. In Protocol B, the FPU cushions were covered with a cotton upholstery fabric. In the tests with the untreated FPU, we found that the larger flakes of char were more likely to generate the HCN rather than the crushed char. Therefore, all of these tests were conducted with char flakes.

4.0 CONCLUSIONS

- Research conducted at BASF indicated that the physical properties of the 1.0% Cu_2O-treated FPU were not significantly different from the comparable untreated FPU. The physical properties examined were tensile strength, elongation, tear strength, resilience, indentation force deflection, support factor, compression sets, and air flow.

- In agreement with earlier studies, under small-scale conditions (i.e., the foams were heated in the cup furnace smoke toxicity apparatus via a two phase thermal decomposition mode), the HCN yields from both 0.1% and 1.0% Cu_2O-treated FPU foams were reduced approximately 85% when compared to the HCN yields from their respective untreated control FPU foams. Toxicity based on LC_{50} values was reduced 40 to 70% in the small-scale tests with 0.1% Cu_2O-treated foams. Toxicity tests were not conducted in the small-scale apparatus with the 1.0% Cu_2O-treated foams.

- Under small-scale conditions, less than 3 ppm of NO_x was generated from the untreated foams, whereas a range of 3 to 33 ppm of NO_x was measured from the Cu_2O-treated foams. Approximately 11% of the HCN produced from the untreated foams was observed in the combustion atmospheres of the foams treated with 1.0% or 0.1% Cu_2O and about 6% of the HCN appeared to be converted to NO_x. In the full-scale room tests, approximately 23% of the HCN appeared to be converted to NO_x. Since we have shown in our laboratory that NO_2 acts as an antagonist to HCN [23], this amount of NO_x may also act to counteract the immediate toxic effects of any residual HCN.

- The use of melamine-treated FPU is becoming more common; it is one of two FPU foams currently allowed in England. Small-scale tests indicated that 20 g/m^3 of a melamine-treated FPU generated 6 times more HCN than an equal amount of an non-melamine treated foam. The presence of Cu_2O reduced the HCN from the melamine foam by 90 percent.

- Small-scale tests with the ambient O_2 concentrations reduced to as low as 6% indicated that the presence of Cu_2O (at the 0.1% level) would still be effective in reducing the HCN levels by as much as 82%.

- Full-scale room burns indicated that the presence of Cu_2O in the FPU reduced the HCN generation by approximately 50 to 70% when the experimental plan was designed to simulate a realistic scenario (the foams contained 1.0% Cu_2O, were covered with a cotton upholstery fabric and arranged to simulate a chair; smoldering was initiated with cigarettes). This reduction in HCN generation was not observed when the experimental plan used 0.1% Cu_2O treated foam cushions stacked one on top of the other and the smoldering was initiated by a heated coil placed between the two cushions.

- One possible explanation as to why the 0.1% Cu_2O-treated foams did not reduce the HCN yields is that the foams were not heated enough to see the effect. This hypothesis is based on the elemental analyses that showed that the 0.1% Cu_2O-treated foams contained the same amount of nitrogen after the smoldering and flaming phases of the full-scale tests as they did prior to the ramped heating phase in the small-scale tests. It is during the ramped heating phase that the HCN in the small-scale tests is primarily generated. In support of this hypothesis were results indicating that ramped heating of the charred residues from the full-scale tests of the untreated foams generated 45 to 120 ppm of HCN; whereas, if Cu_2O was present (0.1% or 1.0%), there was only 1 to 3 ppm of HCN generated.

- Further research is needed to determine the molecular mechanism of how copper acts as a HCN toxicant suppressant.

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Two full-scale protocols (A & B) were tested to determine the efficacy of cuprous oxide (Cu_2O) in reducing the concentrations of hydrogen cyanide (HCN) from flexible polyurethane foams (FPU) when thermally decomposed under "realistic" room conditions. In each Protocol A test, a FPU cushion (untreated or treated with 0.1% Cu_2O) was cut in half, and the two halves were stacked on a load cell in a closed room. The ignition source was a hot wire placed between the two halves. Rats were exposed to the decomposition products to examine the toxicological effects of the foams with and without Cu_2O. Protocol B differed from Protocol A in that chairs were simulated by four FPU cushions attached to a steel frame; the treated FPU contained 1.0% Cu_2O; the cushions were covered with a cotton fabric; the chairs were ignited with cigarettes; and the burn room was open and connected to a corridor. In both protocols, the thermal decomposition progressed through nonflaming, smoldering and flaming phases and the concentrations of HCN and other gases were monitored. Foams used in the full-scale room burns were also examined under small-scale conditions (under flaming or a two-phase nonflaming/ramped heating mode) in the cup furnace smoke toxicity method. Both atmospheric and reduced O_2 conditions were studied. The small-scale tests showed an 87% reduction in the concentration of HCN and a 40 to 73% reduction in the toxicity of the thermal decomposition products when the Cu_2O-treated foams were tested. In the full-scale tests, the concentration of HCN was reduced 70% when the FPU contained 1.0% Cu_2O, but not when the foams contained 0.1% Cu_2O. Investigation into this discrepancy indicated that exposing the charred residues from the full-scale burn room tests to the ramped heating mode in the cup furnace smoke toxicity method would produce significant amounts of HCN (65-90 ppm) from the untreated foam chars and only 1-2 ppm from the 0.1% Cu_2O-treated foam chars indicating that the copper even at this low concentration was still active in reducing HCN generation. Some preliminary experiments comparing a melamine-treated and standard FPU foam (both without Cu_2O) in the two phase cup furnace smoke toxicity method showed 10 times more HCN generated by the melamine-treated FPU than the standard FPU and a 90% reduction of HCN from the melamine-treated FPU when it was treated with Cu_2O.

12. **KEY WORDS (6 TO 12 ENTRIES; ALPHABETICAL ORDER; CAPITALIZE ONLY PROPER NAMES; AND SEPARATE KEY WORDS BY SEMICOLONS)**

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