Degrad

Oxidative Thermal Degradation of Selected Polymeric Compositions

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Tests were performed on (a) polyvinyl chloride-containing materials, (b) neoprene compositions, (c) polyurethane foams, and (d) miscellaneous materials (including jute and fiber glass) using a stagnation burner arrangement. In the case of the chlorinated materials, significant quantities of hydrogen chloride were detected, its rate of evolution being strongly temperature dependent. Once glow occurred, carbon monoxide became the predominant toxic species formed. Urethane foams produced $CFCl_3$ and CO_2 together with some HCl and chlorinated hydrocarbons; whereas jute compositions liberated methyl chloride as well as other products. A composition of resin reinforced with glass fibers ignited spontaneously at 487°C and produced significant quantities of carbon monoxide.

Introduction

THE RESEARCH IN THE AREA OF FIRE toxicology and material off-gassing has been proceeding uninterruptedly ever since World War II as can be attested by the review summarizing the work from 1945 to 1951[1] and other publications.[2-6] The more recent emphasis on this type of an investigation was necessitated by the considerations of hazards inherent to confined locations such as, *e.g.*, aircraft, spacecraft, submarines, and underground mines.[17-25]

Under thermal oxidative conditions, organic compositions decompose to form a variety of gaseous products the nature of which is largely dependent on the composition of the original material and to a certain degree on the concentration of oxygen in the surrounding atmosphere, *e.g.*, the presence of air or pure oxygen. Furthermore, the most widely used flame resistant materials do contain halogens, particularly chlorine. The latter upon thermal degradation is liberated mainly in the form of hydrogen chloride.

In a broad sense the problem of forming decomposition products, including toxic substances, during the pyrolysis and combustion of natural and synthetic materials in a coal mine is the same as that for any other industrial facility. In a coal mine the same type of materials are used under similar conditions as in an industrial plant; therefore, from identical items the same type of toxic products in the same quantities will be formed. In view of the confinement in an underground coal mine and the creation of a defined air flow pattern by the required ventilation, several aspects become of importance that normally can be neglected in above-ground operations. In contrast to above-ground operations, the available space in coal mines is limited, and in case of an accident, egress is not readily accomplished. In addition, the limited space available is taken up to a much larger extent than in an above-ground facility by equipment necessary to carry out the various mine operations such as mining, haulage, and ventilation. Thus, despite ventilation, the danger of accumulating toxic decomposition products at or above threshold limit values is much greater in an underground mine than in an above-ground facil-

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ity, since larger amounts of materials per unit volume of available space are capable of oxidative thermal decomposition accompanied by toxic product formation. Accordingly, the temperature at which specific materials produce significant quantities of volatiles, the nature and toxicity of these volatiles, the onset of glow or the temperature of autoignition, the loss of flame resistance through normal use, and the nature and toxicity of combustion products are of much greater importance in an underground mine than in most other locations.

Most of the aforementioned studies cited above were conducted at rather gradually increasing temperatures either in static systems or at relatively low gas flow rates. In the work reported here more severe conditions were employed to approximate more closely situations that could occur in a mine. To simulate overheating, a preheated, temperature equilibrated test cell was employed. To approximate the condition in which a stream of hot gas, originating from a fire, causes the decomposition of a material downstream, preheated air was passed at a known flow rate over the test specimen. As described in the experimental section, intermittent sampling was employed to determine change of product composition with time and to estimate the rate of toxic product formation as a function of temperature. The studies reported here were preliminary in nature; more extensive investigations are being currently pursued.

Experimental

The oxidative studies were performed using the stagnation burner arrangement, a schematic of which is given in Figure 1. A quartz probe equipped with three ampoules (shown also in Figure 1) was used for sampling. During sampling, the stopcock A to the vacuum pump was closed, and a given ampoule (previously evacuated) was opened to the probe for a period of 5 seconds. All the temperatures presented in Table I are the temperatures recorded by the thermocouples B (gas temperature) and C (block temperature). In Table I only one temperature is denoted, since in all the experiments performed both temperatures were identical. The temperatures were recorded using a CEC 5-124A recording oscillograph after

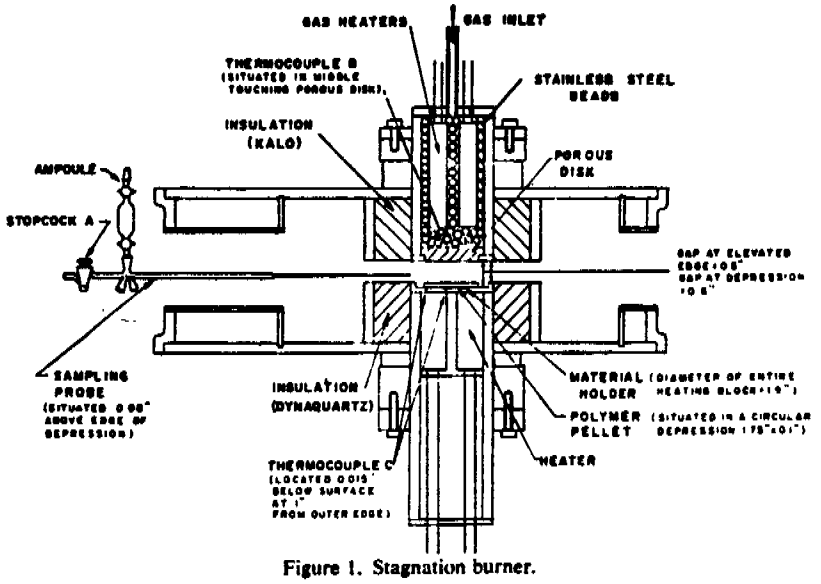

Figure 1. Stagnation burner.

TABLE I

Summary of Thermal Oxidative Tests Performed on Representative Materials[a]

Sample Identification	Temp °C	Sample Wt mg	Heavy Smoke Duration sec	Sampling Time sec	HCl %	CO %	CO_2 %	C_xH_y[b] %	C_2H_4 %	CH_3Cl %	$CFCl_3$ %	SO_2 %	$C_2H_3Cl_3$ %
PVC-Nylon	400	904	45-90	40-45	trace	....	0.04	....	....	....	....	....	....
PVC-Nylon	400	904	45-90	60-65	3.62	0.23	0.16	0.15	0.18	....	....	....	....
PVC-Nylon	490	925	33-85	35-40	3.07	0.36	0.29	0.25	0.09	....	....	....	....
PVC-Nylon	490	925	33-85	55-60	1.36	0.18	0.26	0.21	0.05	....	....	....	....
PVC-Nylon	570	932	28-65	50-55	0.06	0.38	0.29	0.21	0.01	....	....	....	....
PVC-Nylon	570	932	28-65	170-175	....	0.10	0.19	....	....	....	....	....	....
Neoprene Composition	390	2187	165-205[c]	165-170	....	....	0.07	....	....	....	....	....	....
Neoprene Composition	390	2187	165-205	210-215	2.34	0.48	1.07	0.46	trace	....	....	0.04	....
Neoprene Composition	485	2448	60-130	100-105	19.63	1.51	2.77	2.17	0.02	....	....	0.05	....
Neoprene Composition	485	2448	60-130	125-130[d]	3.11	3.74	9.97	0.45	trace	....	....	0.04	....
Neoprene Composition	555	2286	50-90	65-70	7.33	1.06	2.74	1.57	0.01	....	....	0.04	....
Neoprene Composition	555	2286	50-90	150-155[e]	0.38	2.53	5.63	0.10	....	....	....	0.02	....
Jute	475	607	65-150	45-50	....	0.37	1.96	0.20	....	0.31	....	....	....
Jute	475	607	65-150	55-60[f]	....	0.79	2.18	0.44	....	0.20	....	....	....
Jute	555	755	30-45	35-40	....	0.65	2.02	0.14	trace	0.40	....	....	....
Jute	555	755	30-45	65-79[g]	....	0.18	0.59	....	....	0.07	....	....	....
Polyurethane Foam	485	279	10-40	8-13	0.24	0.14	2.41	0.11	n.d.[j]	....	0.06	....	0.11
Polyurethane Foam	485	279	10-40	18-23	....	0.09	0.25	0.01	n.d.	....	....	....	....
Polyurethane Foam	545	260	3-20	5-10	0.13	....	1.91	0.07	n.d.	....	0.04	....	0.07
Polyurethane Foam	545	260	3.20	15-20	....	0.19	0.32	0.05	n.d.	....	trace	....	0.01
Fiber Glass	487	770	75-127	107-112	....	0.71	1.09	1.91	....	....	....	....	....
Fiber Glass	487	770	75-127	130-135[h]	....	2.79	10.60	3.89	0.15	....	....	....	....
Fiber Glass	550	791	35-39	35-40	....	1.88	5.79	1.45	0.03	....	....	....	....
Fiber Glass	550	791	35-39	42-47[i]	....	4.14	9.45	9.44	0.19	....	....	....	....

[a] All the analyses are mole percents of gaseous sample, the remainder is N_2, O_2, Ar.

[b] The hydrocarbons compiled under C_xH_y are ethylene, propylene with lesser amounts of propane and acetylene.

[c] Glow from 4 to 28 min.

[d] Glow from 2 min 10 sec to 28 min; this sample was taken just prior to glow onset.

[e] Glow from 1 min 50 sec to 35 min; this sample was taken during glow.

[f] Glow from 1 min 15 sec to 3 min; this sample was taken just prior to the glow.

[g] Glow from 58 sec to 8 min; this sample was taken during glow.

[h] Combustion from 2 min 7 sec to 2 min 23 sec; this sample was taken during combustion.

[i] Combustion from 39 sec to 1 min 20 sec; this sample was taken during combustion.

[j] n.d.: not determined.

steady state was attained just prior to polymer insertion. In view of the air temperature range of 200-550°C, the actual gas flow varied from 80-150 cc/sec. All times listed in Table I were measured from the moment of polymer insertion. The volatiles collected in the ampoules were analyzed using mass spectrometry (modified CEC Model 21-620) and infrared spectroscopy.

Results and Discussion

In Table I are compiled the results obtained for four representative material compositions used in mines. These were brattice cloth samples (PVC-nylon, jute, "fiber glass"), conveyor belts and cable insulation (neoprene), and ventilation stop sealants (polyurethanes). The fiber glass composition was included to illustrate the unexpected flammability and toxic product formation (in this case CO) from what would appear to be a "safe" material. The actual number of compositions studied under this program was much larger, however, since the data obtained for related compositions (*e.g.*, the various types of brattice cloths composed essentially of polyvinyl chloride-nylon) were not significantly different to alter the general trend only one representative member of each series is discussed.

On both polyvinyl chloride-nylon and the neoprene compositions, tests were performed at 200°C; however, in each instance, after 10 minutes residence in the hot zone, only 1% of sample weight was lost, and no volatile products could be detected by mass spectrometry. In the experiments summarized in Table I at least one sampling at a given temperature was performed during the most intense smoke formation. Examining the data it is apparent that in polyvinyl chloride and neoprene compositions the observance of smoke is associated with hydrogen chloride evolution. As would be expected, at the higher temperature hydrogen chloride is evolved at a much faster rate than at lower temperatures. Consequently, after a shorter time interval the material is depleted of chlorine, resulting in an earlier glow onset. During glow the gaseous effluent was found to be grossly depleted of hydrogen chloride, whereas the relative concentration of carbon monoxide was significantly increased. Thus it seems safe to state that in the case of chlorinated composition, in particular materials such as neoprenes or PVC, hydrogen chloride is the main toxic species produced during the initial stages of decomposition prior to the occurrence of a glow. By the time glow or autoignition can be observed, carbon monoxide, not hydrogen chloride, poses the real toxic hazard. Sulfur dioxide, in case of neoprenes, is produced in sufficiently high concentration to be detected in the highly diluted samples collected. However, in comparison with the hydrogen chloride and carbon monoxide concentrations measured, sulfur dioxide is not the major toxic hazard although it definitely is a contributing factor. On the other hand, in our current studies to be reported at a later date, other toxic sulfur-containing constituents were observed also, such as carbon disulfide, carbonyl sulfide, and hydrogen sulfide. Thus, the sum of all sulfur-containing species amongst the decomposition products may represent a considerable danger in the case of highly cured compositions, since threshold limit values are very low for some of them and the effects are additive.

Jute has been used extensively in the mines, particularly in the form of brattice cloths. As would be expected carbon monoxide is the main toxic species produced here; the surprising aspect is the formation of methyl chloride. This compound most likely arises from the reaction of calcium chloride, incorporated as a fire retardant, with the organic constituents of jute.

Four different polyurethane foam samples were investigated. The mixture of decomposition products found was very similar in each instance. It was known that Fluorocarbon-11 ($CFCl_3$) was the blowing agent used

to produce the rigid foams, thus the finding of this material in the volatile off-gases was not surprising. However, it is noteworthy that it is a potential phosgene precursor. The presence of dichloroethane and hydrogen chloride was unexpected unless it can be assumed that chlorinated hydrocarbons were components of the urethane mixture. Comparing sample weights employed, it is obvious that these products were formed in significant quantities on weight/weight basis.

The "fiber glass" sample used in these investigations is actually an organic resin reinforced with glass fibers to increase structural integrity. The particular sample tested was one of the few materials that were found to burst into flames when exposed to temperature (487°C). It also produced high concentrations of carbon monoxide. As a matter of interest, a typical coal sample failed to glow under these conditions. It should be pointed out that this study was not concerned with material ignition behavior, therefore ignition of this "fiber glass" sample obviously can occur at temperatures lower than 487°C. This material accordingly presents a danger both in view of its ready flammability and its production of large amounts of carbon monoxide. Hydrogen cyanide is of great importance from the toxicology standpoint, yet it is not listed in Table I since the mass spectrometer employed did not resolve the peaks at m/e 27 and 26 to show whether these were HCN and CN or C_2H_3 and C_2H_2 derived. No hydrogen cyanide was detected using infrared spectroscopy, which means that, if it was present, its concentration was below 0.1%.

It should be emphasized that this was an exploratory study concerned mainly with the production of the major toxic components as influenced by temperature and exposure duration. The experimental conditions chosen did not lend themselves to detection and identification of toxic components formed in small quantities, *e.g.*, in concentrations of less than 0,01% in the gaseous effluent. More extensive work aimed at lowering of detection limits and quantitative determination of all major products formed is presently in progress.

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Horace W. Gerarde, M.D., Ph.D.

Dr. Horace Gerarde and his wife, Dotty, died in an airplane crash at Izmir, Turkey, on January 26, 1974. Horace, a long standing member of AIHA, was well known to us for his many significant scientific contributions to our field and for his unstinting work for AIHA committees and projects. He is, perhaps, best known for his extensive research on the toxicology of the hydrocarbons among his many and varied researches.

He was graduated from Beloit College in 1940, then received his M.D. from the University of Wisconsin in 1948 and his Ph.D. from the University of Iowa in 1951. In 1952, he joined the Medical Research Division of Esso Research and Engineering Co., where he did much of his work on the hydrocarbons. Then in 1966 he became the Medical Director of B-D Division of the Becton, Dickinson and Co. and pursued the development of his invention the Unopette. He was Corporate Medical Director for Occupational Health for Becton, Dickinson and Co. and consultant to a number of other firms at the time of his tragic death.

Dr. Gerarde also combined his research and industrial medical activities with a considerable interest in teaching. At various times he held teaching appointments at Fairleigh-Dickinson University, Rutgers University, New York University, and Harvard University.

We join his coworkers and many friends in their grief and loss in the passing of Horace Gerarde, for whom we hold the highest respect as a scientist, as an individual, and most of all as our professional confrere.