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COMBUSTION PRODUCTS EVALUATION FROM HULL INSULATION MATERIALS C--ETC(U)
SEP 80 H G EATON, F W WILLIAMS, P A TATEM

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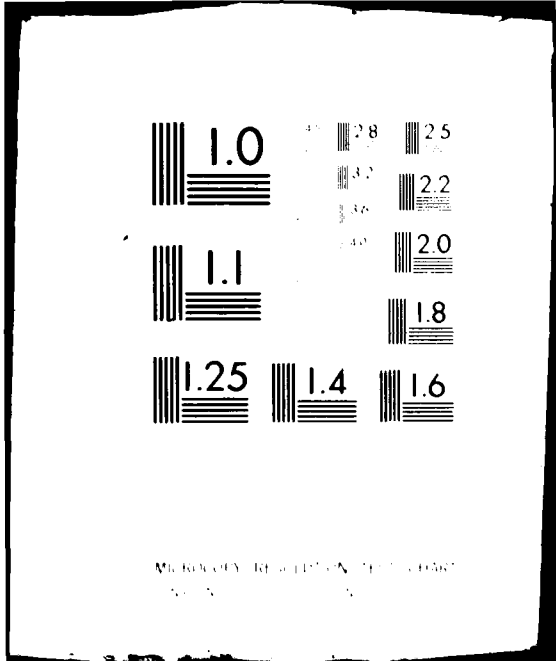
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Combustion Products Evaluation from Hull Insulation Materials Coated with Fire Retardant Paints

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Chemistry Division*

September 8, 1980

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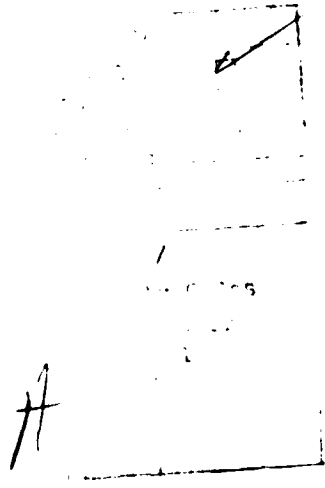
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INTRODUCTION

The threat of a major fire aboard a nuclear submarine is a major concern for the Navy. Because of the submarine's limited volume, it is important that if a fire does occur it be limited to its point of origin until it is suppressed. Of equal concern are the products of a fire: heat, smoke, and the production of combustible and/or toxic gases, which in a submarine could easily be lethal. These gases may be produced directly from the burning of materials or may be the result of "nonflammable" materials being exposed to fire or thermal stress, i.e., pyrolysis.

Aboard the submarine, hull insulation provides a significant area for exposure to an accidental fire. To decrease the ability of this material to contribute to the spreading of a fire, a Ship Alt (NAVSEASYS COM 10902-018-2010 ACN 2-78 of 1 Feb. 77) has been issued that calls for coating hull insulation with an intumescent paint. Although this paint offers the advantage of limiting the spread of a fire, it is possible that the retardants, once subjected to the stresses of fire and heat, will themselves add significant toxicants to the environment.

The Center for Fire Research, National Bureau of Standards (NBS), has recently published its investigation of fire studies involving hull insulation, Foam A, with and without fire retardant paint(s) in a reduced-size model submarine compartment [1]. As reported, the insulation material without the fire retardant paint produced flashover in less than one minute, and with the fire retardant paint approximately ten minutes delay was provided before flashover occurred. In addition, the retardant greatly reduced the overall generation of carbon monoxide, hydrogen cyanide, hydrogen chloride, and smoke. However, no other fire products were investigated.

In an extension of this work, the Naval Research Laboratory was tasked by the Naval Sea Systems Command (Code 92D) to evaluate other gases produced from fire stressed insulation materials with and without fire retardant paints. Previous reports on this subject have been issued [2-9].

MATERIALS EVALUATED

The insulation materials evaluated were: Foam A, an acrylonitrile - butadiene rubber-based material with the fire retardant polyvinyl chloride added; Foam B, a nitrile rubber material; Foam C, cork; and Foam D, a new class of polymer known as polyphosphazene.

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The flame retardant paints* evaluated with the insulation materials are designated as: intumescent, oil base, O-987 and O-9788; intumescent, latex, O-3342; and paints used primarily for undercoating, A-207, O-634, and chlorinated alkyd.

In general, the samples were subjected to two environmental fire tests: (a) an indirect fire exposure was simulated with the aid of radiant heaters which generated fluxes of 0.15, 0.5 and 5.0 W/cm² at the material's surface; and (b), direct exposure of the sample to a fire was obtained with the use of a hydrogen torch.

EXPERIMENTAL PROCEDURES

Gas Sampling

Both environmental fire tests outlined above were conducted in a 270-l stainless steel combustion chamber shown in Fig. 1. The operation of this system has been reported previously [10]; however, for completeness, it is described here.

The back and bottom of the chamber are equipped with assorted inlets for electrical connections, gas admissions, and product sampling. The chamber atmosphere is continuously sampled via the closed-loop manifold shown schematically in Fig. 2. The gas samples from the chamber flow, in order, through a 0.3- μ m soot filter (Gelman), bleed valve, and a pressure regulator operated at a pressure differential of about 3.5 psi. The reference side of the regulator is maintained at about 10.7 psia, so that the sample loop is under a slight vacuum during the continuous sampling process. Beyond the regulator, the sample flow is divided along two pathways: the first leading through a flowmeter into CO₂ and CO analyzers (Beckman Instruments, Model 315A), and the second leading through an O₂ analyzer (Beckman Model F3). The flow is maintained at 250 cm³/min into the O₂ analyzer and 900 cm³/min into the CO₂ and CO analyzers by the individual needle valves ahead of the circulating pump.

After leaving the analyzers, the gas flow is recombined at the circulating pump and returned to the chamber. The pressure can be monitored at four points along the sampling manifold: on the reference side of the regulator, in the sample loop immediately after leaving the regulator, after the O₂ analyzer, and after the CO₂/CO analyzers. The closed-loop system operates under a slight vacuum during calibration as well as during sampling, so that no corrections to the analyzer readings are necessary. The CO₂ and CO analyzers have 0-10% and 0-4000 ppm scales, respectively. The O₂ analyzer range is 0-25%. Auxiliary valves in the chamber provide an outlet for intermittent gas sampling with colorimetric tubes (Dragerwerk Lubeck, 53/55 Moislinger Allee, Lubeck 24, Germany) for HCl and HCN gases and whole gas samples [11].

The nonflaming heating condition was accomplished with a radiant panel heater (Pyropanel, Research Inc.) controlled via a Variac to produce a maximum heat flux of

*The identifying numbers used here are the same as those used in Reference 1.

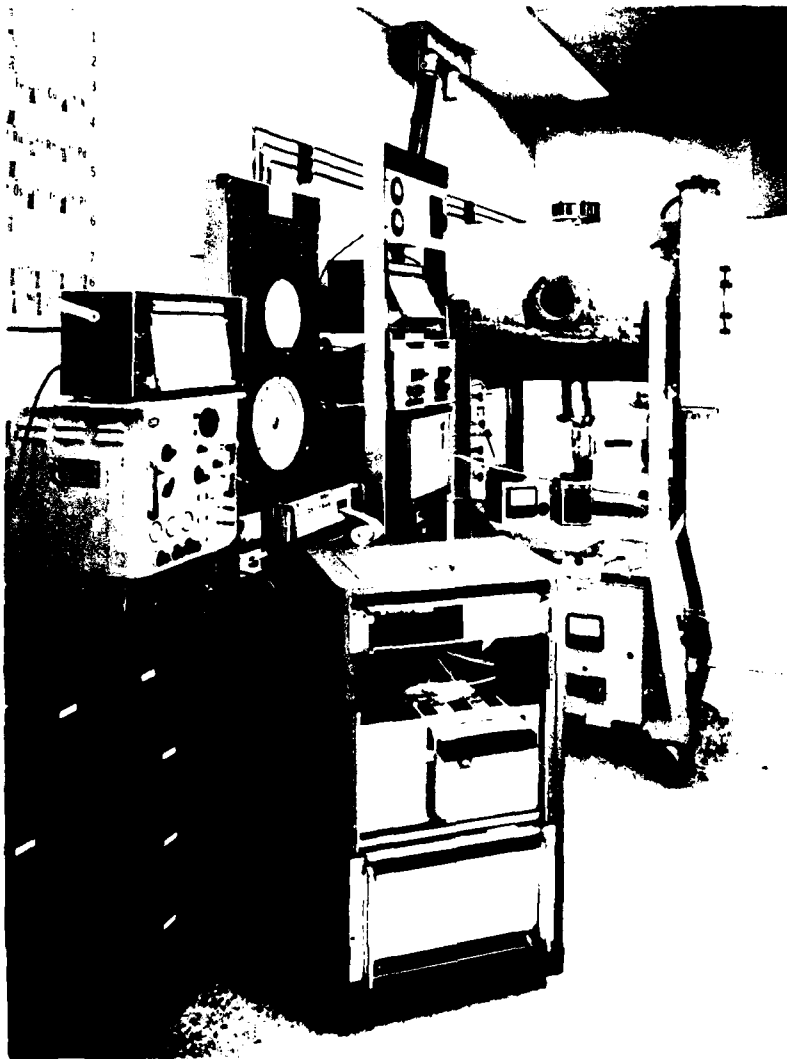


Fig. 1 270-1 stainless steel combustion chamber with associated gas handling equipment and analyzers.

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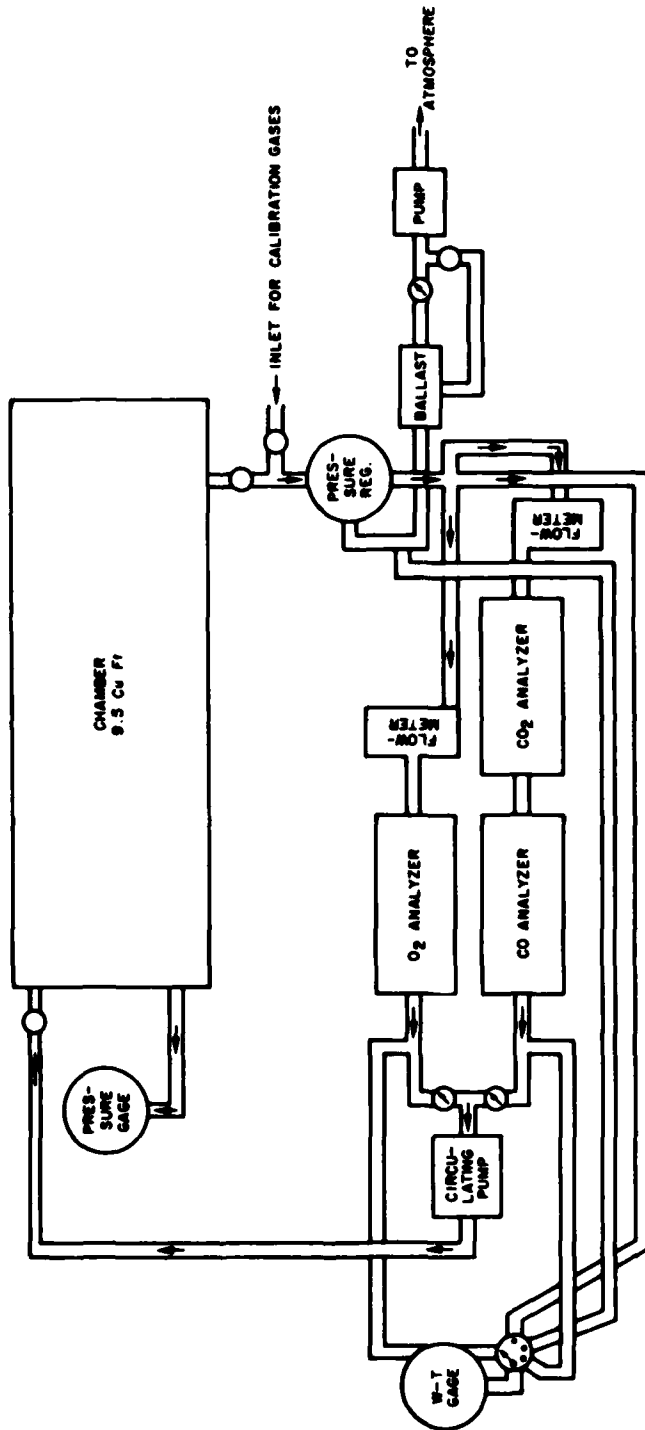


Fig. 2 — Schematic diagram of the chamber and sampling system

5.0 W/cm² at the sample surface. This maximum output from the heater was determined with a water-cooled radiometer (Hy-Cal Engineering) prior to the experimental runs. The actual fluxes produced at the sample surface, therefore, were dependent upon the amount of smoke produced by a given sample. The nonflaming mode was carried out at 21% oxygen concentration in the chamber. Although the initial oxygen concentration was at the stated level, studies have shown that materials ignited within an enclosed space will be burning in an atmosphere containing less and less oxygen as time progresses. This oxygen depletion alters the burning process and, thus, the product profile [12].

The flaming environment was produced by use of a hydrogen-air diffusion flame ($\cong 2100^{\circ}\text{C}$). The hydrogen flame was chosen to avoid contamination of the combustion products from the samples with products from the flame. The hydrogen flame in the combustion chamber depleted the chamber oxygen, requiring oxygen to be added (constantly monitored with the oxygen analyzer) to maintain 21% oxygen in the interior. A 10-cm (4-inch) burner was designed with five jets along its height. The flames from these jets impinged directly across the vertical sample surface during an experimental run, exposing the entire height of the sample at any given time. During the exposure period the flame was moved horizontally across the width of the sample surface.

A typical experimental run is carried out in the following manner. A vertically supported sample of dimensions 15.2 \times 15.2 \times 1.3 cm (6" \times 6" \times 0.5") was positioned in the chamber and exposed for 25 min to one of two stresses. The two stresses were 21% oxygen-flaming and 21% oxygen-nonflaming. During the exposure time, the chamber atmosphere was continuously monitored through the closed system gas sampling line for changes in concentration of oxygen, carbon dioxide, and carbon monoxide. Following each exposure, the chamber was allowed to equilibrate to room temperature while being mixed with a fan and then analyzed with colorimetric tubes for the presence of HCl and HCN. The chamber atmosphere was also batch-sampled with evacuated stainless steel 1.7- ℓ gas bottles at the end of each exposure for quantitative analyses [11] by gas chromatography.

Due to the low concentration of product generated during the stresses, the batch samples could not be used for product identification. To collect sufficient quantities of the combustion gases generated under the stress conditions for qualitative analysis, a glass tube containing Tenax adsorbent was inserted in the closed sampling loop. After allowing the chamber contents to equilibrate following exposure and withdrawing whole gas samples for quantitative analyses, the gas stream from the chamber was pumped across the Tenax for approximately 1 h to concentrate the gases [13]. The concentrated gases were analyzed by gas chromatography/mass spectrometry (GC/MS).

Gas Chromatographic Analysis

Gaseous products collected in the 1.7- ℓ stainless steel bottles were analyzed by a Perkin-Elmer, Sigma 2 model, gas chromatograph (GC) which was equipped with dual hydrogen flame ionization detectors and Carle gas sampling valves. This analyzer was used to verify and quantitate the gaseous products identified by gas chromatography/mass spectrometry (GC/MS) from retention times of known standards.

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Two chromatographic columns were used. One detected nonpolar products, a 4.5 m × 0.3 cm od (15 ft × 1/8 in. od) column with 3% OV-1 on chromosorb G, 80/100 mesh. The other detected low molecular weight products and polar components, a 60 cm × 0.3 cm od (2 ft × 1/8 in. od) Porapak Q column, 100/120 mesh. Elution and separation of the products on the columns were obtained with helium carrier gas and programmed temperatures.

The GC analyzer was calibrated with known concentration and pressures of pure heptane. Flame ionization detector response factors from the literature were used to calculate absolute concentrations of the contaminants in the gas sample bottles. Those contaminants whose response factors were not available were determined experimentally. Further, the contaminants not identified by GC or GC/MS were reported as "unknown" and their responses were reported as equivalent to heptane.

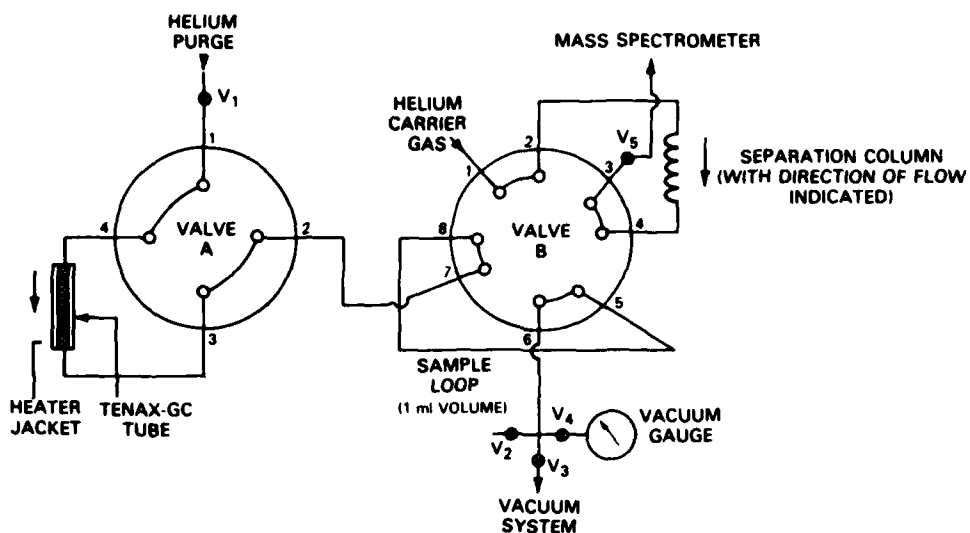
Gas Chromatograph/Mass Spectrometer (GC/MS) Analysis

Qualitative determinations of the evolved combustion gases were conducted by concentrating the sample products on adsorption Tenax-GC tubes and subsequently analyzing these tubes on a Hewlett-Packard 5993 GC/MS. This analyzer was equipped with the following major components: a microprocessor controlled GC, model 5700A, interfaced to the MS by a jet separator, an electron-impact ionization source, quadrupole mass filter system, and an electron multiplier. The data system was controlled by a HP 21 MX-E computer, a HP 7900A dual disc drive, and a Tektronic 4012 Graphics Terminal.

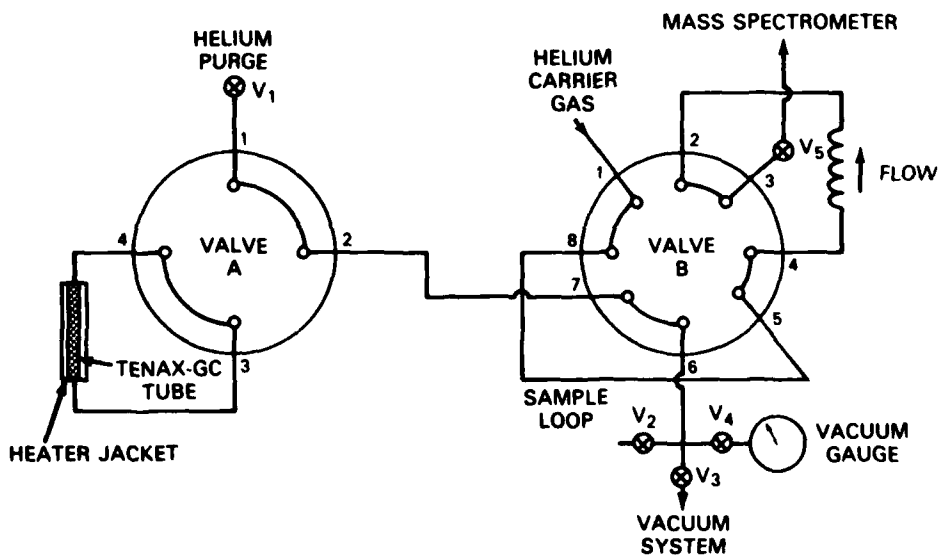
The GC/MS was operated in a continuous scanning mode. The separation column, 3% OV-1, and condition for operation was similar to that used in the GC analyzer. Mass spectra were identified by a mass spectral library with search capabilities and by published compendia of mass spectral data.

The analysis of the concentrated vapors on the Tenax-GC tubes presented a problem in that the contaminants not only varied in volatilities but in concentrations as well. Thus, when the entire sample was conventionally flash heated and desorbed and injected into the GC/MS [14-16], the vapor pressure from the high concentration constituents, mainly benzene and toluene, exceeded the normal operating vacuum (10^{-4} - 10^{-5} Torr) of the MS causing it to automatically shut down to prevent damage to the cathode and electron multiplier. To overcome this situation, a gradient or step-wise heat desorption technique of the sampling tube was developed to allow the detection of minute quantities of contaminants in the presence of the more concentrated components.

A schematic flow diagram of the gradient sampling system is presented in Figs. 3a and 3b. Gas valve A, a flow switching valve, and valve B, a combination sampling and backflush valve developed by Eaton, et al. [17], are housed in an oven compartment (Carle Instruments, Inc., Fullerton, CA) at a temperature of 150°C. Valve V5 and the separation column are housed in the GC/MS. This valve serves as a restrictor to raise the column outlet pressure which tends to decrease the inlet to outlet ratio. In this manner, when the sampling valve B is actuated and flow of carrier gas is reversed through the column (Figs. 3a and 3b), there is no sudden pressure output sensed by the MS causing this system to cease operation due to a sudden pressure fluctuation.



a — Position of valve A for helium purge or, after heating the Tenax tube, to pass the contaminants to the previously evacuated sample loop of valve B



b — Position of valve A when Tenax tube is being heated. Position of valve B when sample is injected into GC/MS

Fig. 3 — Schematic flow diagram of desorption and GC/MS sampling systems

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The advantages of such a valving operation when chromatographing a sample of unknown volatilities are: by backflushing the column after a reasonable time in the fore-flush mode, one can determine if all components in the sample have been eluted. This is accomplished by the fact that any remaining components will be regrouped and eluted from the column as one peak. This technique was used by Eaton, et al., in the analysis of total hydrocarbons [17]. Another advantage is the fact that this is the best way to insure that the chromatographic column is "clean" and that subsequent analysis will not be contaminated from a previous injection of a sample.

The adsorption tube with Tenax-GC packing material functions like a chromatographic column. The orientation of the sample flow through the tube during the concentration process is preserved when connecting the tube to valve A as shown in Fig. 3a. In this manner, the more volatile contaminants are analyzed first. Additionally, the sample tube is heated (Chromalytics 1074 Concentrator, Spex Industries, Inc., Metuchen, N.J.) in the gradient mode which is described below. An analysis of the desorbed sample is conducted after each heat interval.

In a typical sequence of operation, the adsorption tube is inserted into the heater jacket as shown in Fig. 3a. At room temperature, the sampling system is purged of air with helium by opening V1 and V2 and then both V1 and V2 are closed. Valve A is turned to a closed position (Fig. 3b). The remaining system is evacuated by opening V3 and then is closed. The sampling tube with an approximate pressure of 1 atm of helium is heated to the desired temperature (starting at 200°C) for 1 min and then opened (Fig. 3a) to the evacuated sample loop of valve B. At this point, heating of the sample tube is discontinued. Under these conditions, the sample loop pressure is approximately 170 Torr.

Valve B is turned (Fig. 3b) to position the sample loop into the helium carrier gas flow and separation column. Separation and elution of the components into the MS are accomplished by programmed temperature from 50°C (held for 5 min) to 150°C at 10°C/min.

At the completion of the analysis, the system is returned to the configuration shown in Fig. 3a. For subsequent analyses of the same Tenax tube, the sampling tube, which now is at subambient pressure and at room temperature, is repressurized with helium to one atmosphere, closed, heated at a 50° higher temperature (250°C), desorbed into the evacuated sample loop, and injected into the GC/MS as described above. These steps are repeated at 50° intervals to a final temperature of 350°C with the analysis procedure of the sample conducted after each heating interval.

The results and advantage of this gradient heating technique of the sampling tube are shown in comparing the total ion chromatograms of a sample in Fig. 4. In this sample, the major components are benzene, toluene, and o-xylene with retention times of 16, 20, and 24 min, respectively. The temperature of the sampling tube for test runs 5000-5003 was 200°, 250°, 300°, and 350°C, respectively.

If this sample had been initially heat-desorbed at 300°C, the composite concentration and hence the vapor pressure of benzene (runs 5001 and 5002) would have exceeded the normal vacuum pressure of the MS. The consequent shut-down of the system would

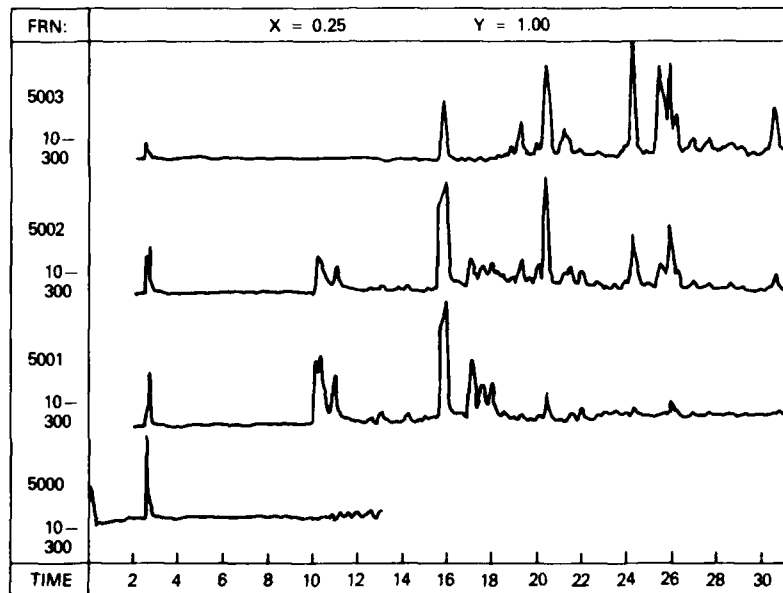


Fig. 4 — Profile of total ion chromatograms. Tenax tube heat desorbed at 200°, 250°, 300° and 350°C.

thus prevent the detection of the less volatile components. By using a gradient method of heating the sample as shown in Fig. 4, the concentration of the more volatile components, including benzene, are progressively decreased after each increased heat interval while the less volatile components increase in response and concentration. From the retention times of components in the composite total ion chromatogram in Fig. 4, and by mass spectral analysis, it was found that no decomposition of components resulted from this gradient heat desorption technique.

RESULTS AND DISCUSSION

Evaluation of Insulation Foams Without Fire Retardant Paints

Of primary concern during these fire stress experiments was the generation of potentially toxic or corrosive products. In general, aromatic hydrocarbons are undesirable because they tend to affect bone marrow resulting in numerous blood changes [18,19]. Chlorinated hydrocarbons affect the central nervous system and may cause liver, heart, and kidney damage [19]. Additionally, in one segment of the Navy's Fleet, the nuclear submarine, catalytic air purifiers are used in conjunction with other systems to purify the atmosphere. We have found that acids and other undesirable products may be produced in passing chlorinated hydrocarbons through the catalytic purifier [20-22].

An evaluation of the insulation materials of interest without fire retardant paint systems is presented in Table 1. Contaminant concentrations are expressed in milligrams per

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Table 1 — A Comparison of the Toxic Products Generated
In a Fire Environment from Insulation Foams
Without Retardants (Expressed as milligram of
contaminant/gram of material consumed \pm 10%)

Contaminant	Foam A	Foam B	Foam C	Foam D, No. 1	Foam D, No. 2
	Thermal Stress (Fire Stress)				
Carbon monoxide	76 (34)	8 (63)	131 (37)	9 (44)	19 (42)
Carbon dioxide	1050 (1600)	405 (1104)	500 (1843)	441 (1162)	540 (1026)
2-Chlorobutane	—	0.3 (+)	0.9 (+)	0.3 (+)	0.3
1-Chlorobutane	—	0.1	—	—	0.1
Benzene	1.2 (0.4)	19.6 (2.3)	1.1 (0.2)	0.2 (0.9)	(1.1)
Toluene	0.1 (0.2)	5.9 (0.9)	2.9 (0.3)	9.3	0.8
Chlorobenzene	—	0.3 (+)	—	—	—
Chloropropane	—	0.8 (0.1)	—	—	(+)
Trichloroethylene	—	0.6 (0.1)	—	0.2	0.2 (0.1)
p-Xylene	—	0.2 (0.1)	0.1	—	—
o-Xylene	—	1.2 (0.2)	(+)	—	—
Chlorohexane	—	—	1.1 (0.1)	—	—
Allyl benzene	—	0.5 (0.1)	—	—	—
Ethyl benzene	—	—	0.1 (0.1)	—	—
Trichloropropane	—	—	0.4	—	—

+ Present but less than 0.1 mg/g
—Not detected

gram of material consumed. Concentrations for both test conditions are listed with those in parentheses denoting values obtained from the direct fire exposure test. The material generating the most hazardous environment based on aromatic and chlorocarbon products is Foam B followed by Foam C. Foam D, sample number 1, generated the highest concentration of toluene.

Evaluation of Insulation Foams With Fire Retardant Paints

Foam A: This polyvinyl chloride-nitrile rubber material is currently used in the Fleet. This material was tested with all of the candidate fire retardant paints of interest. As seen in Table 2, approximately 50 products were identified.

Table 2 — Evaluation of Foam A Samples — Products Generated In a Fire Environment (Expressed as milligram of contaminant/gram of material consumed, ± 10%)

Contaminants Identified	No Coating	Thermal Stress (Fire Stress)									
		A-207	O-9788	A-207 & O-9788	A-207 & O-987	O-634 & O-3342	O-634 & O-9788	O-634 & O-987	O-634 & Chlorinated Alkyd	O-634 & Chlorinated Alkyd & O-9788	
Ethane, Ethylene	1.1 (1.0)	1.0 (1.0)	1.9 (2.0)	2.0 (1.4)	1.1 (7.0)	1.0 (1.3)	0.9 (1.4)	1.9 (1.2)	0.9 (2.0)	1.9 (1.2)	1.2 (1.7)
Propane, Propylene	0.5 (0.7)	0.9 (0.7)	0.6 (0.5)	0.7 (0.3)	0.9 (2.1)	0.6 (0.6)	0.5 (0.6)	0.5 (0.2)	0.7 (0.4)	0.9 (0.2)	0.7 (0.4)
Isobutane	+	0.5	+	0.4	0.2 (0.5)	0.5 (+)	+	+	0.1	0.1	+
2-Methylpropene, 1-Butene	0.2 (0.1)	1.3 (0.1)	0.2 (0.1)	2.0 (0.2)	1.4 (1.9)	2.8 (0.5)	1.2 (0.1)	0.3 (0.1)	0.7 (0.2)	0.9 (0.2)	0.3 (0.3)
2-Butene	-	0.3	-	0.6	0.4 (+)	0.2	0.2	+	+	+	-
Butane	-	0.3 (+)	(0.1)	1.2 (0.1)	0.2 (1.4)	-	-	0.2 (0.1)	+	+	(0.3)
2-Methylbutane	-	-	-	-	-	+	+	-	-	-	-
1-Pentene	-	-	-	-	-	(0.1)	(0.1)	-	-	-	-
3-Methyl-1-butene	-	-	-	-	-	0.4	0.3	-	-	-	-
Neopentane	+	0.6	-	-	0.9	-	-	-	0.3	-	-
Pentane	-	-	-	-	-	-	-	-	-	-	-
2-Methyl-1-butene	+	+	-	-	+	-	-	-	+	-	-
2-Methyl-2-butene	+	+	-	-	+	0.4 (+)	0.3 (0.1)	-	+	-	-
Cyclopentene	-	-	-	-	-	0.1 (+)	0.1 (0.1)	-	-	-	-
Cyclopentane	-	-	-	-	+	-	-	-	-	-	-
2-Methylpentane	-	-	-	-	-	+	-	-	-	-	-
3-Methylpentane	-	-	-	-	-	-	-	-	-	-	-
Hexene-1, 4-Methyl-1-pentene	-	-	-	-	+	0.1 (0.1)	+	0.1 (0.1)	-	-	-
Hexane, 2-Chlorobutane	-	-	-	-	-	0.2 (+)	0.1 (0.1)	-	-	-	-
Methylcyclopentane	-	-	-	-	-	(+)	(+)	-	-	-	-
1-Chlorobutane	-	0.6	-	1.4	1.4 (0.1)	1.9	1.2	-	+	0.3	-
Benzene	1.2 (0.4)	1.1 (0.4)	0.5 (0.9)	0.7 (0.5)	0.6 (2.3)	1.1 (0.7)	1.4 (1.1)	0.6 (0.9)	0.7 (0.2)	1.2 (0.4)	0.8 (0.7)
Cyclohexene	-	-	-	-	-	+	+	-	-	-	-
Heptene-1	-	-	-	-	-	0.3 (0.1)	0.2 (0.1)	-	-	-	-
2,4,4-Trimethyl-pentene-1, trans-Heptene-2	-	-	-	-	-	0.2 (+)	0.2 (0.1)	-	-	-	-
2,4,4-Trimethyl-pentene-2	-	-	-	-	-	0.1 (+)	0.1	-	-	-	-
Toluene	0.1 (0.20)	0.2 (0.2)	2.9 (0.9)	3.5 (0.3)	0.2 (0.8)	4.5 (0.6)	2.6 (1.4)	1.7 (0.8)	0.2 (0.3)	8.0 (0.5)	1.0 (2.0)

(Continues)

Table 2 — Evaluation of Foam A Samples — Products Generated in a Fire Environment (Expressed as milligram of contaminant/gram of material consumed, ± 10%)—(Continued)

Contaminants Identified	No Coating	A-207	O-9788	A-207 & O-9788	A-207 & O-987	A-207 & O-3342	O-634 & O-9788		O-634 & Chlorinated Alkyd O-9788
							O-634 & O-3342	O-634 & O-9788	
Thermal Stress (Fire Stress)									
Octene-1	—	—	—	—	—	0.1 (0.1)	0.1 (0.1)	—	—
Cycloheptane	—	—	—	—	—	0.1	0.1	—	—
Octane	—	—	—	—	—	0.1 (+)	0.1 (0.1)	—	—
Chlorobenzene	—	—	—	+	—	0.1 (+)	+	+	+
Ethylbenzene	—	—	—	—	—	0.3 (0.2)	0.3 (0.1)	—	—
p-Xylene	—	—	—	—	—	0.1 (+)	+	—	—
o-Xylene	—	—	—	—	—	0.2 (0.5)	0.3	—	—
1-Nonene	—	—	—	—	—	0.1 (0.1)	0.1 (0.1)	—	—
n-Propylcyclohexane	—	—	—	—	—	0.1	+	—	—
Allyl benzene	—	—	—	—	—	0.1 (+)	+	—	0.9 (0.7)
1,2,4-Trimethylbenzene	—	—	—	—	—	0.2 (0.2)	0.1 (0.1)	—	—
n-Butylcyclohexane	—	—	—	—	—	—	0.1	—	—
Carbon monoxide	76 (34)	50 (36)	28 (42)	58 (36)	3 (25)	38 (27)	2 (10)	45 (43)	60 (63)
Carbon dioxide	1050 (1600)	750 (750)	885 (1250)	606 (1150)	100 (530)	58 (1800)	27 (1080)	620 (1360)	400 (1650)
Hydrogen chloride*	(+)	(0.1)	+	+	+	N/A	N/A	+	0.1 (0.2)
Hydrogen cyanide*	(+)	(0.4)	0.4 (0.1)	1.4 (1.0)	(1.6)	N/A	N/A	1.6 (1.0)	1.3 (0.5)

* HCl and HCN analyses are accurate to within ± 20%
 + Present but less than 0.1 mg/g
 — Not detected
 N/A Not analyzed

In terms of the number and quantity of organic products generated, Foam A with no protective coating generated the least hazardous environment. However, as was stated previously, such a system is undesirable for use because of its ability to support combustion. In general, the greatest number of products was obtained when O-3342 was used as the top coating with either primers A-207 or O-634.

Table 3 — Summary from Table 2 of Contaminants of Interest Produced by Fire Retardant Paint Systems on Foam A

Effects of Contaminants	Radiant Panel Heat Test	Hydrogen Torch Test
Least conc. for CO and CO ₂	O-634 & O-3342	A-207 & O-987
Highest conc. for CO and CO ₂	O-634 & Chlorinated Alkyd	O-634 & O-987
Highest conc. for HCN and HCl	O-634 & Chlorinated Alkyd & O-9788	A-207 & O-987
Highest conc. for aromatic hydrocarbons	O-634 & Chlorinated Alkyd	A-207 & O-3342

A summary of the contaminants of interest from Table 2 is presented in Table 3 and discussed in the following two paragraphs.

In the thermal stress test, the products carbon monoxide (CO), carbon dioxide (CO₂), and aromatic hydrocarbons were highest in concentration with the application of O-634 as the primer coat and chlorinated alkyd as the top coat. This same paint combination with the addition of O-9788 generated the highest concentration for hydrogen cyanide (HCN) and hydrogen chloride (HCl). The combination of O-634 and O-3342 produced the least amount of CO and CO₂.

In the hydrogen torch test, different responses or effects of the paint systems were obtained. With O-987 as the top coating and A-207 as the primer, HCN and HCl were highest while CO and CO₂ were lowest in concentration. However, CO and CO₂ were highest with the application of O-634 as the primer. The paint system A-207 and O-3342 generated the highest concentration for aromatic hydrocarbons.

The best systems overall (Table 2) appear to be those containing O-9788 alone or in combination with primers A-207 or O-634.

Foam B: This nitrile rubber material was evaluated with A-207 alone, and with the combination primer O-634 and top coat O-9788 (Table 4). With no coating, benzene and toluene were quite high in concentration. Both paint systems reduced these concentrations considerably but were still higher than the same configurations used with Foam A.

Foam C: Cork samples were evaluated with paint combination O-634 and O-9788 (Table 5). There were only slight reductions in concentration for the aromatic hydrocarbons with the application of the fire retardant paints.

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Table 4 - Evaluation of Coated Foam B Samples - Products
Generated in a Fire Environment (Expressed as milligram
of contaminant/gram of material consumed, + 10%)

Contaminants Identified	No Coating	With O-634 & O-9788	With A-207
Ethane, Ethylene	0.8 (1.2)	0.4 (1.4)	1.3
Propane, Propylene	0.3 (0.3)	0.2 (0.5)	0.9
1-Butene, 2-Methylpropene	8.5 (0.7)	3.1 (0.3)	8.3
2-Methyl-1-butene	(+)	(+)	-
2-Methylbutane	(+)	+ (+)	+
3-Methyl-1-butene, 2-Chloropropane	0.8 (0.1)	0.3 (0.1)	0.6
2-Methyl-2-butene, Methylene chloride	2.0 (+)	1.7 (+)	0.9
2,2-Dimethylbutane	0.1	+	0.1
Cyclopentene	0.2 (+)	0.1 (+)	0.1
Cyclopentane	-	+	+
4-Methyl-2-pentene, 2-Methyl pentane	+ (+)	(+)	-
3-Methylpentene	0.6	0.5	1.0
Hexene-1, 4-Methyl-1-pentene	(+)	+ (+)	1.0
Hexane, 2-Chlorobutane	0.3 (+)	0.1 (+)	0.1
1-Chlorobutane	0.1	0.2 (+)	2.4
Benzene	19.6 (2.3)	6.4 (3.5)	6.9
Cyclohexene, 3-Methylhexane	(+)	+ (+)	+
Trichloroethylene, 1-Heptene	0.6 (0.1)	0.1 (0.1)	0.3
2,4,4-Trimethylpentene-1, trans-2-Heptene	0.5 (+)	0.1 (+)	0.2
2,4,4-Trimethylpentene-2	0.2	0.1	0.1
1-Chloropentane	-	-	1.2
Toluene	5.2 (0.9)	1.5 (1.1)	0.6
2-Ethylhexene-1, 2,2-Dimethylhexane	(0.1)	0.2 (0.1)	0.3
Octene-1	0.5	-	-
Cycloheptane	0.4 (+)	0.2 (+)	0.2
Octane	(+)	(+)	-
Octene-2	(+)	(+)	-
4-Ethylcyclohexene, Ethylcyclohexane	(0.1)	(0.2)	-
Chlorobenzene	0.3 (+)	0.6 (0.1)	0.1
p-Xylene	0.2 (0.1)	+ (0.1)	0.1
o-Xylene	1.2 (0.2)	0.4 (0.2)	0.8
Cumene	0.6	-	-
Allyl benzene	0.5 (0.1)	0.2 (0.1)	0.2
Nonane	-	0.4 (+)	0.6
1,2,4-Trimethyl benzene	(0.1)	0.1 (+)	0.1
Decene-1	-	0.1 (+)	0.1

(Continues)

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Table 4 — Evaluation of Coated Foam B Samples — Products
Generated in a Fire Environment (Expressed as milligram
of contaminant/gram of material consumed, ± 10%) (Continued)

Contaminants Identified	No Coating	With O-634 & O-9788	With A-207
	Radiant Panel Heat Test (Hydrogen Torch Test)		
Diethyl benzene	0.1	—	—
n-Butylcyclohexane	3.1	—	—
Carbon monoxide	8 (63)	22 (73)	341 (N/A)
Carbon dioxide	405 (1105)	131 (1287)	347 (N/A)

— Not detected
+ Concentration less than 0.1 mg/g
N/A Not analyzed

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Table 5 — Evaluation of Coated Foam C Samples — Products
Generated in a Fire Environment (Expressed as
milligrams of contaminant/gram of material consumed, ± 10%)

Contaminants Identified	No Coating	With O-634 & O-9788
	Radiant Panel Heat Test (Hydrogen Torch Test)	
Methane	0.3	0.3
Ethane, Ethylene	2.7 (0.7)	(1.0)
Propane, Propylene	0.8 (0.2)	0.2 (0.2)
Isobutane	—	+
1-Butene, 2-Methylpropene	0.7 (0.1)	0.6 (0.2)
cis-2-Butene, 2,2-Dimethylpropane	+	+
2-Methyl-1-butene	+	(+)
2-Methylbutane	0.1	(+)
1-Pentene	0.5 (+)	+ (+)
Pentane	0.5 (+)	0.2 (+)
2-Methyl-2-butane, Methylene chloride	—	(+)
2,2-Dimethylbutane	0.1	0.1
1-Chloropropane	—	+
Cyclopentene	0.2 (·)	+ (+)
4-Methyl-2-pentene	0.1 (+)	0.1
3-Methylpentane	(+)	(+)
Hexene-1, 4-Methyl-1-pentene	0.5 (0.1)	0.1 (0.1)
Hexane, 2-Chlorobutane	0.9 (+)	0.2 (+)
Methylcyclopentane	0.1	—
1,2-Dichloroethane	—	1.2
Methylchloroform	0.4	0.1 (1.4)
1-Chlorobutane	—	1.9 (0.2)
Benzene	1.1 (0.2)	1.1 (0.7)
Cyclohexene, 3-Methylhexane	0.2 (+)	0.1 (+)
1-Heptene	1.3 (+)	0.1 (0.1)
Methylcyclohexane	0.5	0.1
3-Methylcyclohexene	0.2	+
1,1,2-Trichloroethane	—	0.2
Toluene	2.9 (0.3)	1.6 (0.4)
3-Methylheptane	—	0.1 (+)
Cycloheptatriene	(+)	—
2-Ethylhexene-1, 2,2,5-Trimethylhexane	(+)	0.9 (0.2)
Octene-1	0.5	—
Cycloheptane	—	0.5
Octane	0.3	(+)
Chlorobenzene	—	0.1
4-Ethylcyclohexane, Ethylcyclohexane	—	(0.4)
1-Chlorohexane	1.1 (0.1)	—

(Continues)

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Table 5 — Evaluation of Coated Foam C Samples — Products
Generated in a Fire Environment (Expressed as
milligrams of contaminant/gram of material consumed, ± 10%)—(Continued)

Contaminants Identified	No Coating	With O-634 & O-9788
	Radiant Panel Heat Test (Hydrogen Torch Test)	
Ethylbenzene	0.1 (0.1)	0.1 (+)
p-Xylene	0.1	0.3 (0.1)
o-Xylene	(+)	(0.1)
1-Nonene	0.5 (0.2)	—
1,2,3-Trichloropropane	0.4	—
Nonane	0.1	+ (+)
Cumene	—	0.1
Allyl benzene	—	0.1 (+)
1,2,4-Trimethylbenzene	—	0.7 (0.1)
Decane	0.1	0.8 (0.1)
Undecene-1	—	0.2
Carbon monoxide	131 (37)	27 (48)
Carbon dioxide	500 (1843)	265 (1189)

— Not detected

+ Concentration less than 0.1 mg/g

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Table 6 — Evaluation of Foam D — Products Generated in a Fire Environment (Expressed as milligram of contaminant/gram of material consumed, ± 10%)

Contaminants Identified	Sample No. 1	Sample No. 2
	Radiant Panel Heat Test (Hydrogen Torch Test)	
Methane	0.4	—
Ethane, Ethylene	(0.6)	0.2 (0.7)
Propylene	0.1 (+)	0.1 (+)
Isobutane	—	0.1
1-Butene, 2-Methylpropene	0.8 (+)	0.1 (+)
cis-2-Butene	(+)	(+)
2-Methyl-1-butene	—	(+)
1-Pentene	+ (+)	(+)
2-Chloropropane, 3-Methyl-1-butene	—	+
trans-Pentene-2	—	0.2
Hexene-1	(+)	(+)
Hexane, 2-Chlorobutane	0.3 (+)	0.3
1-Chlorobutane	—	0.1
Benzene	0.2 (0.9)	(1.1)
Trichloroethylene, 1-Heptene	0.2	0.2 (0.1)
1,1,2-Trichloroethane	1.0 (+)	—
2,3,4-Trimethylpentane	—	0.1
Toluene	9.3	0.8
Octene-1	—	(+)
Octane	(+)	+ (+)
1-Nonene	1.8	0.2 (0.1)
1,2,4-Trimethylbenzene, Decene-1	0.4 (0.1)	(0.1)
Decane	0.2	—
Carbon monoxide	9 (44)	19 (42)
Carbon dioxide	442 (1162)	540 (1026)

— Not detected
+ Concentration less than 0.1 mg/g

Foam D: Two sources for polyphosphazene were evaluated without fire retardant paints. The products found are listed in Table 6. With the exception of the high concentration of toluene generated by sample number 1 during the thermal stress test, the samples are similar in products generated in a stress environment. Sample number 2 appears to be comparable to Foam A for use in closed environments. No tests were conducted for painted specimens of polyphosphazenes.

CONCLUSION AND RECOMMENDATIONS

In general, all of the uncoated insulation materials generated less potential toxic or corrosive products in the fire stress tests than when coated with fire retardant paint systems

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if the results are expressed on the basis of equal quantities of material consumed. However, previous studies have shown that such materials left unprotected with fire retardant paints contribute to the spread of a fire [1]. Thus, our main concern was to assess the best combination of insulation foam and retardant paint system that could be used aboard ship which would limit the spread of a fire and at the same time contribute the least to contamination of the enclosed environment.

Of the insulation foams and fire retardant paint systems tested, Foam A with fire retardant paint O-9788 used alone or in combination with primers O-634 or A-207 generated the least hazardous environment.

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