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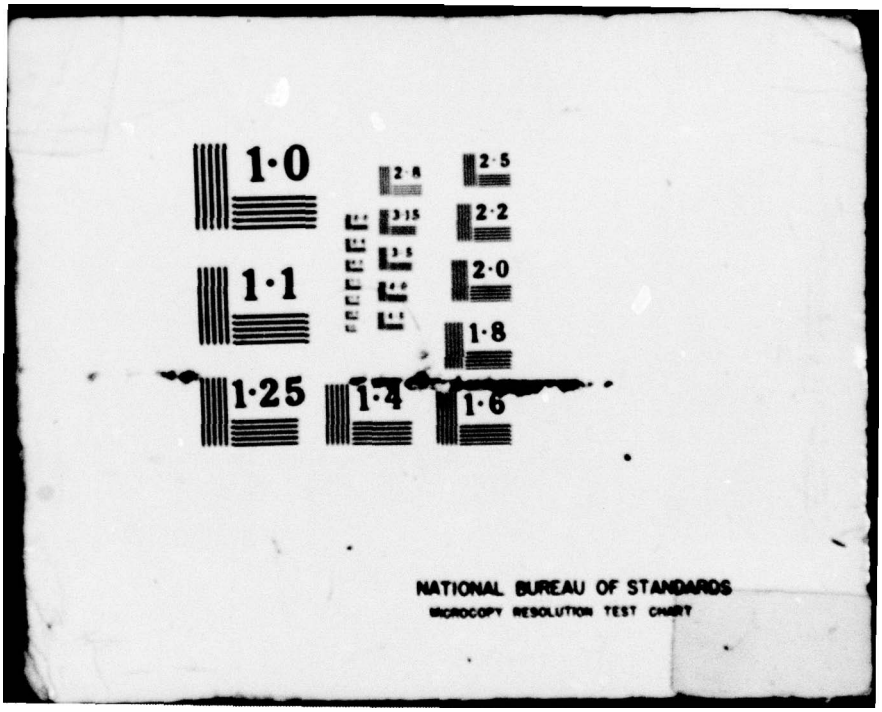
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"TOXICITY OF THE DEGRADATION PRODUCTS FROM POLYPHOSPHAZENE COPOLYMERS"*

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Part IV Submitted to

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December, 1979

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Polyphosphazene copolymers have been degraded under dynamic air flow up to temperatures of 700°C at a heating rate of 35° per minute. A few experiments were also conducted up to 1000°C. Animal inhalation screening tests with mice (Swiss Webster) were made under these test conditions. An air flow rate of 20 ℓ/min was employed in the toxicological studies where the temperature in the animal chamber was always held below 45°C, a condition which did not adversely affect the animals under test. Simultaneously,

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The results clearly show that there is not a significant correlation between CO-evolved and the induced toxicity in these animals. A similar conclusion follows for the evolution of HCN gas. Correlations with both these gaseous products indicates that other more lethal products may be responsible for the observed LC_{50} results. The complexity of the decomposition products has not yet been elucidated, but it has been demonstrated clearly that an animal test model properly applied can be used to screen complex polymeric systems.

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"Toxicity of the Degradation Products from Polyphosphazene Copolymers"

Part IV

by

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ABSTRACT

Polyphosphazene copolymers have been degraded under dynamic air flow up to temperatures of 700°C at a heating rate of 35° per minute. A few experiments were also conducted up to 1000°C. Animal inhalation screening tests with mice (Swiss Webster) were made under these test conditions. An air flow rate of 20 ℓ/min was employed in the toxicological studies where the temperature in the animal chamber was always held below 45°C, a condition which did not adversely affect the animals under test. Simultaneously, thermogravimetric measurements were made on decomposing polyphosphazenes in order to assess the rate of sample decomposition at different temperatures. Quantitative analytical measurements of the evolution of HCN and CO gases from the polymers (some without fillers) were made under identical thermal and environmental conditions.

The results clearly show that there is not a significant correlation between CO-evolved and the induced toxicity in these animals. A similar conclusion follows for the evolution of HCN gas. Correlations with both these gaseous products indicates that other more lethal products must be responsible for the observed LC_{50} results. The complexity of the decomposition products has not yet been elucidated, but it has been demonstrated clearly that an animal test model properly applied can be used to screen complex polymeric systems.

Descriptors: Polyphosphazene copolymers, toxicity (animal) studies, quantitative HCN and Co gas analysis, thermogravimetric analysis fillers.

INTRODUCTION

Of the many thousands of fire-related fatalities occurring annually in this country, asphyxiation due to oxygen depletion and inhalation of toxic gases evolved during the burning process, is believed to be the major cause rather than direct burns. The increased use of man-made polymeric materials in construction, home furnishings, and clothing coupled with their potential fire hazard have caused a great deal of concern among the public. Many conventional synthetic organic polymers either lack thermal stability, like polyethylene, or give rise to toxic fumes on thermal decomposition as found, for example, in polyvinyl chloride and polytetrafluroethylene. The toxicity of the degradation products of many of these polymeric materials has been examined.[1-9]

The lack of thermal stability and potential fire hazard of many common organic polymers have motivated the synthesis of inorganic polymers containing silicon, nitrogen and/or phosphorus in the chain backbone instead of carbon atoms.[10, 11] Technical developments have made these inorganic polymers qualitatively compatible with conventional organic polymers in many applications. Relatively lower combustion toxicity and higher thermal stability have been reported for these newer materials.[12, 13]

The overall combustion toxicity of polyphosphazenes has been studied by exposing mice to the gaseous combustion products of polyphosphazenes.[13] The LC_{50} and relative toxicity of these polymers as compared to Douglas fir have been determined. In these experiments, the two highly toxic gases, namely HCN and CO have been detected amongst the decomposition

products of polyphosphazenes. The physiological effects of these two gases are mentioned briefly. For instance, carbon monoxide is readily absorbed by the red blood cells and is more firmly bound by the hemoglobin than is oxygen. For this reason. the body suffers reduced oxygen supply and the brain and nerve tissues are quickly damaged whenever CO is present in the air at abnormally high levels. HCN is known to be a very potent poisonous compound which can combine with oxidation enzymes and cuases death in a short period of time even when it is present at very low concentrations. By way of summary of literature data, LC_{50} values for HCN and CO are presented in Table 1. With the exception of two result, the data cited concerns rats.

In contrast to what one might have expected, it has been established that there is no synergistic effects when HCN and CO are combined. Lynch[17], who has exposed rats to HCN and CO separately as well as in combination at various concentrations, has concluded that the toxicities of these two gases appear to be purely additive. The toxicity of gases such as HF, HCl, NO_2, and HCN,with or without CO, have also been studied by Higgins, et al.[18] These workers reported that CO when present in combination at levels are not hazardous to life, do not enhance the toxic response of any of the four substances just mentioned. Furthermore, the LC_{50} values for CO combined with any of the four gases just mentioned are only slightly lower than the LC_{50} values of the pure compound, again indicating an important result that no synergistic effect exists between HCN and CO.

MATERIALS AND METHODS

Polyphosphazene samples studied in this investigation are listed in Table II. Their respective chemical structures and filler content(s) are also given.

1. Determination of LC_{50}

Detailed descriptions of apparatus and experimental conditions used for screening polyphosphazenes are to be found in previous publications.[13] Briefly, four mice were exposed simultaneously to the thermal decomposition products of polyphosphazenes under dynamic heating conditions in air in a box-type furnace. The heating rate was maintained at 35°C/min. throughout the exposure. The maximum temperature reached was 700°C. The animal exposure period was 20 minutes. It was initiated when the furnace temperature reached 100°C and was terminated at 700°C. A constant air flow of 20 liters per minute through the exposure chamber was maintained by an exhaust pump. The air flow was composed of 9 liters of cooling air form an ice bath to keep the temperature inside the exposure chamber below 45°C. By varying the polymer sample load, a dose-response (mortality) curve was obtained. Six to ten experiments (with four animals in each instance) were generally required to construct a satisfactory dose-response curve. The sample loading where 50-percent mortality occurred was interpolated from the dose-response curve and was defined as LC_{50}, based upon original weight. An equation was fitted to the data points for each polyphosphazene by least square statistics.

2. Measurement of HCN and CO

Polyphosphazene materials were decomposed thermally following the procedure used previously for obtaining the dose-response curves for mice. In order to obtain meaningful and consistent comparisons between materials, sample loadings corresponding to 50 percent mortality levels were used.

Carbon monoxide was measured quantitatively by a portable CO analyzer from Energetic Science, Inc. HCN concentrations are determined by gas chromatography (GC). Successful resolution of HCN by GC and the reliability of GC analysis of HCN have been well documented.[19,20] A special nitrogen-phosphorous flame ionization detector (N-P FID) was employed in this study. This type of FID is a very sensitive and selective means for measuring nitrogen and phosphorous containing organic substances, and thus it enhances the accuracy of HCN determinations. Twelve gas samples collected from the exposure chamber at different temperatures for each material were analysed for HCN using a Hewlett-Packard 5730A gas chromatograph equipped with an N-P FID.A six-foot Porapak N glass column was used and the column oven temperature was maintained at 150°C. Helium carrier gas at a flow rate of 40 cc/min. was applied. The sampling frequency was based upon the decomposition rate of the polymer under investigation from the thermal gravimetric analysis (TGA) for every polyphosphazene studied.

Since CO concentrations were continuously monitored throughout the exposure period, the total amount of CO as well as the maximum CO concentration and duration of CO concentration above a critical level was obtained from the curve. Curves of HCN concentrations vs. temperature

or time were constructed from GC analysis results to provide the same type of information as in the CO determinations. It is believed that HCN curves so obtained by GC analysis closely resemble a continuous curve because a very dense sampling frequency (about one sample every minute) was used. The results therefore provide quantitative, meaningful information about the degradation products of our polyphosphazenes.

RESULTS AND DISCUSSION

Typical TGA curves for a polyfluorophosphazene (PNF) film, a polyarylozyphosphazene (APN) gum, and an APN foam along with the measured concentrations of HCN and CO generated during thermal decomposition in air are shown in Figures 1, 2, and 3, respectively.

The toxicity effect of smoke and gaseous products is naturally related to the quantity of these ingredients evolved during the sampling period. In particular, the total amount of HCN and CO measured during the animal exposure (20-minute period), corresponding LC_{50} values together with relative toxicity, maximum concentration and percent yield of these two gases are all presented in Tables III and IV for comparison among and between the polymers studied. Note that LC_{50} and relative toxicity values are based upon original sample loadings which are used as a basis for sample comparisons in our screening studies. However, values derived from the actual amount of polymer in each sample are also provided in Tables II and IV for the sake of completeness or for use by the interested reader. For assessing relative toxicity, we have always used actual sample loadings bearing in mind that because of the influence of additives, such as fire

retardants, stabilizers, and plasticizers, the chemistry of burning and the toxicity of a given polymer with or without filler may differ significantly.

1. Correlation Between Relative Toxicity and Total HCN and CO Concentrations

This correlation was attempted to test if the 50-percent mortality rate, caused by the degradation products of the more toxic polyphosphazenes, was due to either the high HCN or CO concentrations found in these samples. In Tables III and IV, samples are listed in order of decreasing toxicity. These results clearly demonstrate that there is not a significant relationship between CO or HCN concentrations and induced toxicity, which is a significant finding. Note, too, that the LC_{50} values are different for each sample. This comparison based upon sample loading is justified because the purpose of the current study was to compare the materials as they exist at a weight level where 50 percent of mortality was induced in mice. From Tables III and IV, it is shown that a significantly smaller amount of HCN and CO is found for the most toxic polyphosphazenes (namely, samples A and B of Table II, et seq.). At first sight, this result is unexpected.

2. Is HCN or CO the Cause of Death?

Our results indicate that in general only a small amount of HCN is detected at temperatures below 400°C (Figures 1, 2, and 3). The peak concentration of HCN, which is usually of short duration, is attained about 550-600°C, after which it rapidly drops off beyond 600°C. The maximum HCN concentration found for each sample and the period where the HCN concentration exceeds 200 ppm can be found in Table III. Comparing

values with the literature results in Table I, where it takes a five-minute exposure for mice (30-35g) at a 323-ppm HCN level in order to induce the 50-percent mortality, it is concluded that none of the polyphosphazenes tested have an HCN concentration sufficient in itself to cause death.

In Figures 1, 2, and 3 which contain typical results, there is also a general pattern of CO evolution from the polyphosphazenes tested. As in the case of HCN, a negligible amount of CO is evolved below 400°C. Clearly, the concentration of CO reaches a maximum value in the vicinity of the autoignition temperature of each polymer and afterwards diminishes rapidly. The exposure periods for mice that are subjected to CO concentrations above 2000 ppm are listed in Table IV. The longest period during which the concentration is above 2000 ppm is five minutes. Comparing these results (Table IV) with LC_{50} values reported for CO using Swiss Albino mice in Table I which cites 3750 ppm for a 30-minute exposure, our conclusion is that the CO concentration monitored during the exposure period for any of the polyphosphazene samples tested is considerably less than what is required to cause fatalities in mice. The maximum CO level found for sample D is about 9750 ppm. Although this concentration prevails for less than one minute, the actual CO received by the animals in the vicinity of this peak, corresponds to about 6000 ppm over a 3 minute interval. Such a CO level may be lethal.

Since no synergistic effects are found for HCN and CO gases in combinations and because the potency ratio[17] of HCN:CO = 45.5:1, these gases can be treated as an additive mixture of these components, as if only one gas were present. The effect of HCN and CO from the polyphosphazenes tested in this investigation would only account for about half the toxicity required to reach the LC_{50} level for the last four

polyphosphazenes that we have classified as "toxic of wood" in Table III. An even smaller contribution for the first three materials is noted for those placed in the category "more toxic than wood" polyphosphazenes. These results clearly indicate that for the polyphosphazenes studied other toxic substances must exist in the products of degradation. This is particularly true for the "more toxic" polymers. Since all the "more toxic" polyphosphazenes contain either chlorine or fluorine, it is suspected that a halogenated compound may be responsible for the enhanced toxicity of these polymers. Whether or not this is true or whether other phosphorous or nitrogen containing substances together with HCN and CO gases are responsible for the observed mortality rates will be answered only after more extensive chemical analysis of the combustion products of polyphosphazenes are completed in our laboratories using GC/MS methods.

3. Comparison of Total HCN and CO Values Amongst the Polyphosphazenes

Tukey's Honest Significance Difference (HSD) test[21] has been applied to the HCN and CO measurements (corresponding to LC_{50} levels). Results are listed in Tables V and VI along with calculated HSD values based upon one-percent type-I error (see Appendix I for details). Comparisons of the total HCN concentration (Table V) detected at LC_{50} level for all polyphosphazenes examined indicate that the differences which exist among the first four samples of Table III are not significant. However, the total amounts of HCN for the last three samples of this Table seem to be quite different from that in the first four specimens. Comparison of the total CO content, among all possible pairs of means, places the polyphosphazenes into the following four groups:

Group 1: Samples 210877 and 210878, which are polyfluroalkyloxy-phosphazenes

Group 2: Aryloxpolyphosphazene with chlorine attached, i.e., poly(phenoxy-2,4, -dichlorophenoxy) phosphazene

Group 3: Aryloxypolyphosphazene with bulky side group, poly(phenoyx-2-naphthoxy) phosphazene

Group 4: Arloxypolyphosphazenes containing fillers, Navy sample and samples 208896 and 208898

The difference for total CO concentrations detected at an LC_{50} level is significant among these four groups. Where there is more than one sample in a group, the difference among samples within the group is statistically insignificant (e.g., Group 1 and Group 4).

The HSD tests on the total HCN and CO concentrations found during thermal degradation of polyphosphazenes reveal that additives as well as side groups must play an important role in determining the overall toxicity of these samples. How these factors affect the decomposition of polyphosphazene and to what extent they influence the toxicity is only partially understood. Only when a comprehensive analysis of the combustion products and mechanism of degradation of polyphosphazenes are made as a function of temperature in isothermal and nonisothermal studies will the details of the chemistry of degradation be elucidated.

However, the animal test carried out so far has provided a relatively rapod technique for screening these polyphosphazenes without the recourse to the complexities of degradation kinetics, which have not yet been fully understood for these polymers.

CONCLUSIONS

1. High toxicity is not necessarily correlated with high HCN or CO content for the polyphosphazenes studied.

2. Total HCN and CO concentrations measured during exposure period of 20 minutes (except perhaps for sample D) are not sufficient to cause death in the animals tested. Other toxic substances must be present in the decomposition products. When these are combined with HCN and CO in sufficient amounts, they produce lethal results. This is especially true for the halogenated polyphosphazenes, which are more toxic than the others.

3. Screening of the toxicity of decomposition products of polyphosphazenes using an animal test model have once again provided useful results for complex polyphosphazene systems (with and without fillers). More detailed studies of the products of degradation by GC/MS are needed to fully comprehend the problems.

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FIGURE LEGENDS

Figure 1 -- Typical curves showing the weight loss-temperature relationship for Sample A, number 210877 film, which is predominately $-OCH_2CF_3$ with other fluoralkoy side groups. Filler 30 phr silica; concentrations of HCN and CO evolved as a function of temperature up to 700°C; heating rate 35° min^{-1}. LC_{50} sample size used (see Table III).

Figure 2 -- Typical weight loss-temperature curves for polyphosphazene foam, Sample G, number 208896. Copolymer with phenoxy and ethyphenoxy substituents. Filler level 192 phr of of Al_2O_3, $3H_2O$, and $Mg(OH)_2$ in the ratio 3:1. HCN and CO concentrations evolved as a function of temperature up to 700°C at 35° min^{-1} heating rate. LC_{50} sample size used (see Table III)

Figure 3 -- Typical weight loss-temperature curves for polyphosphazene copolymer foam, Sample D, with phenoxy and 2-naphthoxy side groups. HCN and CO concentrations evolved as a function of temperature up to 700°C at a heating rate of 35°C min^{-1}. LC_{50} sample size used (see Table III).

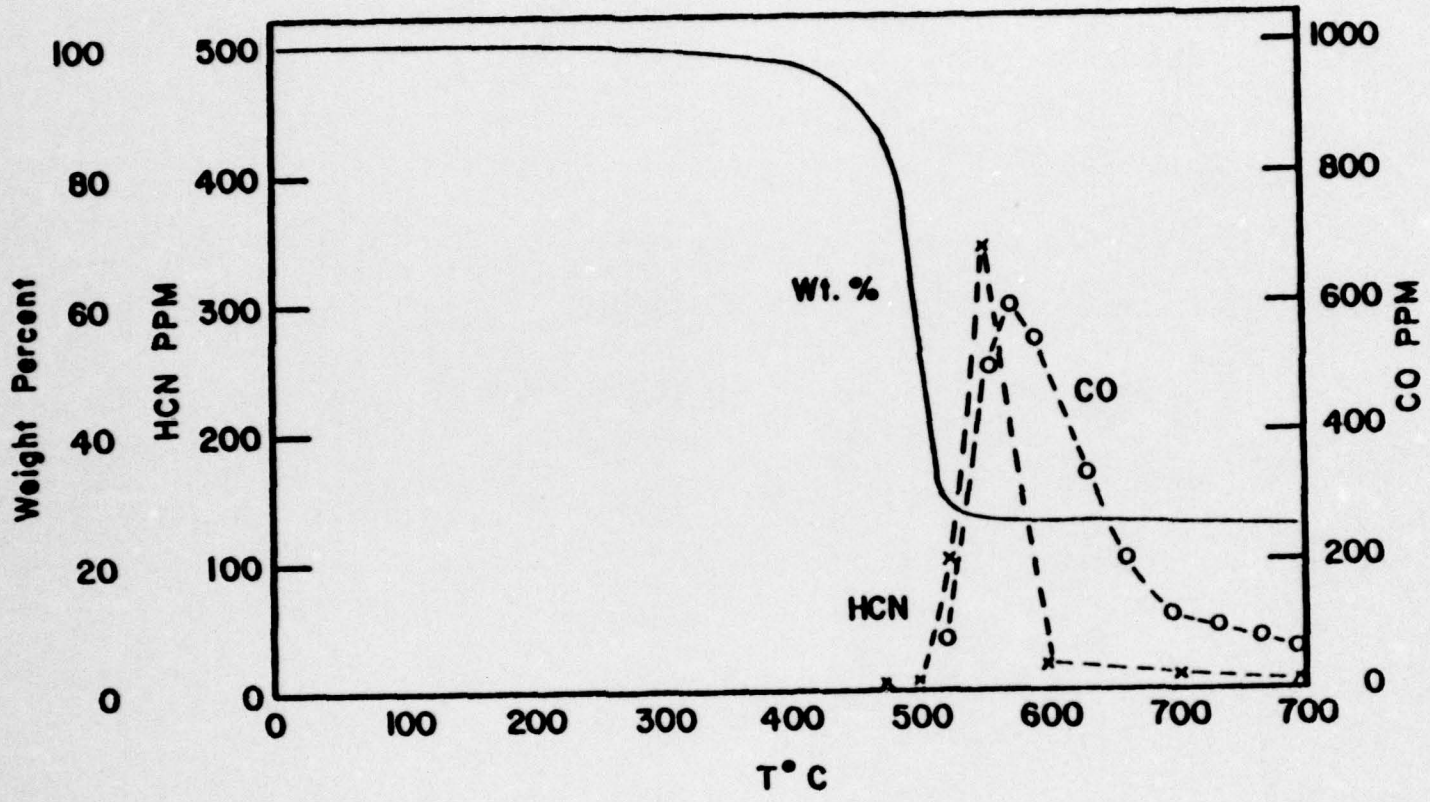

Figure 1 Typical curves showing the weight-loss - temperature relationship for Sample #210877 film which is predominately $-OCH_2CF_3$ with other fluoroalkoxy side groups. Filler 30 phr silica.[3] Concentrations of HCN and CO evolved as a function of temperature up to 700°C; heating rate 35° min^{-1}.

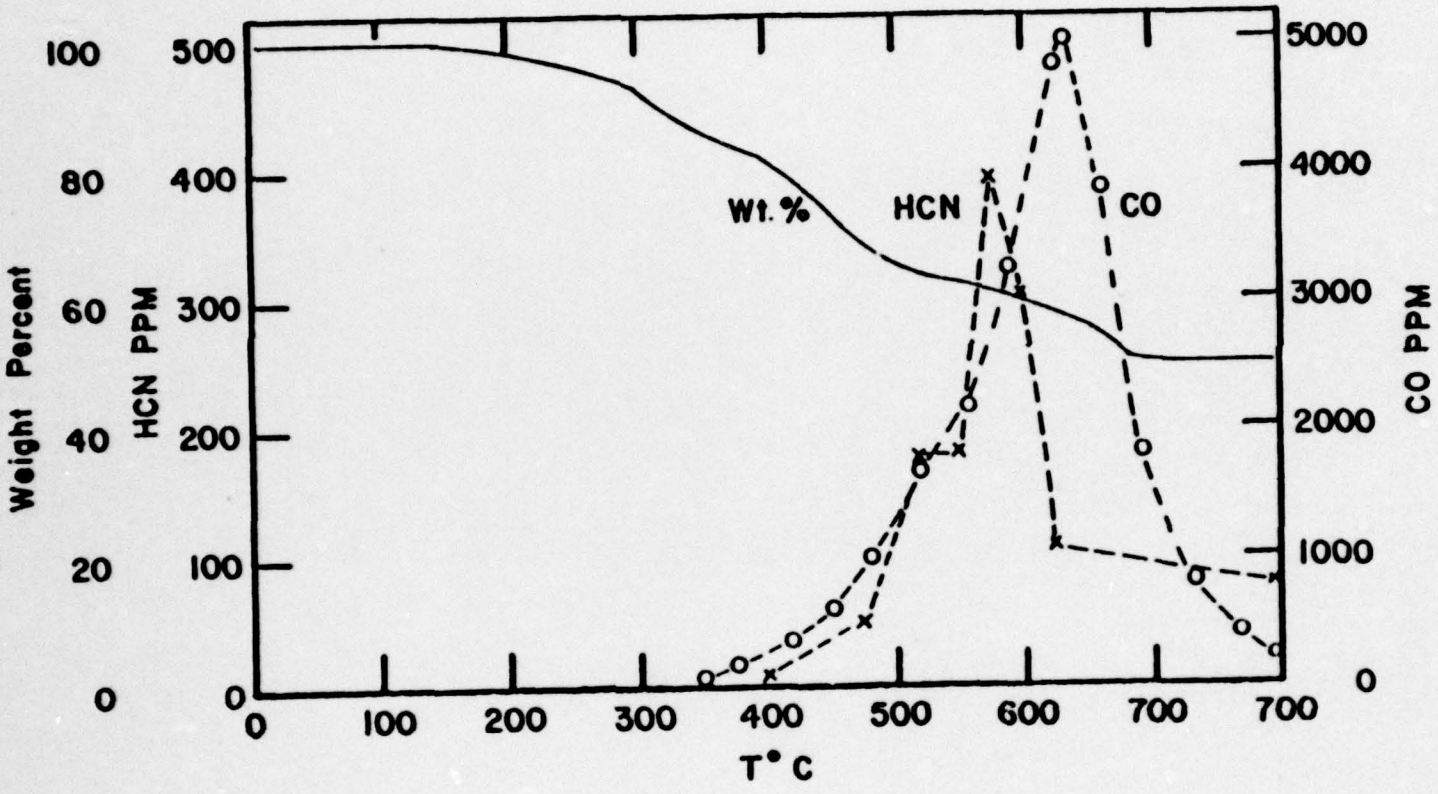

Figure 2 Typical weight loss-temperature curves for polyphosphazene foam, sample #208896. Copolymer with phenoxy-and ethylphenoxy-substituents. Filler level 192 phr of Al_2O_3, $3H_2O$ and $Mg(OH)_2$ in the ratio 3:1. HCN and CO concentrations evolved as a function of temperature up to 700°C at 35° min^{-1} heating rate.

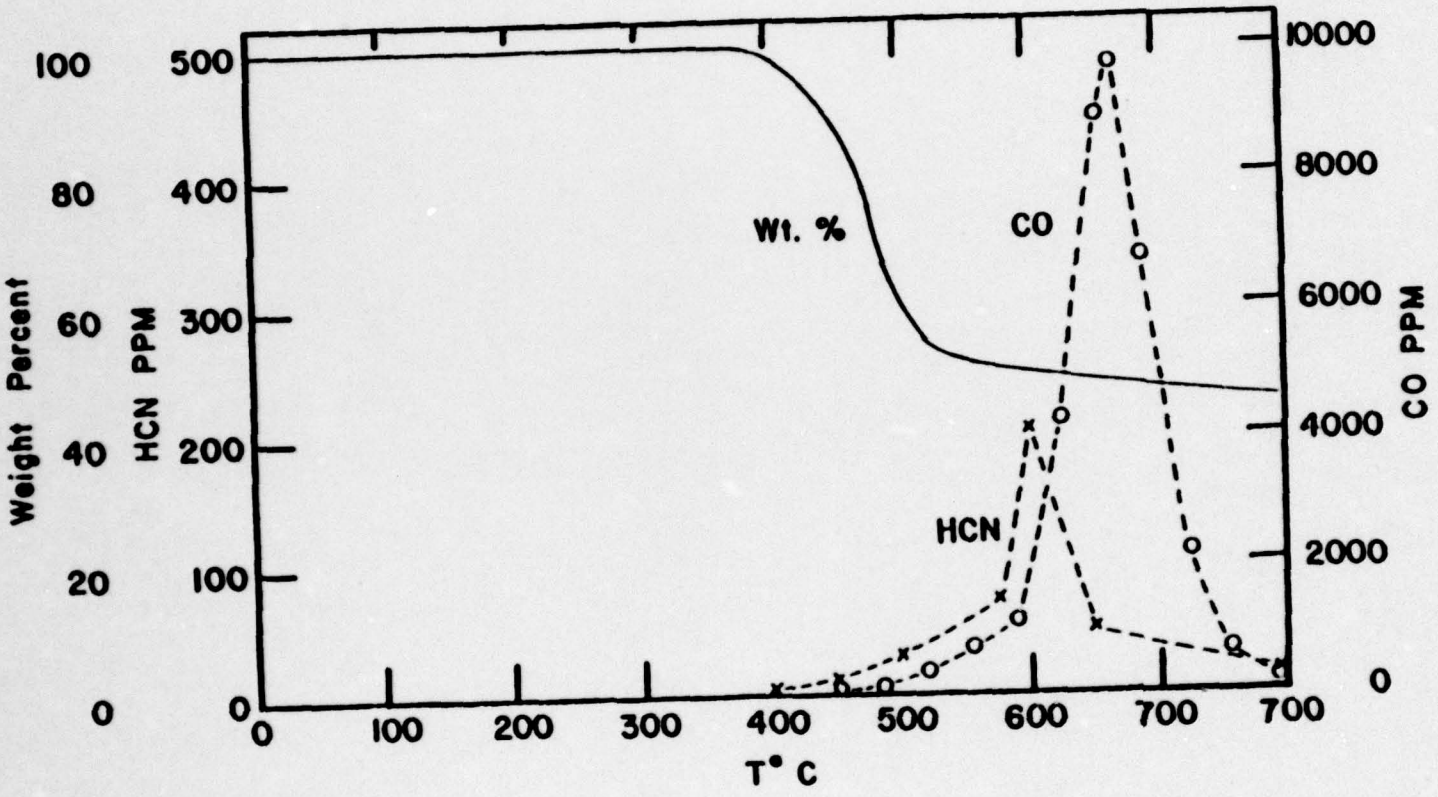

Figure 3 Typical weight loss - temperature curves for polyphosphazene copolymer foam with phenoxy and 2-naphthoxy - side groups HCN and CO concentrations evolved as a function of temperature up to 700°C at a heating rate of 35°C min^{-1}.

Table 1. LC_{50} Values of HCN and CO

Gas	Species	Concentration ppm	Exposure Time Min.	Reference
HCN	rats	480	5	14
	rats	200	30	15
	rats	142	30	15
	rats	100	30	17
	mice	323	5	18
CO	rats	4800	30	17
	rats	5500	30	15
	mice	3570	30	16
	rats	14200	5	14
	rats	8800	10	15

TABLE II Details of polyphosphazene samples used in this study

	Sample	Type	Side Groups	Filler
A	210877	film	$-OCH_2CF_3$ with other fluoroalkyoxy groups	30 phr silica
B	210878	film	Same as A	30 phr carbon black
C	phenoxy-2,4-dichloro	gum	R_1 = phenoxy R^1 = 2,4,-dichlorophenoxy	none
D	phenoxy-2-naphthoxy	gum	R = phenoxy R^1 = 2-naphthoxy	none
E	Navy	foam	R = phenoxy R^1 = ethylphenoxy	unknown
F	208898	foam	same as E	144 phr of 1:1 $Al_2O_3 \cdot 3H_2O$ and $Mg(OH)_2$
G	208896	foam	Same as E	192 phr of 3:1 $Al_2O_3 \cdot 3H_2O$ and $Mg(OH)_2$

TABLE III Results of HCN determinations

Sample[a]	LC_{50}[b] (gm)	Relative Toxicity	% Polymer	Total HCN Detected (mg)	Maximum HCN (ppm)	Period for HCN>200 ppm (Min.)	% yield[d]	% yield[e]
A	2.12	18	77	12	346	1	0.554	0.719
B	2.60	15	77	4	105	0	0.138	0.180
C	10.36	3.5	100	9	196	0	0.085	0.085
D	18.23	2.0	100	10	205	0.2	0.054	0.054
E	20.85	2.0	---	46	345	3	0.221	-----
F	24.57	1.5	34	29	260	1.5	0.116	0.341
G	24.77	1.5	40	33	395	2	0.135	0.338

a. See Table I for sample descriptions

b. Based upon original weight

c. Relative to LC_{50} of Douglas fir (37. gm)

d. Based upon total sample bonding, i.e. LC_{50} values

e. Based upon actual polymer in sample

TABLE IV Results of CO determinations

Sample[a]	LC_{50}[b] (gm)	Relative Toxicity[c]	% Polymer	Total CO Detected (mg)	Maximum CO (ppm)	Duration of CO>2000 ppm (min.)	% yield[d]	% yield[e]
A	2.12	18	77	46	600	0	2.17	2.82
B	2.60	15	77	80	700	0	3.06	4.10
C	10.60	3.5	100	256	3750	3.5	2.50	2.50
D	18.23	2.0	100	576	9750	4	3.16	3.16
E	20.85	2.0	---	439	2950	3.5	2.11	----
F	24.57	1.5	34	420	4450	4	1.71	5.03
G	24.77	1.5	40	478	5090	4	1.93	4.82

*See Table III for footnote descriptions.

TABLE V Pairwise comparison of HCN means. HSD = 16.68

Sample[a]	A	B	C	D	E	F	G
A(12)[b]	-	8	3	2	34*	17*	21*
B(4)[b]		-	5	6	42*	25*	29*
C(9)[b]			-	1	37*	20*	24*
D(10)[b]				-	36*	19*	23*
E(46)[b]					--	17*	18*
F(29)[b]						--	4
G(33)[b]							--

[a] Sample descriptions given in Table I.

[b] Total HCN detected in mg.

* Indicates differences is statistically significant, i.e. >16.68

TABLE VI Pairwise comparison of total CO at LC_{50} levels.
HSD = 108.01; 1% type I error

Sample[a]	A	B	C	D	E	F	G
A(46)[b]	-	34**	210	530	393	374	432
B(80)		--	176	496	359	340	398
C(256)			---	320	183	164	118
D(576)				---	137	156	98**
E(439)					---	19**	39**
F(420)						---	58**
G(478)							---

[a]Sample descriptions given in Table I.

[b]Total CO in mg.

** Difference statistically insignificant, i.e. <108.01.

Appendix 1

In the Tukey procedure we first of all carried out an F-test based upon the hypothesis that $\bar{x}_j - \bar{x}. = 0$, where the subscript j refers to the number of samples studied. In our case $\bar{x}_j$ represents the average HCN or CO concentration based upon duplicate results for a particular sample, and $\bar{x}.$ is the grand average of the HCN or the CO concentration for all the results being tested.

The statistics of the F-test are listed below. The analysis clearly rejects the hypothesis of $\bar{x}_j - \bar{x}. = 0$, thus indicating that a significant difference exists among the HCN or CO concentrations.

	Source	SS[a]	df[b]	MS[c]	F[d]
HCN	Between (among) samples (BS)	2937	7 - 1 = 6	489.5	51.91*
	Within samples (WS)	66	14 - 7 = 7	9.43	
	Total	2997	14 - 1 = 13		
CO	Source				
	Between (among) (BS) samples	502002	7 - 1 = 6	83667	211.58*
	Within samples (WS)	2768	14 - 7 = 7	395.43	
	Total	504770	14 - 1 = 13		

*Significant at 1% type 1 error ($\alpha = 1\%$). Type I error is defined as the error that occurs when the experimenter rejects the hypothesis when it is true.

[a] Sum of squares

[b] Degree of freedom

[c] Mean of sum of squares

[d] $F = [MS_{BS}] / [MS_{WS}]$

Tukey's test was used to make all pairwise comparisons of samples and to locate the source of the difference in the F test. Tukey's formula

$$HSD = q_{\alpha v} \sqrt{\frac{SS_{WS}/df._{WS}}{n}}$$

where in our study

$n = 2$ (duplicate experiments)

$q_{.01,7} = 7.68$ (from Tukey's table)

$SS_{WS} = 66$ and 2768 for HCN and CO respectively

$df.WS = 7$ for both HCN and CO

Based on this formula, the calculated HSD's for HCN and CO are 16.68 and 108.01 respectively. If the absolute difference of HCN or CO concentrations between any two samples is greater than the corresponding HSD value, then the difference is said to be statistically significant. Results of the HSD tests are found in Table V and VI.