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THERMAL DEGRADATION AND TOXICITY ASPECTS
OF VARIOUS POLYMERIC MATERIALS

C. R. Schmitt

UNION CARBIDE CORPORATION
NUCLEAR DIVISION
OAK RIDGE Y-12 PLANT

operated for the ATOMIC ENERGY COMMISSION under U. S. GOVERNMENT Contract W-7405 eng 26

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C. R. Schmitt

Oak Ridge Y-12 Plant

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ABSTRACT

The thermal degradation characteristics of a flexible polyurethane foam, two polyethylene trash containers, and a polystyrene packaging material were evaluated by thermogravimetric, mass spectrographic, and emission spectrographic analyses with regard to the toxic gaseous products evolved.

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SUMMARY

An ignition testing apparatus was used in conjunction with mass spectrographic analyses to evaluate the toxic gaseous products evolved from the thermal degradation of various packaging materials in common use at the Oak Ridge Y-12 Plant.^(a) Mass spectrographic analyses of vapors liberated from a flexible polyurethane foam at the temperature of melting and just prior to ignition showed that toxic hydrogen cyanide was present. After ignition, a relatively large increase in the hydrogen cyanide content of the gaseous degradation products occurred.

Mass spectrographic, thermogravimetric, and other analytical data were also obtained on two samples of polyurethane used as trash containers and on a sample of polystyrene used as a packaging material.

(a) Operated by the Union Carbide Corporation's Nuclear Division for the US Atomic Energy Commission.

INTRODUCTION

The flammability and combustion aspects of the many new types of synthetic polymeric foams and packaging materials have received considerable attention in recent years. Toxicity aspects that may be associated with the burning or thermal degradation of many of these materials, however, have not been generally recognized or studied.

For example, a fire at a Cleveland, Ohio clinic in 1929 involving X-ray film (a plastic composed of nitrocellulose) brought death to 125 persons. Subsequent medical studies, however, showed that most of the deaths were not due directly to the fire, but were a consequence of the production of poisonous carbon monoxide and various nitrogen oxides.⁽¹⁾ Other fires have also occurred which have caused deaths that have been attributed to the gaseous products evolved from man-made materials, rather than from the flames.

Information on inhalation hazards from the toxic gases or vapors produced by plastic, wooden, or other cellulosic or polymeric materials is of vital importance to plant emergency squad, fire fighting, and production supervision personnel. In real fire situations, it becomes advantageous to have some knowledge of what gases are formed so that proper precautionary measures can be applied for protection against inhalation of these gases as well as for preparing for obscuration by dense smoke.⁽²⁾

Research on the toxicity aspects of the gaseous pyrolysis and thermal degradation products of various plastic and polymeric materials that are in current use at the Y-12 Plant was, therefore, initiated.

Of special interest were: (1) a flexible polyurethane foam used as a cushioning and packaging material for shipping various production items, (2) two plastic containers used for the collection and incineration of miscellaneous combustible paper waste materials, and (3) a polystyrene packaging material. Other information on the comparative life hazards resulting from inhalation of the combustion and thermal decomposition of certain plastic, wooden, and cellulosic building materials under fire conditions has been reported previously by Dufour.⁽³⁾

EXPERIMENTAL STUDY OF THE VARIOUS MATERIALS

THERMAL DEGRADATION APPARATUS AND PROCEDURE

The equipment used to study the evolution of gaseous thermal degradation products from the polyurethane and polyethylene materials consisted of an ignition test apparatus⁽⁴⁾ for solids that was used in conjunction with a 6-inch, 60-degree magnetic-sector, gas mass spectrometer. Weight-loss data resulting from the thermal degradation were obtained with a recording therm analyzer which records the changes in weight as the temperature is increased at a controlled gas flow rate or in a vacuum environment.

A cross-sectional view of the thermal decomposition and sampling apparatus is presented in Figure 1, and consists of a vertical, electrically heated furnace tube that is 22 centimeters long and has a 10-centimeter bore. The tube was

Figure 1. THERMAL DEGRADATION TEST APPARATUS FOR SOLIDS.

lined with an asbestos sleeve and embedded in refractory cement. An inner refractory tube was placed inside of the furnace tube and was made to rest on small blocks in the bottom of the furnace.

The space between the two tubes was used for circulation and heating of the air, which was admitted tangentially to the inner refractory tube from below. The top of the refractory tube was covered with a divided refractory disc having an opening for observation and for the passage of smoke and gases. A small gas flame was kept lit above the opening and was used for igniting the evolved gases. The temperature of the air rising in the inner tube was indicated by Thermocouple T₂ placed below the specimen. Another thermocouple (T₁) was located in front of the heating coils and a third thermocouple (T₃) was either attached to the surface or inserted within the lower part of the specimen.

TEST MATERIALS

Flexible Polyurethane Foam

As the first material of interest, a flexible polyurethane foam in widespread use as a packaging material at Y-12 was studied because of the possibility that toxic hydrogen cyanide (HCN) could be formed by the thermal degradation of the cyanate groups comprising the polyurethane molecule.

Thermal Degradation and Ignition Studies - A thermogram of the flexible polyurethane foam showing its thermal degradation characteristics in a flowing helium atmosphere is given in Figure 2. An inspection of Figure 2 shows that extensive losses in weight began at approximately 140° C and continued until a temperature of approximately 400° C was attained. At this temperature, the foam showed an overall weight loss of 92 percent. Time-temperature plots of the thermal degradation and ignition of the flexible polyurethane, evaluated in a flowing air atmosphere at air flow rates of 5 and 10 ft/min, are presented in Figures 3 and 4, respectively. As shown, the ignition temperature or temperature at which the polyurethane foam first caught fire was lowered significantly (from 625 to 607° F) as the air flow rate was increased to 10 ft/min.

During the air flow degradation test at 5 ft/min, gas samples were taken at: (1) the melting point of the polyurethane foam, (2) the point at which white fumes were observed, and (3) at the ignition point temperature when the sample caught fire. These samples were obtained by holding the stem of an evacuated gas sampling bulb (100 mls) into the exhaust end of the thermal degradation test apparatus, opening a stopcock to allow the bulb to attain atmospheric pressure, and then closing the stopcock.

Figure 2. THERMOGRAM OF POLYURETHANE FOAM IN A FLOWING HELIUM ATMOSPHERE. (4 liters/hour)

Mass Spectrographic Analyses - Mass spectrographic analyses, made of the trapped gases in the bulbs (see Figure 5), indicate a major peak for Mass 27, thereby confirming the presence of hydrogen cyanide. The presence of water vapor (Mass 18), carbon monoxide or nitrogen (Mass 28), and carbon dioxide (Mass 44) was also evidenced in the gaseous products that were evolved.

A comparison of the relative peak heights shown in Figure 5 for hydrogen cyanide (Mass 27) shows a relatively small peak corresponding to the sampling temperature of 400° F, a larger peak at 625° F prior to ignition, and a much larger peak at the sampling temperature of 650° F after ignition had occurred. These changes in the relative peak heights indicate, qualitatively, that the amount of hydrogen cyanide evolved increased significantly after the polyurethane foam had ignited.

Figure 3. TIME-TEMPERATURE PLOT DURING THERMAL DEGRADATION AND IGNITION OF POLYURETHANE FOAM. (Air Flow Rate of 5 ft/min)

Hydrogen Cyanide Analyses - After the mass spectrographic analyses were run (which consumed approximately one half of the bulb sample), the remaining gas and condensed liquid in the bulbs were flushed with distilled water and analyzed for hydrogen cyanide by a standard colorimetric, water-analysis method for cyanide employing pyridine-pyrazolone.⁽⁵⁾ The analytical results are reported in Table 1. These data indicate a 27-fold increase in the amount of hydrogen cyanide liberated after ignition, compared to the amount liberated just after the polyurethane had melted and the first smoke became visible. A time-temperature plot showing air and foam temperatures corresponding to the three gas bulb samples taken is given in Figure 3.

Spectrographic Analyses - Emission spectrographic and other analytical data were obtained on the flexible polyurethane foam. Results, summarized in Table 2, show a phosphorus content of 2,000 ppm. According to Lyons,⁽⁶⁾ phosphorus-containing polyols are easy to manufacture from inexpensive raw materials and thus are often used as a component in polyurethane foams. A common catalyst used for rigid polyurethane foam is an amine and, for flexible polyurethane foams, a tin salt is often used.⁽⁶⁾

Figure 4. TIME-TEMPERATURE PLOT DURING THERMAL DEGRADATION AND IGNITION OF POLYURETHANE FOAM. (Air Flow Rate of 10 ft/min)

Figure 5. MASS SPECTROGRAMS OF THERMAL DEGRADATION PRODUCTS EVOLVED FROM POLYURETHANE FOAM SHOWING RELATIVE AMOUNTS OF HYDROGEN CYANIDE (Mass 27) PRESENT.

Table 1
RELATIVE AMOUNTS OF HYDROGEN CYANIDE PRESENT IN THE
GASES EVOLVED FROM THERMAL DEGRADATION OF
FLEXIBLE POLYURETHANE FOAM

Sample Number	Foam Temperature (° F)	Gas Bulb Sampling Conditions	Total µgs HCN in Gas Bulb Sample(1)
1	400	First Fumes after Melting	0.1
2	625	Fumes before Ignition	0.3
3	650	Fumes after Ignition	2.7

(1) By a pyridine-pyrazolone colorimetric method. Total volume of the bulb was 100 milliliters.

Table 2
ANALYTICAL DATA ON FLEXIBLE POLYURETHANE FOAM

Percent H ₂ O(1)	0.12		
Percent Ash	0.096		
Emission Spectrographic Results(2)			
<u>Element</u>	<u>Concentration (ppm)</u>	<u>Element</u>	<u>Concentration (ppm)</u>
P	2,000	Ti	< 3
Si	55	Ni	< 2
Sn	20	Zr	< 1
K	10	Mn	< 0.5
Mg	10	Mo	< 0.5
Al	8	Ag	< 0.5
Fe	8	B	< 0.5
Ca	5	Ba	< 0.5
Zn	< 30	Be	< 0.5
Co	< 10	Cr	< 0.5
Cu	< 5	Cd	< 0.5
Li	< 5	V	< 0.5
W	< 5		

(1) By Karl Fischer titration.

(2) Arranged in decreasing order of concentration, followed by those elements for which only "less than" values could be obtained.

Thus, from the relatively high phosphorus and tin contents shown in Table 2, it is suspected that phosphorus comprised a portion of the polyol component and a tin salt comprised the catalyst.

Polyethylene Trash Containers

Infrared Analyses - Two different varieties of plastic trash containers used at the Y-12 Plant for the collection and incineration of paper and cellulosic wastes were characterized by infrared analyses in order to identify the fundamental chemical nature of the plastic material. Infrared spectrograms are presented in Figure 6. As shown in Figure 6, both the light-buff and black

plastic trash containers were readily identified as polyethylene, as evidenced by the close agreement of their infrared spectrograms with the standard.

Figure 6. INFRARED SPECTROGRAMS OF STANDARD POLYETHYLENE AND OF THE POLYETHYLENE TRASH CONTAINERS.

Thermogravimetric Analyses - Vacuum thermograms obtained on the light-buff and black plastic waste containers are given in Figures 7 and 8, respectively; a summary of the comparative thermogravimetric data obtained on the two plastic materials is given in Table 3. Although both of the waste containers were identified to be predominantly polyethylene by infrared analyses, large differences were found in their thermogravimetric degradation characteristics, as Figures 7 and 8 and Table 3 point out.

Figure 7. VACUUM THERMOGRAM OF THE LIGHT-BUFF PLASTIC WASTE CONTAINER.

Spectrographic and Analytical Data - Differences in the inorganic constituents of the polyethylene samples were also found, as shown by the spectrographic and analytical data presented in Table 4. The 2,250-ppm titanium content shown in Table 4 for the buff-colored polyethylene sample indicated that a titanium pigmentation agent may have been used. Since the black polyurethane waste container showed a 6.6-to-1 carbon-to-hydrogen weight ratio, it was indicated that carbon black particles probably were added to obtain the black pigmentation in this sample inasmuch as the stoichiometric carbon-to-hydrogen ratio for the polyethylene molecule is only 6.0 to 1.

Polystyrene

Another packaging material in common use at the Y-12 Plant is polystyrene. This plastic is received from various commercial vendors in a wide assortment of physical shapes and colors. Spectrographic analyses, showing the major inorganic elements that are present in a white, yellow, and green-pigmented polystyrene packaging filler material, are summarized in Table 5. As shown in Table 5, the major inorganic elements detected were sodium, calcium, silicon, and potassium, and it is indicated that organic addition

Figure 8. VACUUM THERMOGRAM OF THE BLACK PLASTIC WASTE CONTAINER.

Table 3
SUMMARY OF THE THERMOGRAVIMETRIC DATA ON
PLASTIC WASTE CONTAINERS

	Black Plastic(1)	Light-Buff Plastic(1)
Sample Weight (mgs)	50.2	104.4
Initial Weight (gms)	3.36176	2.2539
Final Weight (gms)	3.35893	2.2485
Weight Loss (gms)	0.00283	0.0054
Percent Weight Loss	5.6	5.2
Degradation Temperature (° C)	401	365
Initial Vacuum (torr)	1.5×10^{-5}	1.5×10^{-5}
Heating Rate (° C/min)	8	8
Lowest Temperature Corresponding to a Rapid Weight Loss Condition (° C)	247	170

(1) Both were identified as polyethylene by preliminary infrared analyses.

Table 4
SPECTROCHEMICAL ANALYSES OF COMMERCIAL
POLYETHYLENE WASTE CONTAINERS

Element	Material(1) (ppm)	
	Black Plastic(2)	Buff-Colored Plastic
Ag	< 0.02	< 0.9
Al	5	36
B	< 0.06	< 0.9
Ba	0.2	9
Be	0.003	0.9
Ca	40	7.2
Cd	< 0.1	36
Co	< 0.2	< 18
Cr	9.2	< 0.9
Cu	0.2	< 9
Fe	8	63
K	1.0	180
Li	0.6	< 18
Mg	4	< 9
Mn	0.2	< 1.8
Mo	0.03	< 0.9
Na	1.0	360
Ni	0.2	< 3.6
P	< 3	< 90
Pb	0.3	< 0.9
Si	30	36
Sn	0.1	< 0.9
Ti	0.4	2,250
V	0.02	< 0.9
W	0.02	< 9
Zn	1.0	< 54
Zr	0.04	1.8

(1) Differences in the lower limits of detectability shown are due to different sample quantities used.

(2) The black sample analyzed 87.3 percent carbon, 13.2 percent hydrogen, and less than 0.001 percent ash after ignition.

Table 5
SPECTROGRAPHIC ANALYSES OF PIGMENTED POLYSTYRENE.

White Pigmented		Yellow Pigmented		Green Pigmented	
Element(1)	Concentration (ppm)	Element(1)	Concentration (ppm)	Element(1)	Concentration (ppm)
Na	2,000	Na	150	Na	170
Ca	20	Ca	15	Ca	17
Si	15	Si	9	Si	10
Al	10	K	8	K	7
K	6	Al	4	Fe	5
Fe	3	Fe	3	Mg	3
Li	2	Mg	2	Al	2
Mg	2	Ti	0.9	Ti	1
Sn	0.3	Pb	0.2	Pb	0.3
B	0.2	Cr	0.2	P	< 17
Pb	0.2	P	< 15	Zn	< 10
Cr	0.2	Zn	< 9	Co	< 3
Mn	0.1	Co	< 3	Li	< 2
Mo	0.1	Cu	< 2	W	< 2
Ba	0.1	Li	< 2	Ni	< 0.7
Ag	0.1	W	< 2	Zr	< 0.3
P	< 10	Ni	< 0.6	Ag	< 0.2
Zn	< 6	Zr	< 0.3	B	< 0.2
Ca	< 2	B	< 0.2	Ba	< 0.2
Co	< 2	Ag	< 0.2	Be	< 0.2
W	< 1	Ba	< 0.2	Cd	< 0.2
Cu	< 1	Be	< 0.2	Cr	< 0.2
Ni	< 0.4	V	< 0.2	Mn	< 0.2
Zr	< 0.2			Mo	< 0.2
Be	< 0.1			Sn	< 0.2
Ba	< 0.1			V	< 0.2

(1) Arranged in decreasing order of concentration, followed by those elements for which only "less than" values could be obtained.

agents such as vegetable dyes may have been used to produce the differences in color.

Polystyrene ignites easily and the primary products of its combustion are carbon monoxide and carbon dioxide;⁽⁷⁾ thus, no extensive tests were made in this preliminary study other than to identify these gaseous pyrolysis products by quadrupole mass spectrographic analyses. In addition to the inorganic constituents contained in commercial polystyrene foam, as shown in Table 5, other constituents such as the chloro-fluoro hydrocarbons may also be present in some polystyrene foams which could cause a more serious toxicity hazard upon ignition. Since some commercial polystyrene foams use these chloro-fluoro hydrocarbons as the foaming agents, toxic phosgene gas (COCl_2) could be liberated. It has been estimated, for example, "that a commercial polystyrene egg carton containing one percent Freon would burn theoretically to about two thirds carbon dioxide, one third water, and 125 ppm phosgene in the combustion gases".⁽⁸⁾

DISCUSSION

The flexible polyurethane foam evaluated in this study was made at the Y-12 Plant by reacting a commercial polyurethane prepolymer mix (which contains isocyanate, polyol, and polyester ingredients) with a catalyst in a 1:1 volume ratio. This combination gave a flexible polyurethane foam having a bulk density of four pounds per cubic foot.

For a simple isocyanate such as toluene diisocyanate (TDI), the general reaction is:

where x is an integer and R is an alkyl group.

Although extensive work on the burning of polyurethane foam has been reported in the literature,^(7, 9-13) analytical and thermal degradation characterization data of the specific flexible polyurethane foam in use at the Y-12 Plant was needed because of the wide variety of isocyanate, polyol, polyester, and catalyst components of the many different proprietary commercial foam formulations.

As shown in Figure 4, the first smoke emitted from the Y-12 flexible polyurethane foam occurred at a temperature of approximately 350° F, and extremely heavy smoke evolution occurred at approximately 700° F. According to Lyons,⁽⁶⁾ smoke generation is a serious deterrent to effective fire-fighting operations since it "often obscures the route to safety and displaces oxygen in the lungs, both leading to death, and is often more hazardous than any other factor in a fire".

The literature references^(7, 9-13) state that the structure of the polyhydroxy compound and of the polyisocyanate has a great effect on the flame or flammability characteristics, char formation, and smoke density. All of these characteristics are of primary importance to Y-12 Plant operations for such problems as proper design, formulation of emergency fire-fighting procedures and equipment, and building ventilation requirements.

Polyurethanes made from TDI give the poorest chars and produce the least smoke.⁽⁴⁾ Polyester linkages have a profound influence on the type and amount of volatile and flammable fragments produced by thermal degradation. Although degradation of the foam is complex, "unzipping" of the polyurethane molecule to isocyanate and polyol occurs with loss of carbon dioxide and the formation of olefins and various amines. These reactions are:

In the presence of oxygen, Backus⁽¹³⁾ states that further degradation occurs and many other volatiles are produced. Since carbon, hydrogen, and nitrogen are all present in the initial isocyanate degradation products of a polyurethane foam, it is not very surprising that toxic carbon monoxide and hydrogen cyanide are formed, as was found in this study. The toxicity level of carbon monoxide and hydrogen cyanide in air has been reported as 100 and 10 ppm, respectively.⁽¹⁴⁾

Dufour⁽³⁾ cites the results of tests in which rats were exposed to the combustion or thermal decomposition products of a polyester-type polyurethane foam. The air combustion products included carbon monoxide, hydrogen cyanide, and the oxides of nitrogen, all of which were also identified in this study. It was also reported that hydrogen cyanide is also produced by the pyrolysis of many other natural and synthetic consumer products including cotton, wool, and paper.

Interest in the thermal degradation and toxicity aspects of the two types of plastic waste containers, also in common use at Y-12, has been of special concern recently because of several incidents where thermal degradation had occurred in offices by the inadvertent direct contact that had been made against electric baseboard wall heaters.

The results of this preliminary laboratory evaluation have been limited to only a few selected polymeric packaging materials of current interest. In

future studies, thermal degradation-toxicity tests on other polymeric materials will also be needed and will probably involve the use of a thermal decomposition-toxicity index developed by Epstein and Heicklen.⁽¹⁵⁾ The toxicity index, I , has been defined as:

$$I = k \sum_i P_i / LC_{50}^i ,$$

where:

k represents the rate constant for the decomposition of the polymer in hours⁻¹ and is a function of the decomposition temperature, T ;

P_i the mole percent of the decomposition product, i , in the product gases; and

LC_{50}^i the toxicity of the product, i , in ppm.

In view of the extremely heavy smoke evolution from flexible polyurethane over the temperature range from 350 to 700° F, an engineering study has been initiated on the adequacy of building ventilation and exhaust fans in those buildings at the Y-12 Plant where flexible polyurethane and other combustible packaging materials are being used and stored in large quantities.

ACKNOWLEDGEMENTS

The assistance of the following people at the Y-12 Plant Laboratory is gratefully acknowledged: E. C. Creech and J. H. Hamilton for the ignition testing, gas bulb sampling, and thermogravimetric analyses; and L. M. Steckel and Miss M. G. Davis for the gas mass spectrographic analyses.

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