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(NASA-TM-78458) TOXICITY OF PYROLYSIS GASES
FROM SYNTHETIC POLYMERS (NASA) 26 p HC
A03 F A01 CSCL 06T

N78-18127

Unclas
G3/23 05677

Toxicity of Pyrolysis Gases from Synthetic Polymers

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December 1977



National Aeronautics and
Space Administration

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NASA TM-78,458

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SUMMARY

The toxicity of the pyrolysis gases from some synthetic polymers was investigated, using the screening test method developed at the University of San Francisco. The synthetic polymers were polyethylene, polystyrene, polymethyl methacrylate, polycarbonate, ABS, polyaryl sulfone, polyether sulfone, polyphenyl sulfone, and polyphenylene sulfide.

Changing from a rising temperature program (40° C/min) to a fixed temperature program (immediate exposure to 800° C) resulted in shorter times to animal responses. This effect is attributed in part to more rapid generation of toxicants.

The toxicants from the sulfur-containing polymers appeared to act more rapidly than the toxicants from the other polymers. It is not known whether this effect is due primarily to differences in concentration or in the nature of the toxicants. The carbon monoxide concentrations found do not account for the results observed with the sulfur-containing polymers.

Polyphenyl sulfone appears to exhibit the least toxicity among the sulfur-containing polymers evaluated under these test conditions.

INTRODUCTION

Synthetic polymers are used in a wide variety of applications because of their unique properties, versatility, processability, and economic advantages. The materials intended for many applications must be evaluated with regard to various fire response characteristics. The toxicity of the gaseous products of pyrolysis and combustion is an important fire safety consideration.

Earlier work at the University of San Francisco showed that synthetic polymers exhibited a wide range of toxicity (ref. 1), and that test conditions affected test results and could affect relative rankings (ref. 2).

This paper presents the results of studies of the toxicity of the pyrolysis gases from a variety of synthetic polymers. A gradual heating rate, intended to simulate the pre-flashover conditions of a developing fire, was provided by the rising temperature program at 40° C/min. A rapid heating rate, intended to simulate the post-flashover conditions of a fully developed fire, was provided by the fixed temperature program at 800° C.

The plan of investigation consisted of the following steps: (1) performance of experiments on the synthetic polymers using both the fixed temperature and rising temperature programs; (2) analysis of the animal responses to determine the effect of heating rate on animal response times, and on time intervals between specific responses for the different polymers; (3) relation of animal response times to thermal stability data obtained through thermogravimetric analysis; (4) comparison of the animal response times with the response times reported for known concentrations of the various toxicants expected from specific polymers; and (5) comparison of the toxicant concentrations required to produce the observed effects with the concentrations of those toxicants found by gas analysis of the chamber atmospheres.

MATERIALS

The synthetic polymer samples evaluated in this study were identified as follows:

1. Polyethylene, 1: low density polyethylene pellets, El Rexene, Type 106, lot 31894, origin Rexene Polymers Company, Paramus, New Jersey.
2. Polyethylene, 2: polyethylene pellets, Bakelite 1142, origin Union Carbide Corporation, Bound Brook, New Jersey.
3. Polystyrene, 1: polystyrene pellets, Natural Styron 402, D 27 7, origin Dow Chemical Company, Torrance, California.
4. Polystyrene, 2: polystyrene sheet.
5. Polymethyl methacrylate: polymethyl methacrylate sheet, Plexiglas G, origin Rohm and Haas Company.
6. Polycarbonate: bisphenol A polycarbonate pellets, Lexan 100-111, lot F767D1, origin General Electric Company, Mount Vernon, Indiana.
7. Acrylonitrile-butadiene-styrene (ABS): ABS pellets, Dylel 702, natural, lot A 54000, origin Sinclair-Koppers Company, Kobuta, Pennsylvania.
8. Polyaryl sulfone: polyaryl sulfone pellets.
9. Polyether sulfone, 1: polyether sulfone pellets, 212-P.
10. Polyether sulfone, 2: polyether sulfone pellets, 200-P.
11. Polyphenylene sulfide: polyphenyl sulfide pellets.
12. Polyphenyl sulfone: polyphenyl sulfone pellets, Radel R-5000, origin Union Carbide Corporation, Bound Brook, New Jersey.

APPARATUS

A Lindberg horizontal-tube furnace is used for pyrolysis. The sample material is pyrolyzed in a quartz boat centered in a quartz tube, closed at

one end with a cap, and connected at the open end to the animal exposure chamber.

The animal exposure chamber is of a design developed and patented by NASA, and is made of clear polymethyl methacrylate so that continuous observation of the animals is facilitated. The activity of the free-moving mice in the chamber allows observation of natural, unrestrained behavior which can be recorded by the average lay person. This spontaneous activity appears to result in fairly uniform distribution of the gases throughout the chamber volume.

The polymethyl methacrylate is superior to glass in ease of fabrication, light weight, resistance to shock, and inertness to hydrogen fluoride, which is a pyrolysis effluent from some synthetic polymers. The chamber has a total free volume of 4.2 liters, and is made of an upper dome section and a lower base section, both with a diameter of 203 mm (8 in.).

The upper dome section is removable, and is connected to the base section by means of a conventional toggle-snap ring; the joint is sealed by a O-ring. Access to the chamber is provided by two horizontal cylinders of different diameter mounted on the dome section. The larger horizontal cylinder, having a diameter of 59 mm (2.38 in.), is fitted with an adapter to accommodate the open end of the pyrolysis tube. The smaller horizontal cylinder, having a diameter of 39 mm (1.56 in.), is fitted with an adapter to accommodate the probe of a Beckman-process oxygen analyzer, and serves also as the entry port for the test animals. A perforated polymethyl methacrylate plate across the larger horizontal cylinder prevents movement of the mice into the pyrolysis tube.

The upper end of the dome section is provided with apertures and a clear polymethyl methacrylate cylinder having a cover plate. The cover plate is connected to a bubbler to permit venting of pressure exceeding 25 mm (1 in.) of water and prevent entry of fresh air, and is provided with fittings for a thermometer and for gas sampling.

PROCEDURE

The pyrolysis tube, pyrolysis boat, animal exposure chamber, and all fittings and adapters are thoroughly cleaned and dried before each test. The pyrolysis boat is weighed with and without the sample under test. A sample weight of 1.00 g is normally used for screening studies, and was used in this study.

The test animals are received in plastic cages with each test group in its own cage. Each animal is removed, inspected for freedom from abnormalities, weighed, and marked on some part of the body with different colors of ink for identification. Four Swiss-Webster male mice, 25 g to 35 g body weight, are used for each test. Four appears to be the optimum number of mice which can be used for each test without excessive oxygen consumption during the test period as well as being the largest number which can be satisfactorily observed by a single operator.

Each experiment is repeated two or more times. This replication provides measures of variation between test animals and between experiments.

The mice are placed in the animal-exposure chamber and given a minimum of 5 min to accustom themselves to their surroundings. The entire system is sealed (except for the safety vent) and all joints are checked for proper seating. The pyrolysis tube containing the sample is introduced into the furnace which is preheated to 200° C in the case of the rising temperature program, or 800° C in the case of the fixed temperature program. In the case of the rising temperature program, the furnace is turned on at the start of the test at the predetermined heating rate of 40° C/min; when the furnace approaches or reaches 800° C, this temperature is maintained by either automatic or manual control until the end of the test. The test period is 30 min unless 100% mortality occurs earlier. The test is terminated upon the death of the last surviving animal, and any samples for gas analysis are taken at that time before the system is opened.

Time to first sign of incapacitation is defined as the time to the first observation of loss of equilibrium (staggering), prostration, collapse, or convulsions in any of the test animals.

Time to staggering is defined as the time to the first observation of loss of equilibrium or uncoordinated movement in a specific test animal.

Time to convulsions is defined as the time to the first observation of uncontrolled muscular movements in a specific test animal.

Time to collapse is defined as the time to the first observation of loss of muscular support in a specific test animal.

Time to death is defined as the time to the observed cessation of movement and respiration in a specific test animal.

Temperatures and oxygen concentration in the animal-exposure chamber are recorded at 1-min intervals throughout the entire test period.

After the test is terminated and the animals are removed from the chamber, the pyrolysis boat containing the sample is removed. It is then allowed to cool, and is weighed to permit calculation, by difference, of the weight of sample pyrolyzed. Surviving animals are observed daily for a 14-day period after the test and any significant changes from normal appearance, behavior, or weight are noted.

RESULTS AND DISCUSSION

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Animal Responses

The results of toxicity tests on 12 synthetic polymers are presented in tables 1 and 2. Test results using the fixed-temperature program are

presented in table 1, and test results using the rising-temperature program are presented in table 2. The values given for individual tests, as indicated by a test reference, are mean \pm standard deviation within experiment (between animals); the mean values given for individual polymers are mean \pm standard deviation between experiments.

The mean values for the different polymers listed in order of increasing time to death for each temperature program are presented in table 3. The values given are mean \pm standard deviation between experiments with n being the number of experiments.

Changing from a rising-temperature program to a fixed-temperature program resulted in shorter times to animal responses. This effect is attributed in part to more rapid generation of toxicants. The differences between polymers in the extent to which response times were reduced may in some cases reflect their relative thermal stability because the rising-temperature program tends to result in longer times to polymer decomposition and toxic effects with the more thermally stable polymers.

With the rising-temperature program, the polymers divided into three groups: (1) those with times to death between 10 min and 15.5 min (the sulfur-containing polymers), (2) those with times to death between 15.5 min and 18 min (PMMA and ABS), and (3) those with times to death between 19 min and 27 min (polyethylene, polystyrene, and polycarbonate).

With the fixed-temperature program, the polymers could be divided into the same three groups: (1) those with times to death between 2 min and 6.3 min (the sulfur-containing polymers), (2) those with times to death between 7.7 min and 9.5 min (PMMA and ABS), and (3) those with times to death between 9.6 min and 22 min (polyethylene, polystyrene, and polycarbonate). Although the rank order of the three groups remained the same, the rank order within the third group was different from the fixed-temperature program in that polycarbonate and polyethylene appeared to be significantly more toxic than polystyrene.

Listing the polymers in order of increasing time to convulsions or increasing time to collapse, produced essentially the same rank order as increasing time to death with both temperature programs. Listing the polymers in order of increasing time to the first sign of incapacitation or increasing time to staggering, produced slightly different rank orders; the sulfur-containing polymers consistently exhibited the shortest times to the first sign of incapacitation and times to staggering.

The reductions in times to different animal responses resulting from the change from the rising-temperature program to the fixed-temperature program are presented in table 4. The reductions in response times were greatest with polyethylene, polycarbonate, and ABS.

The reductions in response times were essentially the same for convulsions, collapse, and death with all the polymers studied. With polycarbonate, ABS, and the sulfur-containing polymers, the reductions in response times

appeared essentially the same for all responses recorded. With respect to the reductions in response times, there seemed to be significant differences between the two samples of polyethylene, between the two samples of polystyrene, and between the two samples of polyether sulfone.

The time intervals between convulsions and death, and between the first sign of incapacitation and death, are presented in table 5. The time intervals between convulsions and death for each polymer were, in general, not significantly affected by temperature program. The time intervals between the first sign of incapacitation and death seemed unaffected by temperature program in the case of the sulfur-containing polymers, and showed no consistent difference between temperature programs in the case of the other polymers.

On the basis of the animal response data alone, the same toxicants or combinations of toxicants may account for the observed times to convulsions and death; but the observed times to incapacitation may be due to different toxicants or combinations of toxicants.

Relation to Thermal Stability

Thermogravimetric analysis (TGA) indicated that with a heating rate of 40° C/min in nitrogen or air, ABS decomposed above 300° C, and bisphenol A polycarbonate, polyether sulfone, polyaryl sulfone, and polyphenylene sulfide decomposed above 500° C (ref. 3). This difference of 200° C corresponds to a difference of 5 min in a rising-temperature program at 40° C/min; however, the 3 min to 7 min difference in time to death between the sulfur-containing polymers and ABS with the rising-temperature program is opposite in direction, and would indicate that the toxicants from the sulfur-containing polymers produced death 8 min to 12 min more rapidly than did those from ABS.

Although the sulfur-containing polymers and bisphenol A polycarbonate decomposed at approximately the same temperature, and therefore at approximately the same during the rising-temperature program, the toxicants from the sulfur-containing polymers produced death 8 min to 12 min more rapidly than did the toxicants from polycarbonate.

With immediate exposure to 800° C in the fixed-temperature program, the differences attributable to differences in thermal stability below 800° C would appear to be essentially eliminated. The sulfur-containing polymers, however, produced death by 4 min to 7 min more rapidly than did ABS and polycarbonate.

The more rapid deaths with the sulfur-containing polymers seem to indicate the presence of more rapidly acting toxicants. It is not known whether the more rapid action is due primarily to higher concentrations or to differences in the nature of the toxicants.

The 8 min to 12 min difference with the rising-temperature program and the 4 min to 7 min difference with the fixed-temperature program appear to indicate that the two heating rates may produce different toxicants,

different combinations of toxicants, or different concentrations of toxicants from one or more of these polymers.

Possible Gaseous Toxicants

A review of some available information on the gaseous toxicants evolved from these synthetic polymers is appropriate at this point.

The volatile combustion products of polysulfone heated in air at a heating rate of 50° C/min were carbon dioxide, sulfur dioxide, carbon monoxide, and methane, and smaller amounts of benzene, toluene, ethylene, ethylbenzene, and ethane. Carbonyl sulfide was identified in the temperature range of 490° C to 550° C, where most of the sulfur dioxide was formed (ref. 4).

The thermal decomposition products of polysulfone pyrolyzed in vacuum from 200° C to 600° C included sulfur dioxide (primarily formed at 500° C), hydrogen sulfide (primarily formed at 600° C), and carbon monoxide (primarily formed at 600° C) (ref. 5).

The main decomposition products of aromatic polysulfones thermally degraded in vacuum were carbon dioxide and sulfur dioxide (ref. 6).

Sulfur dioxide was produced by the thermal degradation of four types of polysulfones in helium at 5° C/min to 300° C (ref. 7).

The gaseous combustion products of polyphenylene sulfide at 700° C in air were carbon dioxide, sulfur dioxide, and carbon monoxide, and a small amount of carbonyl sulfide (ref. 8).

An acrylonitrile-butadiene-styrene (ABS) polymer containing 22% acrylonitrile, 19% butadiene, and 59% styrene, when pyrolyzed in the presence of air, produced hydrogen cyanide (HCN) and nitrogen dioxide (NO₂) over a temperature range of 500° C to 1200° C; high amounts were produced at 800° C, where 100 g of polymer produced 4.62 g HCN and 14.9 mg NO₂ (ref. 9).

The volatile combustion products of bisphenol A polycarbonate heated in air at a heating rate of 50° C/min were carbon dioxide, carbon monoxide, and methane, and smaller amounts of benzene, toluene, ethylene, ethylbenzene, and propylene (ref. 4).

The major products obtained in the thermal degradation of bisphenol A polycarbonate were benzene, toluene, ethylbenzene, phenol, p-cresol, p-ethylphenol, and p-isopropylphenol (ref. 10).

The gaseous combustion products of polyethylene and polystyrene at 700° C in air were carbon dioxide and carbon monoxide, and smaller quantities of hydrocarbons (ref. 8).

The combustion products of low-density polyethylene heated in air at a heating rate of 50° C/min were carbon dioxide, carbon monoxide, ethylene,

propylene, 1,3-pentadiene, 1-butene, methane, 1-hexene, 1-pentene, and ethane, in order of decreasing amount (ref. 11).

Carbon monoxide can be evolved from most of the synthetic polymers in this study. The toxicants which would be expected from the sulfur-containing polymers, but not from the other polymers are sulfur dioxide, hydrogen sulfide, and carbonyl sulfide. The differences in time to death between the sulfur-containing polymers and ABS indicate that these sulfur-containing toxicants may act more rapidly than hydrogen cyanide or nitrogen dioxide, if the difference is due to the nature rather than concentration of toxicants.

Nitrogen dioxide levels in excess of 10,000 ppm appeared necessary to produce deaths in Swiss albino mice within 5 min (ref. 12). On the other hand, a study of the effect of sulfur dioxide on Swiss albino mice showed that approximately 15,000 ppm of SO₂ produced death in about 2 min (ref. 13), and carbonyl sulfide (COS) has been reported to produce deaths in mice in 1.5 min at levels of 2900 ppm COS (ref. 14).

While the preceding information may strengthen the proposition that the nature of the toxicants from the sulfur-containing polymers is the cause of the more rapid deaths, the importance of carbon monoxide should not be overlooked. A study of the effect of carbon monoxide on Swiss albino mice showed that approximately 15,000 ppm of CO produced death in 1.7 min (ref. 15).

The short times to death (2.6 min to 5.5 min) observed with the sulfur-containing polymers using the fixed temperature program indicate that carbon monoxide, sulfur dioxide, or carbonyl sulfide could have been important factors, but the data presented at this point are not sufficient to indicate relative importance.

Chamber Gas Analyses

The recorded oxygen concentrations in the animal-exposure chamber during the test consistently decreased with time; the oxygen concentrations obtained by gas analysis at the time of death of the last surviving animal are, therefore, the lowest concentrations encountered by the test animals.

Although the oxygen concentrations obtained during the test by the polarographic-membrane technique provided reliable information on trends, the oxygen analyzer used frequently malfunctioned and the readings were sometimes at considerable variance from the data obtained using a gas chromatograph with thermal conductivity detector. Interference from other compounds and smoke deposits were possible causes of the discrepancies observed. The values obtained by gas chromatography are considered more reliable and are used in this paper.

The concentrations of methane, carbon monoxide, and oxygen in the animal-exposure chamber at the time of death of the last surviving animal are presented in Table 6. Because these analyses are essentially isolated spot values which provide no information about concentration trends, only limited

conclusions can be based on these data (ref. 16). However, because a closed system is used to prevent entry of fresh oxygen and escape of toxicants, it seems reasonable to assume that the oxygen concentrations are the lowest encountered, and that the methane and carbon monoxide concentrations are the highest encountered.

The gas analyses were limited in extent, with samples taken from only 13 tests with the rising-temperature program and 15 tests with the fixed-temperature program. The oxygen concentrations averaged $16.8\% \pm 0.5\%$ with the rising-temperature program and $18.7\% \pm 0.9\%$ with the fixed-temperature program; the values given are mean \pm standard deviation. The higher oxygen concentrations observed with the fixed-temperature program are believed to be due to the shorter times to death and hence reduced oxygen consumption by the test animals.

The methane concentrations obtained ranged from 300 ppm to 16,300 ppm with the fixed-temperature program and from 1,000 ppm to 9,600 ppm with the rising-temperature program. Where comparable data for specific polymers were available, methane concentrations tended to be higher with the fixed-temperature program. Because 10,000 ppm (1%) of methane displaces only sufficient air to reduce oxygen concentration by 0.2%, the contribution of methane as a simple asphyxiant in this study was not considered significant. The contribution of these concentrations of methane to hazard with regard to flammable mixtures (ref. 17) is outside the scope of this study.

Carbon monoxide concentrations reached the 10,000 ppm (1%) level only with polyethylene and polycarbonate; these levels were observed for both the rising-temperature and fixed-temperature programs. With polyether sulfone and ABS using the fixed-temperature program, carbon monoxide concentrations were below 4000 ppm. These CO concentrations, by themselves, could not have resulted in death in less than 7 min (ref. 15), and therefore do not account for the 4.3 min to 5.5 min times to death observed with polyether sulfone using the fixed-temperature program.

The carbon monoxide concentrations from polymethyl methacrylate, ABS, polycarbonate, polyethylene, and polystyrene using the fixed-temperature program were high enough to explain the times to death observed on the basis of the earlier carbon monoxide study (ref. 15).

Chamber Atmosphere Temperatures

The recorded temperatures in the animal-exposure chamber during the test did not exceed 29.5°C in any of the experiments. In only four of the experiments did the chamber temperature exceed 27.0°C . These temperatures are not considered to have a significant effect on animal responses.

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CONCLUSIONS

A more rapid heating rate generally produced shorter times to death, as anticipated. Even with immediate exposure to 800° C, however, there were differences in times to death which may reflect differences in mechanisms of intoxication.

The thermal stability advantages of the sulfur-containing polymers were overshadowed by the more rapid action of the toxicants evolved. It is not known whether this effect is due primarily to differences in concentration or in the nature of the toxicants. Carbon monoxide was not found in sufficient concentrations to be considered the primary cause.

Polyphenyl sulfone appears to exhibit the least toxicity among the sulfur-containing polymers evaluated under these test conditions.

ACKNOWLEDGMENTS

This work was performed at the Fire Safety Center of the University of San Francisco, with the support of the National Aeronautics and Space Administration under NASA Grant NSG-2039.

The authors are indebted to Dr. Arthur Furst and Dr. Henry A. Leon for their assistance and advice, and to Dr. Alfred Buchler for help in searching the literature.

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TABLE I. - TOXICITY TEST DATA ON SYNTHETIC POLYMERS: USF METHOD F:
800° C FIXED TEMPERATURE, NO FORCED AIRFLOW^a

Test reference	Time to first sign of incapacitation, min	Average time to staggering, min	Average time to convulsions, min	Average time to collapse, min	Average time to death, min	Weight of animals, g
Polyethylene, 1						
ANN-53	2.87	4.62 ± 1.37	8.04 ± 0.90	9.22 ± 0.69	12.13 ± 1.33	30.68 ± 1.97
JES-90	4.28	7.33 ± 2.30	9.21 ± .23	8.27 ± 1.60	11.32 ± .57	26.85 ± 1.19
Mean	3.57 ± 1.00	5.97 ± 1.92	8.62 ± .83	8.74 ± .67	11.72 ± .57	
Polyethylene, 2						
ANS-331	7.67	8.57 ± 0.84	8.66 ± 0.63	9.36 ± 1.14	11.09 ± 0.42	27.25 ± 1.94
ANS-333	6.00	6.54 ± .71	7.00 ± .77	7.06 ± .79	8.36 ± .61	27.68 ± 2.07
Mean	6.84 ± 1.18	7.55 ± 1.44	7.83 ± 1.17	8.21 ± 1.63	9.73 ± 1.93	
Polystyrene, 1						
ANN-52	2.53	7.68 ± 3.58	17.34 ± 5.31	21.97 ± 2.44	28.59 ± 1.00	28.5 ± 1.86
ANN-57	4.83	11.09 ± 4.35	18.06 ± 1.62	17.36 ± 2.09	21.56 ± 1.60	28.0 ± 2.77
JES-87	10.62	11.82 ± .98	12.76 ± 1.12	11.90 ± .60	15.38 ± 2.02	28.78 ± 2.60
Mean	5.99 ± 4.17	10.20 ± 2.21	16.05 ± 2.87	17.08 ± 5.04	21.84 ± 6.61	
Polystyrene, 2						
JAS-13	11.45	12.82 ± 1.40	15.75 ± 2.14	14.76 ± 1.48	20.87 ± 3.72	30.70 ± 2.69
JAS-14	13.50	14.30 ± .93	16.68 ± .95	15.76 ± 1.15	18.93 ± 1.66	31.70 ± 1.97
Mean	12.48 ± 1.45	13.56 ± 1.05	16.22 ± .66	15.26 ± .71	19.90 ± 1.37	
Polymethyl methacrylate						
JAS-11	2.38	3.35 ± 1.00	7.42 ± 1.04	7.36 ± 0.89	9.00 ± 1.44	28.63 ± 2.36
JAS-12	3.38	4.07 ± .48	5.16 ± .55	4.70 ± .97	6.47 ± .26	27.30 ± 3.14
Mean	2.88 ± 0.71	3.71 ± .51	6.29 ± 1.60	6.03 ± 1.88	7.74 ± 1.79	

^aValues given are mean ± standard deviation.

TABLE 1.- CONTINUED

Test reference	Time to first sign of incapacitation, min	Average time to staggering, min	Average time to convulsions, min	Average time to collapse, min	Average time to death, min	Weight of animals, g
Polycarbonate						
ANM-54	4.92	5.27 ± 0.38	5.69 ± 0.70	6.22 ± 0.53	10.32 ± 1.41	29.95 ± 2.55
ANM-55	4.34	4.84 ± .48	5.32 ± .62	5.72	6.54 ± .88	26.10 ± .63
JES-85	6.35	7.41 ± 1.54	7.20 ± .39	7.54 ± 1.20	11.58 ± 5.80	27.22 ± 1.16
JES-86	4.23	5.51 ± 1.24	5.81 ± .98	5.57 ± .69	7.30 ± 1.13	27.55 ± 2.79
RMM-20	5.72	6.27 ± .58	6.66 ± .61	7.77 ± .44	10.86 ± 3.94	27.32 ± 2.22
RMM-21	6.33	6.67 ± .34	8.70 ± 2.22	7.77 ± .44	10.73 ± 3.06	26.25 ± .62
Mean	5.31 ± 0.95	5.99 ± .96	6.56 ± 1.25	6.56 ± 1.03	9.56 ± 2.09	
Acrylonitrile-butadiene-styrene						
ANM-51	1.73	1.87 ± 0.16	4.20 ± 1.07	4.39 ± 0.80	9.07 ± 1.21	29.28 ± 0.63
ANM-56	2.30	4.83 ± 2.20	6.01 ± .33	5.13	10.16 ± 2.15	28.80 ± 2.32
JES-88	5.30	6.71 ± 1.27	7.00 ± .65	5.99 ± 1.78	10.62 ± 1.44	29.02 ± 1.79
JES-89	3.02	4.44 ± 1.24	4.79 ± 1.14	4.56 ± 1.20	8.19 ± 2.20	30.60 ± 2.92
Mean	3.09 ± 1.57	4.46 ± 1.99	5.50 ± 1.25	5.02 ± .72	9.51 ± 1.09	
Polyaryl sulfone						
JAS-2	3.42	3.65 ± 0.22	4.22	4.24 ± 0.52	4.63 ± 0.47	32.20 ± 3.61
JAS-5	2.55	2.62 ± .12		3.51 ± .63	4.05 ± .52	29.35 ± 3.66
Mean	2.99 ± 0.62	3.14 ± .73	4.22	3.88 ± .26	4.34 ± .41	
Polyether sulfone, I						
ANS-334	3.78	4.09 ± 0.54	4.61 ± 0.49	4.88 ± 0.61	5.69 ± 1.15	27.50 ± 3.03
ANS-336	2.43	3.06 ± .57	4.54 ± .64	4.69 ± .76	5.30 ± .83	23.62 ± .45
Mean	3.01 ± 0.81	3.58 ± .73	4.58 ± .09	4.79 ± .13	5.50 ± .28	

TABLE 1.- CONCLUDED

Test reference	Time to first sign of incapacitation, min	Average time to staggering, min	Average time to convulsions, min	Average time to collapse, min	Average time to death, min	Weight of animals, g
Polyether sulfone, 2						
JAS-4	3.70		4.24 ± 0.55	4.76 ± 0.97	33.75 ± 2.47	
JAS-7	2.78	2.78	3.48 ± 0.50	3.42	4.25 ± .22	33.10 ± 1.36
JAS-8	2.42	2.68 ± 0.31	3.31 ± .12	3.12	3.81 ± .04	30.10 ± 3.01
Mean	2.97 ± 0.66	2.74 ± .06	3.40 ± .12	3.59 ± .58	4.27 ± .48	
Polyphenyl sulfone						
JAS-32	3.63	4.14 ± 0.62	4.57 ± 0.63	4.68 ± 0.52	6.28 ± 1.47	35.58 ± 1.08
JAS-33	4.10	4.58 ± .67	4.76 ± .40	5.45 ± .89	6.30 ± 1.09	35.95 ± 3.52
Mean	3.87 ± 0.33	4.36 ± .31	4.67 ± .13	5.07 ± .54	6.29 ± .01	
Polyphenylene sulfide						
JAS-3	1.83			2.07 ± 0.16	2.29 ± 0.16	29.96 ± 2.66
JAS-6	2.17	2.27 ± 0.17	2.70	2.42 ± .09	2.87 ± .09	31.40 ± 1.49
Mean	2.00 ± 0.24	2.27	2.70	2.25 ± .25	2.58 ± .41	

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TABLE 2. - TOXICITY TEST DATA ON SYNTHETIC POLYMERS: USE METHOD B:
200° C-800° C RISING TEMPERATURE, 40° C/MIN, NO FORCED AIRFLOW^a

Test reference	Time to first sign of incapacitation, min	Average time to staggering, min	Average time to convulsions, min	Average time to collapse, min	Average time to death, min	Weight of animals, g
Polyethylene, 1						
ANS-328	18.25	19.42 ± 1.00	20.80 ± 0.43	21.08 ± 0.38	22.16 ± 0.46	37.50 ± 1.47
ANS-330	15.10	16.44 ± 1.45	18.72 ± 2.33	18.53 ± .29	23.03 ± 1.59	26.18 ± .62
Mean	16.68 ± 2.23	17.93 ± 2.11	19.76 ± 1.47	19.81 ± 1.80	22.60 ± .62	
Polyethylene, 2						
ANS-335	9.43	12.83 ± 3.25	17.21 ± 0.29	17.92 ± 1.23	19.62 ± 0.99	24.50 ± 1.08
ANS-337	8.30	10.64 ± 3.05	16.83 ± .97	17.55 ± 1.14	20.04 ± 1.50	24.12 ± 1.25
Mean	8.87 ± 0.80	11.74 ± 1.55	17.02 ± .27	17.74 ± .26	19.84 ± .29	
Polystyrene, 1						
ANS-323	18.77	21.04 ± 3.18	23.33 ± 1.79	23.38 ± 2.82	26.08 ± 1.20	26.75 ± 1.44
ANS-329	19.32	20.45 ± 1.14	22.44 ± 1.59		26.25 ± 1.95	28.50 ± .71
Mean	19.04 ± 0.39	20.74 ± .42	22.88 ± .63	23.38	26.16 ± .12	
Polystyrene, 2						
CMN-29-1	15.72	17.86 ± 1.92	18.68 ± 1.40	19.32 ± 1.50	22.13 ± 1.51	27.58 ± 0.52
CMN-29-2	14.65	15.15 ± .45	15.10 ± .58	15.68 ± .53	17.93 ± 1.42	28.86 ± 1.98
Mean	15.19 ± 0.76	16.51 ± 1.92	16.89 ± 2.53	17.50 ± 2.57	20.03 ± 2.97	
Polymethyl methacrylate						
CMN-29-3	12.57	13.41 ± 0.76	13.59 ± 0.52	13.95 ± 0.37	15.41 ± 0.67	27.54 ± 2.48
CMN-31-1	12.65	12.87 ± .30	13.24 ± .34	13.51 ± .45	15.74 ± .87	28.17 ± 1.41
Mean	12.61 ± 0.06	13.14 ± .38	13.42 ± .25	13.73 ± .31	15.58 ± .23	

^aValues given are mean ± standard deviation.

TABLE 2.- CONTINUED

Test reference	Time to first sign of incapacitation, min	Average time to staggering, min	Average time to convulsions, min	Average time to collapse, min	Average time to death, min	Weight of animals, g
Polycarbonate						
MIL-37	15.32	15.38 ± 0.15	16.76 ± 0.06	17.20 ± 0.30	23.13 ± 1.98	28.25 ± 1.76
HJK-1	14.62	16.16 ± 1.14	16.42 ± 1.97	18.08 ± 1.78	21.46 ± 2.65	27.72 ± 2.80
HJK-2	17.67	19.58 ± 1.67	20.99 ± 2.20	21.07 ± 2.12	24.29 ± 2.11	27.92 ± 4.73
HJK-3	14.43	16.76 ± 1.60	18.67 ± .86	19.10 ± .96	23.09 ± 2.73	26.28 ± 2.48
RMM-1	14.88	15.60 ± .85	17.24 ± 1.51		19.36 ± 1.67	29.05 ± 3.20
HJC-26	14.33	14.33 ±	17.28 ± 1.50	.18	19.15 ± 2.00	26.52 ± .85
HJC-28	14.02	14.96 ± 1.15	17.67 ± 1.50	.48	20.36 ± 1.95	30.35 ± 5.71
AMM-42	16.17	17.00 ± 1.38	19.08 ± 1.89	18.60	21.34 ± 3.41	28.95 ± 2.54
JES-72	9.07	16.47 ± 1.61	16.66 ± .61	15.32 ± 4.30	22.44 ± 4.14	28.38 ± .94
JES-73	15.97	17.41 ± 1.34	18.23 ± .41	17.83 ± .65	24.69 ± 1.00	32.00 ± 5.08
HJC-44	16.55	17.78 ± 1.40	22.57 ± 4.32	19.12 ± .44	24.00 ± 3.92	26.45 ± .86
RMM-19	13.43	14.01 ± .45	21.14 ± 6.96	16.94 ± 2.42	23.24 ± 5.29	27.42 ± 1.81
HAK-1	15.00	16.02 ± 1.02	16.79 ± .73	17.19 ± .78	19.19 ± 1.39	26.47 ± 1.82
HAK-14	15.23	16.73 ± 2.10			20.17 ± 1.59	34.65 ± 1.96
ANS-1241	16.37	16.81 ± .53	16.61 ± .27	18.16 ± 1.63	20.49 ± 1.16	34.05 ± 1.45
ANS-1242	15.32	15.65 ± .34	19.45	17.96 ± 1.44	20.45 ± 1.00	33.15 ± .52
PAR-1	15.60	18.00 ± 3.39		18.28 ± 3.46	20.93 ± 2.66	32.88 ± 2.31
BAO-3	16.00	16.42 ± .59	15.17		21.28 ± 2.24	32.00 ± 4.36
NVH-1	18.33	21.32 ± 3.25		24.37 ± 4.89	26.45 ± 4.91	32.88 ± 3.79
ANS-1284	17.57	18.21 ± .73		21.71 ± 1.24	26.02 ± 1.72	33.60 ± 4.11
Mean	15.29 ± 1.93	16.74 ± 1.74	18.23 ± 1.94	18.46 ± 2.23	22.08 ± 2.21	

TABLE 2.— CONTINUED

Test reference	Time to first sign of incapacitation, min	Average time to staggering, min	Average time to convulsions, min	Average time to collapse, min	Average time to death, min	Weight of animals, g
Acrylonitrile-butadiene-styrene						
CMM-45-1	16.33		18.11 ± 2.43	18.09 ± 2.13	20.44 ± 1.96	33.48 ± 1.55
CMM-45-2	13.43		14.82 ± .99		16.50 ± .76	32.84 ± .42
DSD-145	9.32	11.92 ± 0.03	11.62 ± 1.60		13.23 ± 1.78	30.98 ± .03
DSD-147	17.52	21.03 ± .71	21.17 ± 2.60		24.38 ± 2.03	35.45 ± 4.17
GLS-37-2	11.00		11.95 ± 1.34		13.53 ± .80	27.70 ± 2.11
Mean	13.52 ± 3.46	16.48 ± 6.44	15.53 ± 4.09	18.09	17.62 ± 4.77	
Polyaryl sulfone						
JMM-114	9.67		10.05 ± 0.54	9.83	10.78 ± 0.53	34.25 ± 0.87
KYS-1	11.50	11.72 ± 0.19	12.22 ± .51		12.88 ± .37	31.08 ± 1.14
CMM-19	8.87	8.87	9.08 ± .10	11.43 ± 0.09	10.01 ± .14	34.06 ± 2.82
Mean	10.01 ± 1.35	10.30 ± 2.02	10.45 ± 1.61	10.63 ± 1.13	11.23 ± 1.48	
Polyether sulfone, I						
RDG-133	10.65	11.16 ± 0.72	11.61 ± 0.56		12.12 ± 0.62	30.18 ± 1.42
KYS-4-1	8.56	8.98 ± .29	9.78 ± .09		10.22 ± .52	29.23 ± 2.14
KYS-4-2	10.83	10.94 ± .20	11.77 ± .51		12.67 ± .89	31.73 ± 3.12
JMM-138	13.00				13.88 ± .16	31.93 ± 3.13
ANS-332	9.88	10.95 ± .71	11.89 ± .42	12.12 ± 0.39	12.96 ± .36	27.25 ± .50
ANS-338	10.85	11.19 ± .30	12.40 ± .24	12.37 ± .32	12.68 ± .52	23.62 ± 1.49
Mean	10.63 ± 1.45	10.64 ± .94	11.49 ± 1.00	12.25 ± .18	12.42 ± 1.22	

TABLE 2.- CONCLUDED

Test reference	Time to first sign of incapacitation, min	Average time to staggering, min	Average time to convulsions, min	Average time to collapse, min	Average time to death, min	Weight of animals, g
Polyether sulfone, 2						
RDG-132	11.78	12.14 ± 0.51	12.03 ± 0.50		12.77 ± 0.56	30.55 ± 0.95
JMM-139	15.00				16.03 .66	33.83 ± 1.80
Mean	13.39 ± 2.28				14.40 ± 2.31	
Polyphenyl sulfone						
JAS-30	13.03	14.75 ± 1.97	14.56 ± 1.01	15.55 ± 1.52	15.78 ± 1.98	34.95 ± 2.45
JAS-31	13.60	14.08 ± .69	14.43 ± .81	14.73 ± .76	15.14 ± 1.03	35.48 ± 1.69
Mean	13.32 ± 0.40	14.42 ± .47	14.50 ± .09	15.14 ± .58	15.46 ± .45	
Polyphenylene sulfide						
CLS-	11.17		11.60 ± 0.13		12.19 ± 0.10	33.05 ± 1.26
KYS-3	8.83	8.83	9.04 ± .09		9.46 ± .16	30.43 ± 1.82
JMM-137	9.67				11.28 ± .21	28.13 ± 3.17
CMM-27	8.27		8.61 ± .23	8.78 ± 0.34	9.35 ± .08	25.21 ± 1.27
Mean	9.49 ± 1.26		9.75 ± 1.62		10.57 ± 1.40	

TABLE 3. - TOXICITY TEST DATA ON SYNTHETIC POLYMERS LISTED IN ORDER OF INCREASING TIME TO DEATH^a

Synthetic polymer	Time to first sign of incapacitation, min	Time to staggering, min	Time to convulsions, min	Time to collapse, min	Time to death, min	Number of tests
USF Method B: 200° C-800° C rising temperature, 40° C/min, no forced airflow						
Polyphenylene sulfide	9.49 ± 1.26	10.30 ± 2.20	9.75 ± 1.62	10.63 ± 1.13	10.57 ± 1.40	4
Polyaryl sulfone	10.01 ± 1.35	10.64 ± .94	10.45 ± 1.61	12.25 ± .18	11.23 ± 1.48	3
Polyether sulfone, 1	10.63 ± 1.45		11.49 ± 1.00		12.42 ± 1.22	6
Polyether sulfone, 2	13.39 ± 2.28				14.40 ± 2.31	2
Polyphenyl sulfone	13.32 ± .40	14.42 ± .47	14.50 ± .09	15.14 ± .58	15.46 ± .45	2
Polymethyl methacrylate	12.61 ± .06	13.14 ± .38	13.42 ± .25	13.73 ± .31	15.58 ± .25	2
ABS	13.52 ± 3.46	16.48 ± 6.44	15.53 ± 4.09		17.62 ± 4.77	5
Polyethylene, 2	8.87 ± .80	11.74 ± 1.55	17.02 ± .27	17.74 ± .26	19.84 ± .29	2
Polystyrene, 2	15.19 ± .76	16.51 ± 1.92	16.89 ± 2.53	17.50 ± 2.57	20.03 ± 2.97	2
Polycarbonate	15.29 ± 1.93	16.74 ± 1.74	18.23 ± 1.94	18.46 ± 2.23	22.08 ± 2.21	20
Polyethylene, 1	16.68 ± 2.23	17.93 ± 2.11	19.76 ± 1.47	19.81 ± 1.80	22.60 ± .62	2
Polystyrene, 1	19.04 ± .39	20.74 ± .42	22.88 ± .63	23.38	26.16 ± .12	2
USF Method F: 800° C fixed temperature, no forced airflow						
Polyphenylene sulfide	2.00 ± 0.24	2.27	2.70	2.25 ± 0.25	2.58 ± 0.41	2
Polyether sulfone, 2	2.97 ± .66	2.74 ± 0.06	3.40 ± 0.12	3.59 ± .58	4.27 ± .48	3
Polyaryl sulfone	2.99 ± .62	3.14 ± .72	4.22	3.88 ± .26	4.34 ± .41	2
Polyether sulfone, 1	3.01 ± .81	3.58 ± .73	4.58 ± .09	4.79 ± .13	5.50 ± .28	2
Polyphenyl sulfone	3.87 ± .33	4.36 ± .31	4.67 ± .13	5.07 ± .54	6.29 ± .01	2
Polymethyl methacrylate	2.88 ± .71	3.71 ± .51	6.29 ± 1.66	6.03 ± 1.88	7.74 ± 1.79	2
ABS	3.09 ± 1.57	4.46 ± 1.99	5.50 ± 1.25	5.02 ± .72	9.51 ± 1.09	4
Polycarbonate	5.31 ± .95	5.99 ± .96	6.56 ± 1.25	6.56 ± 1.03	9.56 ± 2.09	6
Polyethylene, 2	6.84 ± 1.18	7.55 ± 1.44	7.83 ± 1.17	8.21 ± 1.63	9.73 ± 1.93	2
Polyethylene, 1	3.57 ± 1.00	5.97 ± 1.92	8.62 ± .83	8.74 ± .67	11.72 ± .57	2
Polystyrene, 2	12.48 ± 1.45	13.56 ± 1.05	16.22 ± .66	15.26 ± .71	19.90 ± 1.37	2
Polystyrene, 1	5.99 ± 4.17	10.20 ± 2.21	16.05 ± 2.87	17.08 ± 5.04	21.84 ± 6.61	3

^a Values given are mean ± standard deviation.

TABLE 4. -- REDUCTION IN TIMES TO ANIMAL RESPONSES AS A RESULT OF CHANGE FROM RISING TEMPERATURE PROGRAM TO FIXED TEMPERATURE PROGRAM

Synthetic polymer	Difference, min, in time to						Mean
	Incapacitation	Staggering	Convulsions	Collapse	Death		
Polyethylene, 1	13.11	11.96	11.14	11.07	10.88	11.63 ± 0.92	
Polyethylene, 2	2.03	4.19	9.19	9.53	10.11	9.61 ± .47	
Polystyrene, 1	13.05	10.54	6.83	6.30	4.32	5.82 ± 1.32	
Polystyrene, 2	2.71	2.95	.67	2.24	.13	1.74 ± 1.26	
Polymethyl methacrylate	9.43	9.43	7.13	7.70	7.84	7.56 ± .38	
Polycarbonate	9.98	10.75	11.67	11.90	12.52	11.36 ± 1.00	
ABS	10.43	12.02	10.03	-	8.11	10.15 ± 1.61	
Polyaryl sulfone	7.02	7.16	6.23	6.75	6.89	6.81 ± .36	
Polyether sulfone, 1	7.62	7.06	6.91	7.46	6.92	7.19 ± .33	
Polyether sulfone, 2	10.42	-	-	-	10.13		
Polyphenyl sulfone	9.45	10.06	9.83	10.07	9.17	9.72 ± .40	
Polyphenylene sulfide	7.49	-	7.05	-	7.99	7.51 ± .47	

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TABLE 5. - TIME BETWEEN CONVULSIONS AND DEATH AND BETWEEN INCAPACITATION AND DEATH AS A FUNCTION OF POLYMER TYPE AND HEATING RATE

Synthetic polymer	Difference, min, in time between			
	Convulsions and death		Incapacitation and death	
	Rising temp.	Fixed temp.	Rising temp.	Fixed temp.
Polyethylene, 1	2.84	3.10	5.92	8.15
Polyethylene, 2	2.82	1.90	10.97	2.89
Polystyrene, 1	3.28	5.79	7.12	15.85
Polystyrene, 2	3.14	3.68	4.84	7.42
Polyethyl methacrylate	2.16	1.45	2.97	4.86
Polycarbonate	3.85	3.00	6.79	4.25
ABS	2.09	4.01	4.10	6.42
Polyaryl sulfone	.78	.12	1.22	1.35
Polyether sulfone, 1	.93	.92	1.79	2.49
Polyether sulfone, 2	-	.87	1.01	1.30
Polyphenyl sulfone	.96	1.62	2.14	2.42
Polyphenylene sulfide	.82	-.12	1.08	.58

TABLE 6. GAS CHROMATOGRAPHIC ANALYSES OF CHAMBER ATMOSPHERES AT TIME OF DEATH OF LAST SURVIVING ANIMAL.^a

Test reference	Methane, ppm	Carbon monoxide, ppm	Oxygen, percent
USF Method F			
Polyethylene, 2			
ANS-331	9,500	13,200	18.5
ANS-333	8,500	14,200	17.4
Mean	9,000 ± 707	13,700 ± 707	17.95 ± 0.78
Polystyrene, 1			
AMM-52	3,100	8,700	17.3
AMM-57	3,100	7,200	17.7
JES-87	2,100	5,200	18.2
Mean	2,767 ± 577	7,033 ± 1,756	17.73 ± 0.45
Polystyrene, 2			
JAS-13	10,500	4,500	18.7
Polymethyl methacrylate			
JAS-12	16,300	6,300	20.0
Polycarbonate			
AMM-54	11,450	11,200	19.1
AMM-55	12,380	10,200	18.7
JES-85	5,500	10,600	18.7
RMM-20	7,800	10,600	17.8
RMM-21	6,900	8,500	18.3
Mean	8,806 ± 2,972	10,220 ± 1,026	18.52 ± 0.49
ABS			
JES-88	4,100	3,600	19.5
Polyether sulfone, 1			
ANS-334	600	3,400	19.8
ANS-336	300	2,300	19.2
Mean	450 ± 212	2,850 ± 778	19.50 ± 0.42
Polyphenyl sulfone			
JAS-32	1,800	8,700	20.1
Overall mean (n = 16)			18.69 ± 0.89

^aValues given are mean ± standard deviation.

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TABLE 6. CONCLUDED

Test reference	Methane, ppm	Carbon monoxide, ppm	Oxygen, percent
USF Method B			
Polyethylene, 1			
ANS-328	7,800	9,100	16.4
ANS-330	9,300	13,400	17.0
Mean	8,550 ± 1,061	11,250 ± 3,041	16.70 ± 0.42
Polyethylene, 2			
ANS-335	8,200	16,600	17.8
ANS-337	9,600	13,500	17.2
Mean	8,900 ± 990	15,050 ± 2,192	17.50 ± 0.42
Polystyrene, 1			
ANS-329	1,000	8,600	17.4
Polycarbonate			
MTL-37	5,900	9,800	16.5
RMM-1	7,900	9,950	16.7
HJC-26	5,800	8,500	16.8
HJC-28	3,600	10,600	16.2
AMM-42	6,800	10,200	16.3
JES-72	5,300	11,000	16.5
JES-73	5,700	10,000	16.5
RMM-19	4,400	10,400	16.5
Mean	5,675 ± 1,329	10,056 ± 739	16.50 ± 0.19
Polyphenyl sulfone			
JAS-30	1,100	7,200	17.5
Overall mean (n = 13)			16.81 ± 0.50

1 Report No. NASA TM-78,458	2 Government Accession No.	3 Recipient's Catalog No.	
4 Title and Subtitle TOXICITY OF PYROLYSIS CASES FROM SYNTHETIC POLYMERS		5 Report Date	
		6 Performing Organization Code	
7 Author(s) Carlos J. Hilado,* Jeanne A. Soriano,* Kay L. Kosola,* Demetrius A. Kourtidis,+ and John A. Parker		8 Performing Organization Report No. A-7297	
		10 Work Unit No. 505-08-21	
9 Performing Organization Name and Address *University of San Francisco, San Francisco, Calif. 94117 +NASA Ames Research Center, Moffett Field, Calif. 94035		11 Contract or Grant No.	
		13 Type of Report and Period Covered Technical Memorandum	
12 Sponsoring Agency Name and Address National Aeronautics and Space Administration Washington, D. C. 20546		14 Sponsoring Agency Code	
		15 Supplementary Notes	
16 Abstract			
<p>The toxicity of the pyrolysis gases from some synthetic polymers was investigated, using the screening test method developed at the University of San Francisco. The synthetic polymers were polyethylene, polystyrene, poly-methyl methacrylate, polycarbonate, ABS, polyaryl sulfone, polyether sulfone polyphenyl sulfone, and polyphenylene sulfide.</p> <p>Changing from a rising temperature program (40° C/min) to a fixed temperature program (immediate exposure to 800° C) resulted in shorter times to animal responses. This effect is attributed in part to more rapid generation of toxicants.</p> <p>The toxicants from the sulfur-containing polymers appeared to act more rapidly than the toxicants from the other polymers. It is not known whether this effect is due primarily to differences in concentration or in the nature of the toxicants. The carbon monoxide concentrations found do not account for the results observed with the sulfur-containing polymers.</p> <p>Polyphenyl sulfone appears to exhibit the least toxicity among the sulfur-containing polymers evaluated under these test conditions.</p>			
17 Key Words (Suggested by Author(s)) Toxicity of polymers Fire - resistant polymers Pyrolysis		18 Distribution Statement Unlimited	
		STAR Category - 23	
19 Security Class. (of this report) Unclassified	20 Security Class. (of this page) Unclassified	21 No. of Pages 25	22 Price \$3.00