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Coal Mine Combustion Products: Identification and Analysis

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Coal Mine Combustion Products: Identification and Analysis

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COAL MINE COMBUSTION PRODUCTS: IDENTIFICATION AND ANALYSIS

by

Arthur M. Hartstein [1] and David R. Forshey [2]

ABSTRACT

The Bureau of Mines, through contract with Ultrasystems, Inc., obtained data on the oxidative degradative behavior of a number of materials used in coal mines. Tests were performed using a stagnation burner arrangement. Materials examined included those used in typical coal mining operations such as (1) polyvinyl chloride-containing materials. (2) neoprene compositions, (3) rigid foams (urethanes/isocyanates), (4) miscellaneous materials (including jute, fiber glass, and polyethylene), (5) coal, (6) fluids (phosphate esters, organic esters, oil-water emulsions), and (7) composites. The composite comprised a mixture of a phosphate ester fluid with (1) coal, (2) a representative polyvinyl chloride sample, or (3) a neoprene-type composition. A number of decomposition products are identified that could represent a potential health hazard to miners including HCl, CO, SO_2, and H_2S, if they were generated to exceed toxic levels.

INTRODUCTION

Modern underground coal mining necessitates the introduction of a variety of combustible materials into the mine. Typical materials include brattice cloth and ventilation tubing, conveyor belts, electrical insulation. cellulosic materials such as wood and jute, synthetic resins and foams, hydraulic, lubricating, and cutting oils, and fire extinguishants. In a mine environment, mixtures of such materials in addition to coal dust are found. Many of these materials are treated with fire-retardant chemicals; when subjected to heat, they may decompose into toxic products, which cause a health hazard.

The formation of toxic products is far more dangerous in an underground mine than in surface installations because adequate ventilation in underground operations is much more difficult to achieve than in aboveground facilities. Thus toxic products formed during the thermal degradation of a material can rapidly accumulate in a mine working area with reduced ventilation and reach threshold limit values (TLV's) more readily than in the same type of process in an industrial aboveground working area.

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The in situ identification and analysis of anticipated toxic products directly in the mine environment presents some unique difficulties because of many different species that may occur and problems associated with using analytical instruments underground due to portability and permissibility (safety). Presently most mine air analysis is accomplished (1) by using indicator tubes to obtain approximate gas concentrations in the mine or (2) by obtaining a gas sample for an accurate laboratory analysis. Indicator tubes provide only approximate values. Gas samples present another problem. In addition to having to wait hours or sometimes days for laboratory results, in some instances the sample undergoes a chemical change during the time between sampling and analysis.

This report summarizes the results of an investigation into the identification and analysis of coal mine combustion products.[3] The objective of this study was to determine the toxic products of assorted mine materials when heated to simulate oxidative conditions in underground use. Results will indicate the potential health hazards of such materials. This experimental work was performed under Bureau of Mines Contract H0122009 by Ultrasystems, Inc., formerly Dynamic Science Div. of Marshall Industries, Irvine, Calif.

A literature survey was undertaken to evaluate the type and relative concentration of toxic products expected to be formed upon oxidative degradation of cellulose (wood, cotton, jute), polyvinyl chloride (PVC) resins, polychloroprene (neoprene rubbers), polyurethanes, polyesters, epoxy resins, phenolic resins, melamine-and urea-formaldehyde resins, and polyethylene. The findings of this search are compiled in the appendix to the Final Report.[4] This literature compilation is somewhat unique in that it assembles experimental findings of oxidative degradation processes on the various materials commonly found in underground mines. These results were used as a guideline for determining initial analytical procedures and techniques.

EXPERIMENTAL WORK

The stagnation burner procedure was employed in this study (fig. 1). It was used to simulate conditions of pyrolysis of materials in air under conditions such as overheating or combustion of conveyor belt or brattice cloth. The unit was developed and used in similar prior research by Ultrasystems, Inc. under contract by National Aeronautics and Space Administration (NASA). This unit employs large samples and performs oxidative thermal decomposition or combustion of samples under controlled and reproducible ; conditions. Large samples of the present materials are required because they are not homogeneous (such as laminated conveyor belts). Also a large sample will give sufficient hazardous products to assure unambiguous identification.

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[3] Paciorek, K. L., R. H. Kratzer, and J. Kaufman. Coal Mine Combustion Products, Identification and Analysis. Final Report by Ultrasystems, Inc., Contract No. H0122009, July 1972. Prepared for Bureau of Mines. Available from NTIS, No. PB214124

[4] Appendix of the reference cited in footnote 3.

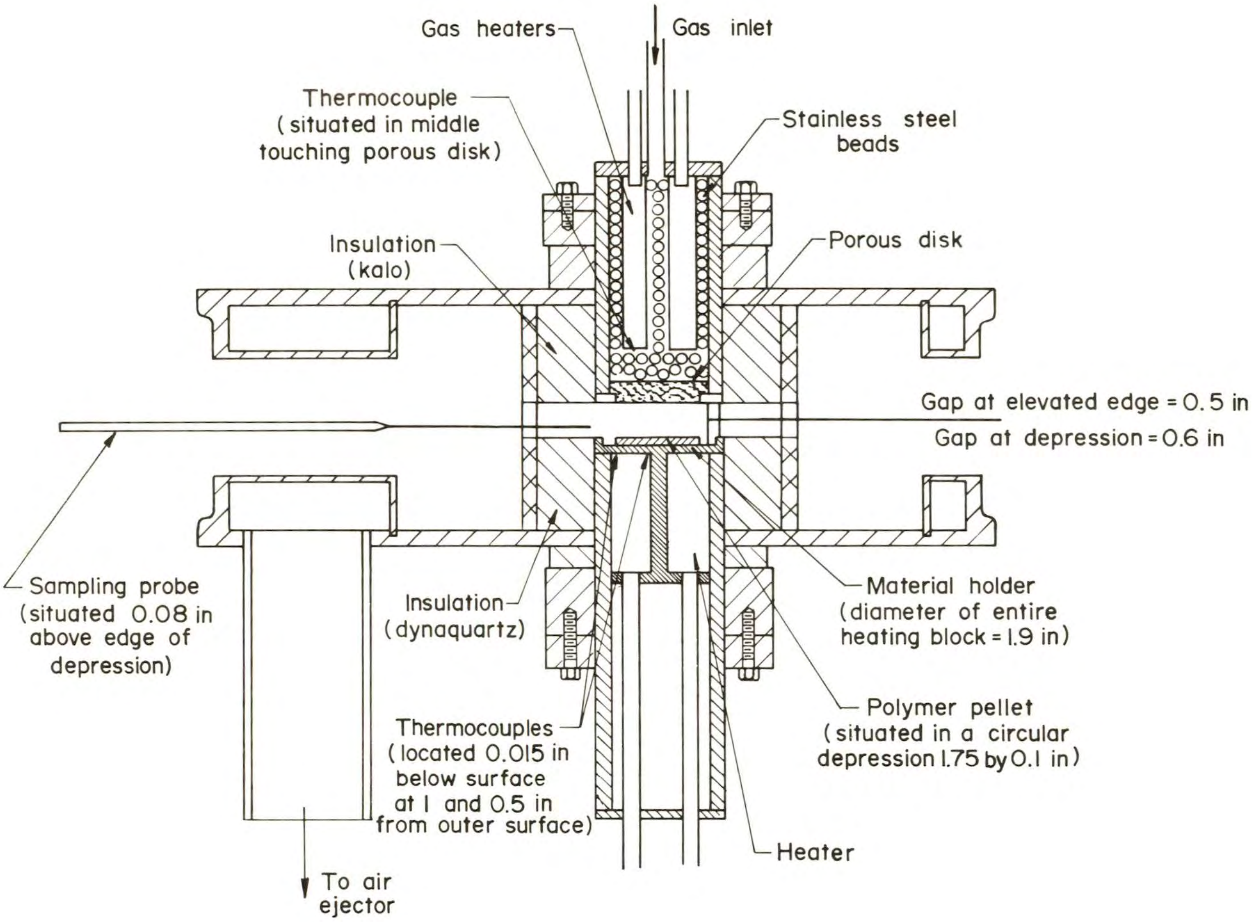

FIGURE 1. - Stagnation burner with sample and probe in place.

Sample size up to about 3 grams[5] were employed in the stagnation burner. The samples are heated to the desired decomposition temperature by placing them into the preheated and temperature-equilibrated system, thus initiating the release of the decompotition products at a well-defined temperature and within a short time interval. The laminar flow of the air used in the stagnation burner results in the compression of the reaction zone close to the sample surface, thereby more closely simulating an actual overheating condition in a mine. A sample probe with three evacuated ampoules shown in figure 2 is introduced into the burner gap with the sampling tip just above the elevated edge of the burner (fig. 1).

In a typical run, the gas and block temperature are equilibrated. Prior to insertion of the sample the probe was placed in the burner and pumped via the 4-mm stopcock. (Each of the ampoules was previously evacuated on the vacuum line.) During sampling the 4-mm stopcock was closed, and each ampoule was opened to the probe for 5 seconds. Between sampling, the system was

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[5] Three-gram samples are large compared with the usual 10 to 20 mg samples used in thermal decomposition studies.

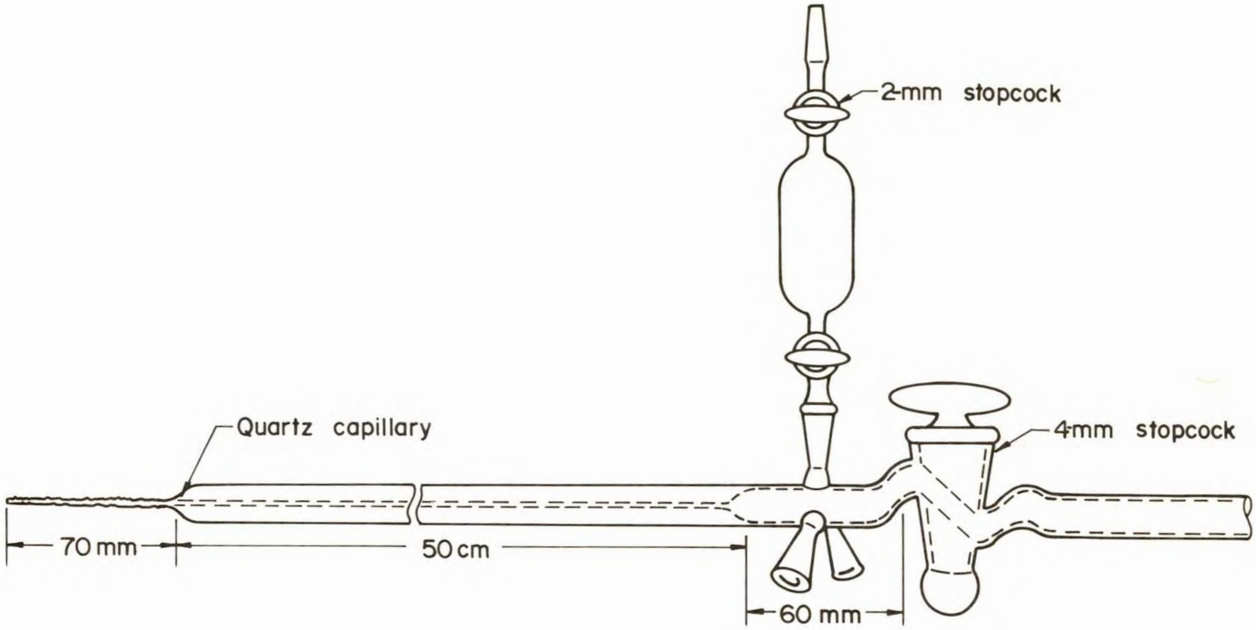

FIGURE 2. - Sampling system.

again evacuated via the 4-mm stopcock. In a specific run, two gas samples are taken, one just before degradation (first visual appearance of smoke) and the second when degradation reached the maximum (maximum visual appearance of smoke); both gas samples are taken prior to ignition of the polymer. A predegradation sample was taken because it is well known that the products formed from a sample prior to ignition are frequently different than those formed during combustion. In addition, prior to ignition, high levels of certain toxicants were found to be produced (for example, carbonyl fluoride from Teflon), whereas the amounts of these materials formed during combustion were neglible. The third ampoule is available for gas sampling if a postignition sample is desired.

A platinum insert tray was used with solid materials and a platinum vessel was used with liquids and composites, thus preventing contamination of the heating block and interferences of residues with succeeding experiments.

During an experiment, data was taken concerning the sample weight, gas temperature, block temperature, onset of smoke, smoke duration, degradation time and weight of residue.

The reproducibility of the stagnation burner technique was proven to be o of the order of 7% by many replicate runs during the prior NASA work (listed in Ultrasystems final report). In the present work, a few duplicate tests also indicated satisfactory reproducibility, and the main thrust of this work was to examine a large variety of these materials.

Mass spectroscopy was the primary analytical tool; these results were confirmed by infrared spectroscopy and gas chromatography.

Inasmuch as the liquids volatilized at relatively low temperatures and the distillate usually condensed at room temperature, mass spectrometric analysis could not be used in many instances. Therefore, the distillate was collected just at the exit of the stagnation burner on sodium chloride windows and analyzed by infrared spectroscopy to see if the original material distilled was unchanged or underwent degradation.

Two experimental temperature ranges were primarily used in this study, 470° to 480° C and 540° to 550° C. The lower temperature range was found to give a relatively fast evolution of preignition products. The higher temperature range was used to obtain, if possible, autoignition or glow, and thus to determine what products are formed during combustion.

With several materials water droplets were observed on the sides of the ampoules. The hydrogen chloride concentrations listed in table 2 must be definitely higher than cited in such cases since any hydrogen chloride dissolved in water formed during the chemical reaction will not be detected by the technique employed in this study.

To asses the synergistic effect that the decomposition of one material has on the simultaneous degradation of another--for example, decomposition of solid material soaked with oil--and to determine the extent, if any, to which the gaseous products of both materials can interact, composite samples were investigates; in each case one of the components was a liquid.

RESULTS AND DISCUSSION

Twenty-two solid materials, thirteen fluids, one coal, and four composite simulated mixtures were subjected to oxidative degradation. These materials represent the broad range of items presently being used in coal mines. The sample materials along with the individual manufacturers are identified in table 1. The relative proportion of oxidative degradation products are listed in tables 2-6.

PVC-based materials are widely used both as "pure" resins or in admixture with other compositions in manufactured articles in coal mines. The oxidative degradation behavior of PVC-containing articles could not be predicted from the behavior of the pure resin. Consequently it was necessary to test individual finished manufactured items, in which, for example, plasticizers, reinforcements, softeners, etc., are present in addition to the "pure" resins. The soundness of this approach is shown by the different results obtained for closely related compositions. Results indicate that hydrogen chloride and carbon monoxide are the major toxic gases released during oxidative degradation of the PVC materials (table 2). The loss of hydrogen chloride at the high temperatures employed here occurs almost instantaneously. This is to be expected since it is known that HCl is liberated readily from PVC materials at temperatures below 200° C. In all materials that glowed at the higher temperature, most, if not all, of the hydrogen chloride had been liberated prior to glowing, indicating clearly the absence of any fire-retarding component[6] once this stage of decomposition is reached. Other products--for example, NO_2, SO_2, COX_2, etc.--if present were not present in measureable amounts to be determined.

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[6] Fire-retardant materials usually contain halogens.

TABLE 1. - Materials tested

Sample	Manufacturer	Sample identification
1	H. K. Porter Thermoid Div.	No. 1-Q-2130, composed of neoprene polymer reinforced with polyester.
2	.....do..................	Hose conduit 1949; composed of neoprene polymer reinforced with polyester.
3	U.S. Steel...............	Labeled D0500W, from Bureau of Mines labeling, contains neoprene.
4	Kaiser Aluminum..........	2340 wire insulation #163 x UPE; composed of cross-linked (with perioxide) pigmented (clay) polyethylene, contains approximately 1/2% amine antioxidant.
5	C. R. Daniels............	Brattice cloth #1800y composed of nylon scrim laminated with thin PVC layer.
6	O'Konite Cable (subsidiary of LTV).	O'Koseal 200 type THW or MTW; composed of PVC.
7	C. R. Daniels............	Conveyor belt; composed of cotton-nylon impregnated with PVC.
8	Not found................	Brattice cloth; from Bureau of Mines labeling composed of fiber glass.
9	Griffolyn Co., Inc.......	Reinforced plastic fabric ripproof #75 clear III, nylon-reinforced PVC.
10	.....do..................	Griffolyn fabric 1800; no composition given, item has been discontinued.
11	Not found................	Brattice cloth; from Bureau of Mines labeling "plastic."
12	Callery Chemical Co......	Urethane-isocyanurate #4 foam.
13	.....do..................	Isocyanurate-urethane 3/1 #3 foam.
14	.....do..................	Polyurethane foam system. Two different data sheets. No sample identification.
15	.....do..................	Polyurethane foam system. Two different data sheets. No sample identification.
16	American Brattice Cloth Corp.	JP-IA (appearance one side white plastic, other jute).
17	.....do..................	18-oz mine duct tubing (appearance yellow plastic).
18	.....do..................	ABC #1 jute
19	Johnston-Morehouse-Dickey Co.	#1 jute 10 oz (composition may be calcium chloride).
20	.....do..................	#3 nylon (Glasstex) (composition PVC-antimony trioxide).
21	.....do..................	#4 plastic 15Y (appearance solid yellow plastic) composition PVC-antimony trioxide).
22	.....do..................	#6 jute (appearance one side plastic, other jute) (composition, PVC calcium chloride and antimony trioxide).

TABLE 1. - Material tested--Continued

Sample	Manufacturer	Sample identification	
23	Monsanto Co..............	Pydraul 135 A (main components phosphate esters, some chlorinated solvents and mineral oils).	
24	.....do..................	Pydraul 312 A (similar in composition to pydraul 135A).	
25	.....do..................	Santosafe 100 (mixture of water, ethylene glycol plus other additives).	
26	D. A. Stuart Co..........	Stuart Dasco FR 300 (phosphate esters plus mineral oil).	
27	Citgo....................	Pacemaker FR30 (composition unknown).	
28	Hulburt Oil and Grease.	Hulsafe 500 (composition unknown).	
29	Quaker Chemical..........	Quintolubric 822 (synthetic organic esters).	
30	Atlantic Richfield Co....	Duro FR HD (oil water emulsion).	
31	Stauffer Chemical Co.....	Fyrquel 90	Mixtures of phosphates esters, aryl substituted.
32	.....do..................	Fyrquel 150	
33	.....do..................	Fyrquel 220	
34	.....do..................	Fyrquel 300	
35	.....do..................	Fyrquel 550	
36	-	Coal; heat value 14,300 Btu/lb.	

Neoprene is one of the few relatively fire-resistant elastomers widely used in coal mines owing to its relatively low cost as compared with that of the expensive fluorinated rubbers. Neoprenes yield products similar to those obtained from PVC, although the relative CO content was lower (table 3). In addition, sulfur compounds evolved were mainly sulfur dioxide (~0.5% of the gaseous mixture).

It was found that the main volatile product formed on thermal oxidative degradation of the urethan/isocyanate foams is carbon dioxide (table 4). The carbon monoxide yield in the majority of instances was found to be relatively low. The toxic products of importance in the decomposition of urethane and/or isocyanate foams are reported in literature to be isocyanates. These compounds, however, are relatively involatile. The present mass spectrometry approach was not suitable for their detection.

The results of the fluid tests are given in table 5. The mineral oil-containing substances were in the form of oil-water emulsions, and these formed products expected from a hydrocarbon-type material. At the lower temperatures, water distilled off preferentially. These compositions autoignited at the elevated temperatures (550° C). The synthetic organic ester fluid, Quintolubric 822, distilled unchanged at 300° C; at 400° C, CO, CO_2 plus hydrocarbons were produced, whereas at 550° C, autoignition occurred giving the usual product mix, namely CO, CO_2, and hydrocarbons.

TABLE 2. - Relative proportion of products formed on oxidative degradation of polyvinyl chloride-containing materials

Sample	Block temperature ° C	Sampling time[5]	Total, %[3]	HCl, %[5]	CO, %	CO_2, %	CH_4, %	C_2H_6, %	C_2H_4, %	C_2H_2, %	C_3H_6, %	C_6H_6, %	H_2O, %
5	476	30-35	1.72	47	10	12	1.2	1.7	(4)	0.6	2.9	0.6	24
	476	55-60	3.36	71	5	10	.6	.9	0.9	.3	2.4	.3	9.2
	551	45-50	1.55	33	-	32	6.5	3.9	9.0	1.3	3.9	.6	10
6	480	45-50	1.44	43	6	17	2.1	2.1	1.4	.7	4.2	2.8	20
	480	90-95	2.84	66	6	12	1.1	.4	.4	.7	2.1	1.8	9
	585	45-50	1.65	33	21	22	3.0	1.2	1.8	.6	3.6	2.4	12
	565	240-245	1.67	17	11	67	1.8	-	-	-	-	-	4
7	487	90-95	2.40	12	30	33	2.1	1.7	2.1	(4)	2.9	.8	16
	487	180-185	2.41	10	25	44	2.1	2.5	2.1	(4)	3.3	.4	11
	555	70-75	3.49	6	31	37	2.9	2.3	4.3	(4)	2.6	.6	13
	555	420-425	2.44	-	11	84	3.7	-	-	-	-	-	2
9	487	35-40	4.35	71	8	7	.7	.5	1.8	.5	2.3	2.1	7
	487	55-60	2.49	56	7	11	1.2	2.0	2.0	.4	2.9	2.0	16
	581	50-55	1.04	6	37	28	1.9	5.8	5.8	2.9	3.8	.1	9
	407	60-65	4.47	81	5	4	.9	.7	1.1	.2	.4	4.0	2.9
11	494	40-45	2.55	73	-	7	.4	1.6	(4)	.8	1.6	.8	15
	494	60-65	1.93	57	5	20	-	.5	2.6	.5	2.6	1.0	10
	573	40-45	3.07	28	15	23	2.0	3.9	2.2	(4)	2.6	.3	23
	573	90-95	2.18	26	12	25	2.8	3.2	1.8	1.4	3.7	.5	24
17	484	70-75	.93	8	10	40	3.2	4.3	3.2	(4)	2.2	1.1	29
	484	95-100	.81	25	-	49	2.5	1.2	2.5	-	3.7	2.5	14
	545	45-50	1.61	12	24	29	1.9	3.1	3.7	1.2	3.1	1.2	20
	545	90-95	1.38	15	20	27	.7	4.3	2.9	1.4	3.6	.7	24
20	479	35-40	.79	9	24	23	5.1	6.3	3.8	3.8	5.1	6.3	14
	479	70-75	1.11	19	9	39	1.8	1.8	1.8	1.8	3.6	6.3	16
	551	35-40	1.62	31	18	19	.6	.6	1.2	.6	3.1	4.9	22
	551	60-65	1.16	19	16	37	1.7	3.4	2.6	1.7	4.3	4.3	9
21	480	45-50	1.34	9	34	19	3.7	5.2	1.5	1.5	6.0	3.0	18
	480	150-155	.47	13	-	53	4.3	6.4	4.3	2.1	4.3	2.1	11
	547	60-65	2.13	20	18	30	5.6	5.6	3.3	.9	5.2	3.8	8
	547	165-170	3.84	4	10	71	6.5	.3	.3	.3	-	(4)	8

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[1] The samples are identified in table 1.

[2] The time is measured from the time of sample insertion. The 5 second interval is the period of time the ampoule was opened to burner atmosphere.

[3] Total products in samples collected.

[4] Trace.

[5] Mole-percent in gaseous sample.

TABLE 3. - Relative proportion of products formed on oxidative degradation of neoprene-containing materials

Sample[1]	Block temperature, ° C	Sampling time[2]	Total, %[3]	HCl, %	CO, %	CO_2, %	SO_2, %	CH_4, %	C_2H_6, %	C_2H_4, %	C_2H_2, %	C_3H_6, %	C_6H_6, %	H_2O, %
1	484	85-90	0.76	-	20	36	1.3	2.6	2.6	5.3	-	2.6	1.3	28
	484	105-110	1.16	-	16	46	.9	3.4	3.4	2.6	-	3.4	-	25
	552	80-85	1.70	-	16	51	.6	4.1	5.3	4.7	-	5.3	(4)	13
	552	130-135	.76	-	-	59	-	10.5	9.2	5.3	-	6.6	-	9.2
2	491	100-105	3.04	63	8	14	1.3	1.6	2.0	.3	1.0	2.0	(4)	6.9
	493	100-105	3.42	66	7	12	1.5	.9	1.5	.9	.6	2.0	(4)	7.9
	491	145-150	4.97	65	8	15	.4	1.4	2.4	.6	.8	3.6	(4)	3.2
	493	145-150	4.65	61	9	15	.6	1.7	2.8	.9	.9	3.2	.2	4.3
3	483	100-105	27.43	72	5	10	.2	2.0	2.1	.7	.1	3.0	.7	4.7
	483	125-130	17.85	17	21	56	.2	1.4	.6	.2	.1	.3	(4)	3.0
	562	65-70	13.57	54	8	20	.3	3.4	2.6	1.1	.5	3.7	.1	6.3
	562	150-155	8.73	4.4	29	64	.2	.2	.5	-	.1	.1	-	1.0
	398	210-215	4.70	50	10	23	.9	1.9	2.1	(4)	2.1	3.6	(4)	6.6

[1] The samples are identified in table 1.

[2] The time is measured from the time of sample insertion. The 5-second interval is the period of time the ampoule was opened to burner atmosphere.

[3] Total products in samples collected.

[4] Trace.

TABLE 4. - Relative proportion of products formed on oxidative degradation of rigid foams

Sample[1]	Block temperature, ° C	Sampling time[2]	Total, %[3]	CO, %	CO_2, %	$CFCl_3$, %	H_2O, %	HCN, %	C_xH_y, %	HCl, %
14	485	8-13	3.24	4.3	74	1.9	8.6	-	3.4	7.4
	485	18-23	.63	14	40	-	44	-	1.6	-
	549	5-10	2.47	-	77	1.6	13	-	2.8	5.3
	549	15-20	1.13	17	28	(4)	50	-	4.4	-
15	486	4-9	6.85	-	86	2.6	3.4	5.0	-	3.1
	486	13-18	2.32	12	45	(4)	25	5.2	4.3	8.6
	564	5-10	2.97	15	68	1.3	6.4	-	-	3.4
	564	15-20	.36	-	61	-	2.8	-	-	36
12	485	5-10	3.25	2.8	81	(4)	8.3	-	5.8	2.2
	485	16-21	.50	38	56	-	6	-	-	-
	553	5-10	1.69	11	76	(4)	3	-	6.5	4.1
	553	15-20	.39	-	77	-	15	-	7.7	-
13	490	5-10	.54	-	56	3.7	26	-	1.9	13
	490	18-23	.67	-	42	(4)	48	-	-	10
	551	5-10	1.03	-	62	1.0	22	-	7.8	6.8
	551	15-20	1.13	16	40	-	37	-	7.1	-

[1] The samples are identified in table 1.

[2] The time is measured from the time of sample insertion. The 5-second interval is the period of time the ampoule was opened to burner atmosphere.

[3] Total products in samples collected.

[4] Trace.

TABLE 5. - Relative proportion of products formed on oxidative degradation of hydraulic fluids

Sample[1]	Block temperature, ° C	Sampling time[2]	Total, %[3]	CO, %	CO_2, %	CH_4, %	C_2H_6, %	C_2H_4, %	C_2H_2, %	C_3H_6, %	C_6H_6, %	H_2O, %
23	405	50-55	0.48	50	31	-	-	-	-	-	-	19
24	554	18-23	2.51	29	25	5.6	4.8	8.0	4.0	17	0.4	5.6
24	554	25-30	3.98	24	70	1.5	.8	.5	.3	1.5	-	1.8
36	546	100-105	.60	-	32	30	10	5.0	3.3	8.3	-	12
36	546	140-145	.91	-	34	35	8.8	4.4	3.3	8.8	-	5.5
26	403	40-45	.41	49	15	4.9	-	2.4	2.4	4.9	-	22
26	403	60-65	.48	40	19	6.3	6.3	4.2	2.1	4.2	-	19
27	400	60-65	.58	50	22	3.4	5.2	3.4	1.7	5.2	-	9
27	400	100-105	.78	49	22	3.8	5.1	2.6	1.3	5.1	-	12
28	302	120-125	.43	44	21	4.7	4.7	2.3	2.3	7.0	-	14
29	406	80-85	.45	22	18	22	4.4	2.2	2.2	6.7	-	42
29	406	110-115	.73	14	22	1.4	4.1	1.4	(4)	4.1	-	53
29	556	10-15	1.86	16	71	.5	1.6	1.1	(4)	.5	-	9
29	556	17-22	11.42	17	80	.7	.9	(4)	1.5	-	.1	1.0
30	298	100-105	.26	-	96	-	-	-	-	-	-	4

TABLE 5. - Relative proportion of products formed on oxidative degradation of hydraulic fluids--Continued

Sample[1]	Block temperature, ° C	Sampling time[2]	Total, %[3]	CO, %	CO_2, %	CH_4, %	C_2H_6, %	C_2H_4, %	C_2H_2, %	C_3H_6, %	C_6H_6, %	H_2O, %
30	405	45-50	1.73	51	16	2.3	4.6	1.7	1.2	5.2	-	17
30	405	60-65	2.59	15	64	.4	.8	.8	(4)	-	-	19
30	547	25-30	10.72	15	63	.9	.9	11	2.8	3.6	.4	1

[1] The samples are identified in table 1.

[2] The time is measured from the time of sample insertion. The 5-second interval is the period of time the ampoule was opened to burner atmosphere.

[3] Total products in samples collected.

[4] Trace.

TABLE 6. - Relative proportion of products formed on oxidative degradation of "composite" materials

Sample[1]	Block temperature, ° C	Sampling time[2]	Total, %[3]	CO, %	CO_2, %	CH_4, %	C_2H_6, %	C_2H_4, %	C_2H_2, %	C_3H_6, %	C_6H_6, %	H_2O, %
3+23	404	60-65	0.29	38	14	3.4	6.9	6.9	(4)	3.4	-	28
	404	160-165	.57	39	58	-	-	-	-	-	-	4
9+23	400	50-55	.41	27	12	4.9	7.3	2.4	(4)	2.4	2.4	41
	400	65-70	.36	31	17	2.8	8.3	2.8	(4)	2.8	2.8	33
33+36	554	80-85	.53	19	9	42	5.7	9.4	1.9	1.9	-	11

[1] The samples are identified in table 1.

[2] The time is measured from the time of sample insertion. The 5-second interval is the period of time the ampoule was opened to burner atmosphere.

[3] Total products in samples collected.

[4] Trace.

The phosphate ester-based fluids from the Pydraul series undergo oxidative degradation more readily than do the Fyrquel phosphate ester-based materials. In both instances, only traces of gaseous products, mainly CO_2, were found. Even at 400° C these fluids distilled virtually unchanged. At 550° C a representative sample of a phosphate ester autoignited whereas the Fyrquel failed to burn.

The composites, which involved phosphate ester fluids admixed with (1) coal, (2) a polyvinyl chloride material, or (3) a neoprene composition, usually exhibited an additive behavior (table 6); that is, the gaseous products were merely the sum of the products found for the individual components. However, the case of composites containing PVC and neoprene and one of the oils tested (Pydraul 135A) did not give an additive effect. Substantial quantities of hydrogen chloride were found at 400° C during degradation of the polyvinyl chloride alone. However, under comparable conditions the composite sample failed to show any hydrogen chloride in the volatiles although the weight loss was in agreement with the other data. It is possible that the composite generates either water or another material that on condensation dissolves hydrogen chloride.

SUMMARY

Typical materials used in coal mines tested during this exploratory program yielded toxic products upon thermal degradation. The products included HCl, CO, SO_2, and H_2S. They represent a potential health hazard to miners when generated underground.

Further work to examine the quantity of toxic products formed, on a gram of product per gram of material basis, is currently being done.

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