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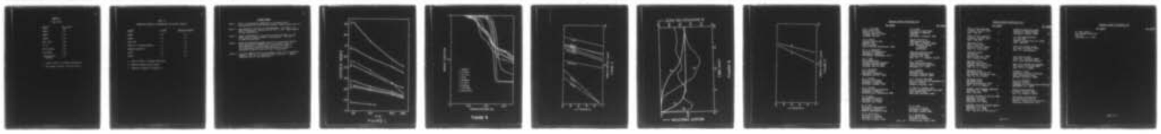

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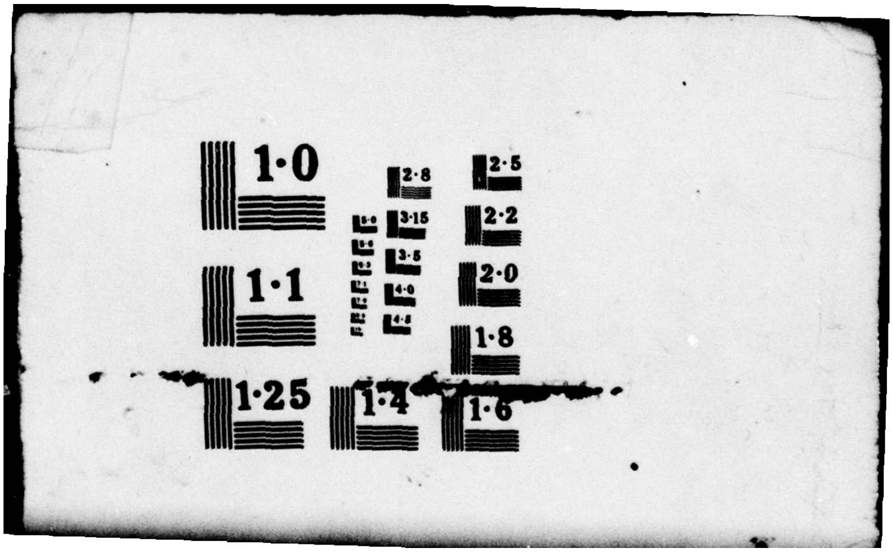
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"TOXICITY AND THERMAL PROPERTIES OF POLYPHOSPHAZENES"*

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Flammability and toxicity of various polyphosphazenes/with and without fillers/have been measured. The performance characteristics of these polymers are compared with other more conventional plastics of commercial interest. Other small scale tests such as limiting oxygen index, at different heat fluxes, have been used as indicators of flammability. Under ambient conditions, polyphosphazenes require a higher oxygen concentration to burn than air alone can supply. LOI values always decrease as heat flux or ambient temperature is raised. Fillers also influence LOI measurements. Foam samples burn more

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$\mathrm{RD}_{(50)}$ and $\mathrm{LC}_{(50)}$ values were obtained by exposing animals (mice) to a gaseous stream of polyphosphazene decompositions products. Dose response curves were obtained. The respiratory response of mice is directly correlatable with the rate of polymer decomposition. The toxicity of a particular polyphosphazene depends strongly upon the type of the side groups on the phosphorus. There is no direct correlation between toxicity hazard and CO concentration in these polymers. Halogen side groups give rise to the most toxic products. The toxicity hazard of a polyphosphazene under programmed linear heating versus isothermal heating (below ignition) have been compared.

Based upon an overall hazard rating involving thermal stability, flammability and toxicity parameters, halogen free polyphosphazenes are favored over halogen containing polymers for high temperature applications.

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TOXICITY AND THERMAL PROPERTIES OF POLYPHOSPHAZENES

ABSTRACT

Flammability and toxicity of various polyphosphazenes/with and without fillers/have been measured. The performance characteristics of these polymers are compared with other more conventional plastics of commercial interest. Other small scale tests such as limiting oxygen index, at different heat fluxes, have been used as indicators of flammability. Under ambient conditions, polyphosphazenes require a higher oxygen concentration to burn than air alone can supply. LOI values always decrease as heat flux or ambient temperature is raised. Fillers also influence LOI measurements. Foam samples burn more readily than films of the same chemical constitutions.

$RD_{50}$and LC_{50} values were obtained by exposing animals (mice) to a gaseous stream of polyphosphazene decomposition products. Dose response curves were obtained. The respiratory response of mice is directly correlatable with the rate of polymer decomposition. The toxicity of a particular polyphosphazene depends strongly upon the type of the side groups on the phosphorus. There is no direct correlation between toxicity hazard and CO concentration in these polymers. Halogen side groups give rise to the most toxic products. The toxicity hazard of a polyphosphazene under programmed linear heating versus isothermal heating (below ignition) have been compared.

Based upon an overall hazard rating involving thermal stability, flammability and toxicity parameters, halogen free polyphosphazenes are favored over halogen containing polymers for high temperature applications.

Descriptors: Toxic hazard, Flammability, Oxygen Index; effect of heat flux (temperature), Isothermal vs. non-isothermal testing.

INTRODUCTION

The increased use of synthetic polymers and their fire hazard potential in applications has caused considerable concern in recent years. Once ignited plastics frequently burn at a rate dependent upon their chemistry and applied heat flux commensurate with a specific situation. Sometimes dense smoke is generated (especially for aromatic systems), but corrosive and toxic combustion products also limit the applicability of many synthetic plastics. Chemical modifications such as halogenation[1,2] have focused on improving fire retardency and reducing flammability often without regard for the toxicity induced. Additives have also been used[3-7] to help suppress ignition, smoke generation and retard burn velocity. While these modifications have proved to be effective for improving fire resistance, they are often responsible for the generation of highly toxic combustion or thermal pyrolysis products. Sometimes they even give rise to increased toxic and corrosive gases such as carbon monoxide and halogenated volatiles.

It should be recognized always that a comprehensive and useful evaluation of the fire hazard of any material must include smoke generation, toxic and corrosive gas production and flammability characteristics.[8,9] The material geometry and the orientation of the polymer during testing often influences such properties as the flame spread velocity, oxygen index level. Again, the specific applications often place demands on material texture[10] depending upon whether the specimen has a foam or film morphology. End-use demands may require that consideration be given to material flexibility, sealability, fire resistance, toxicity or other important parameters associated with product usage. All of these variables should be tested for in the evaluation of the sample performance.

The need for new economically viable polymers with improved thermal stability and low smoke and toxicity and good flame resistance has spurred chemists[11,12] and industrialists [13-15] alike to focus upon inorganic synthetic polymers to fulfill some of these roles. A number of noteworthy developments have been made in polyphosphazene synthesis, [16,17] particularly by Allcock and co-workers. Much of this work has been reviewed [13-16] recently. Some of the behaviorial characteristics of polyphosphazenes with engineering applications have appeared in recent publications.[12,14,18-20] For some time it has been thought that the phosphorous-nitrogen combination in the polymer chain backbone[19] provides innate fire retardant characteristics since phosphorus containing compounds have been widely employed as additives in imparting fire resistance to several commercial plastics. In Japan and in Europe, polyphosphazenes have been blended with other polymers to improve fire resistance. Recently a patent to use polyphosphazenes as a fire retardant has been granted in the United States.*

Some aspects of the fire hazard rating (flame and smoke properties) of polyphosphazenes have been examined within the past few years.[14-15] Parameters such as oxygen index, smoke generation and heat release characteristics have been determined for different kinds of homo and repolymeric speciments. In these evaluations it has been demonstrated that polyphosphazenes rank very favorably with other synthetic materials in regard to these test parameters. They do show potential value in industrial, domestic and military applications where a wide range of physical and mechanical properties are required. Despite their economic disadvantage at this point in time, they appear to be gaining in stature as competitive plastics because of their favorable properties for thermal insulation, comfort cushioning cable jacketing, metal and wire covering, biomedical applications and so on.

At the present time, the complexities and expense of large scale testing

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*U. S. Patent 4,042,561 to Celanese Corp.

present one of the major stumbling blocks in the evaluation polymers with potential. Work on large scale shipboard,[21] aircraft and other domestic fires[22] indicate that a wide spectrum of temperature profiles and presumably toxic products exist in a fire. Changing conditions occur with "time into the burn" and highlight some of the difficulties even in simulating a "real fire". Fires are difficult to classify just as people are complex and individualistic in their traits, personalities and behavior and therefore difficult to categorize. Still, the need exists to try and characterize as scientifically and meaningfully as possible, the critical factors involved in hazardous situations. Full scale screening of materials for all eventualities is virtually impossible so that viable small scale tests must be employed. Eventually valued judgements will be required after the pertinent data have been collected.

For polyphosphazenes, we have attempted to obtain new experimental results that should assist in their fire hazard evaluation. Limiting Oxygen index determined as a function of heat flux (temperature) and toxicity monitoring under isothermal and non-isothermal conditions are reported for the first time for these polymers. The short comings* of small scale testing are well recognized, but the availability of material limits the present program. Nevertheless comparative and reproducible results have been obtained in this work to provide a better perspective on their performance. The work complements and extends the results of other workers in polyphosphazene evaluations.

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*The fire hazard testing of polymers is so complex that even the E84 Tunnel test suffers several disadvantages for screening purposes. Recent work[24] clearly points to some of the short comings in this test procedure.

EXPERIMENTAL

MATERIAL

Most of the polyphosphazene copolymer samples used in this work were kindly supplied by Firestone Tire and Rubber Company, Akron, Ohio. A few were obtained from DeSoto Company and from Dr. Widenor of Naval Research Laboratory. The polyphosphazene samples tested are listed in Table 1. Commercially available polyethylene, polytetrafluoroethylene, and Douglas fir were used for comparisons of material performance with these polyphosphazenes.

METHODS

Oxygen Index: Limiting oxygen index values (L.O.I.) were obtained according to the procedure[25] specified in ASTM D2863-74, on "Flammability of Plastics Using the Oxygen Index Method." Film samples were tested as received. Foam samples were cut into strips of 1-3 mm thickness approximately. The effect of environmental temperature (or heat flux) on the oxygen content requirement to just sustain burning were investigated by measuring L.O.I. values at 25°C, 100°C, 200°C, and 250°C, respectively. To perform this task the apparatus was enclosed by a circular heater with a window slit opening used to observe the sample during testing.

TOXICITY

Apparatus and detail of the techniques involved in the toxicity study has been reported in previous publications.[23,26,27] For each test at any temperature a minimum of four 24-28 gm male Swiss Webster mice were exposed to the products of polymer decomposition for a 20 minute period. Animal response during a 10 minute interval prior to exposure was used to provide a reference base for each test. A 20 minute post-exposure period was also used.

Two modes of polymer thermal decomposition were employed in these toxicity studies. The test exposure condition included:

(a) Gradual linear heating of the sample at 35°/min. between 100°C and 700°C. This procedure was used in order to simulate a smoldering fire situation before passing through the ignition temperature regime about 600°C.

(b) Isothermal heating here the furnace was preheated to 500°C (i.e. below the polymer ignition temperature). The exposure was started immediately after the sample was placed in the furnace. Again a 20 minute exposure was employed. This test procedure tended to simulate thermal decomposition and toxicity associated with flash pyrolysis.

Five to ten individual runs were usually required on each sample in order to construct a reliable dose-response curve. A constant air flow of 20 liters/minute was maintained through the exposure chamber by means of an exhaust pump. The flow was measured with a rotameter and was comprised of a "mix" of 9 liter/minutes from the furnace containing the decomposing polymer and 11 liters/minute of ice cooled air. This procedure prevented overheating in the animal chamber where the maximum temperature reached during exposure was below 43°C. Previous calibration work has indicated that chamber temperature of up to 45°C does not adversely effect the animal response.[28] Usually the chamber temperature increases gradually during the exposure interval reaching its maximum level for a short period towards the end of the exposure period. Equipment have already been described in detail in the literature.[26]

The carbon monoxide level in the decomposition gases was monitored using an Ecolyser detector manufactured by Energetic Science Company, since it was necessary to know if this gas played a significant role in the test.

RESULTS AND DISCUSSION

OXYGEN INDEX

Oxygen index has been widely used as an flammability indicator since its introduction by Fenimore.[30] Limiting oxygen index values (L.O.I.) ranging from 31.9 to 67.0 were recorded in this study (Table 2) for polyphosphazenes tested under ambient environments. The group of polyphosphazenes tested, all required higher oxygen concentration than air itself can provide so these polymers may be considered to be self-extinguishable materials in the conventional sense.

Foam specimens are found to be more flammable than film samples with identical chemical constitutents and filler contents. Compare for example samples C and F of Figure 1. The only difference between these two specimens is that F contains blowing agent and is fabricated in the form of a foam. The sponge-like configuration of foam sample which provide more surface area, enhances its flammability.

As the ambient temperature of the test specimen was increased, the oxygen requirement for flaming combustion decreases for polyphosphazenes. An almost linear dependence of temperature on L.O.I. is well illustrated in Figure 1 for many polymers. Similar reports have been published for other polymeric materials[30] Figure 1 indicates that generally the higher the L.O.I. value at room temperature, the steeper the reduction in the L.O.I. as the temperature is raised. A drop in L.O.I. of 45% is observed for Teflon between 25°C and 250°C. Smoother less steep reduction in slopes are observed for polyphosphazene samples which have lower initial L.O.I. values at room temperature, which polyethylene showing the lowest and shallowest slope at room temperature.

Relative stability of several polyphosphazenes have been presented by Allcock[32] according to the substituent groups present. They fall in order:

$$-CH_2CF_3 > -C_6H_5 > -C_2H_5 > -CH_3$$

Allen et al[33] claim that an aryloxy group is more stable than an alkoxy side group. TGA studies (Figure 2) of the present work indicate that polyphosphazenes with halogenated side groups when heated in air, the weight loss occurs rapidly over a narrow temperature interval leaving little char or residue. On the other hand, the aromatic structure enhances char formation and consequently this intrumescent residue naturally furnishes stability to degradation at higher temperatures compared to alkoxy-polyphosphazenes (Figure 2). Where both samples have aromatic side groups, the presence of halogen improves the stability relatively at lower temperatures, but exhibits less favorable fire resistance at higher temperatures since it leaves little residue. This was clearly shown in Figure 2 in accord with earlier results.[8] Aside from fillers there are three functional fire retardants moities in the polyphosphazene samples examined in this work. They are halogen and/or aromatic side groups and the phosphorous-nitrogen backbone. How they interact or couple functionally with one another is still a complex and an interesting subject for further study.

L.O.I. values indicate the fluoroalkoxy polyphosphazene film filled with 30 phr carbon black has a significantly higher L.O.I. (67.0) than the aryoxypolyphosphazene film (55.0) filled with 144 phr of a 3:1 mixture of aluminum trihydrate and magnesium hydroxide. On the other hand, the 30 phr silica filled fluoroalkoxyphosphazene has a lower L.O.I. (52.0) than the aryloxyphosphazene.

TGA results and L.O.I. data both suggest that halogenated side groups exhibit improved thermal stability in these inorganic polymers to temperatures as high as 350°C. Presumably this behavior is attributed to the fire-retardent effect of halogen on the pyrolysis process per se.[8,20] The observed higher thermal stability of aryloxy-substituted over the halogenated polymers under similar test conditions is consistent with the amount of residue that is formed which functions as a thermal barrier against further degradation in these materials. Whether or not the $-CH_2CF_3$ side groups is more stable than $-C_6H_5$ is still debatable. However the results of our study do show that filler contributes significantly to the thermal stability and that aryloxy groups in general provide higher thermal stability than alkoxy substituents in polyphosphazenes. It is further anticipated that directly substituted aryl or alkyl group to phosphorus will result in enhanced thermal resistance and lower toxicity performance over the alkoxy and aryloxy substituted polymers. Polyphosphazenes of this kind synthesised recently by Allcock et al[34] should when tested, establish if this is correct or not.

TOXICITY

RD_{50} results defined as the concentration level of irritant products which induces a 50% decrease in respiratory rate in mice are calculated from the respective regression equations for the concentration (dose) response curves. For the purpose of screening different polymers, it has been estimated elsewhere that an RD_{50} value in mice corresponds to a rapidly incapaciating condition in humans, with choking and a burning sensation of the eyes, nose and throat. Values for the polyphosphazene examined here are reported in Table III as a function of nominal concentration* (N.C.). From these results, it appears that the decomposition products of polyphosphazene samples have irritating properties similar to Douglas Fir. The LC_{50} values, which provide the concentration level where 50% mortality

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*Note that NC is defined here as total weight loss (mg)/total air flow during exposure (in this experiment 400 liters).

occurs in the animals exposed to the polymeric degradation products generated under the conditions specified in the experimental part of this paper, are shown in Figure 3 and Table 2.

Douglas fir is used as a standard reference material for comparing the toxicity among the different polyphosphazenes as well as for making comparisons with other polymers tested under slightly different conditions(27) (see Table II). It is clear from this table and Figure 3 that the halogenated polyphosphazenes are more hazardous than the non-halogenated variety. Those with the highest halogen content (PNF type polymers) lie to the extreme left in Figure 3 with the 2:4 dichlorophenoxy material falling at an intermediate position between PNF and the other aromatic (APN type) phosphazenes which are approaching the performance of the reference standard (Douglas fir) in their behavior. Using the classification evolved in earlier work(27), the LC_{50} rating of many of our polyphosphazene can be cited to be "as toxic as" wood. In making the comparison in Table II we have assumed that with respect to Douglas fir (D.F.), $LC_{50}(A)_X : LC_{50}(DF)_X = LC_{50}(B)_y : LC_{50}(DF)_y$ where A and B denote two different materials and X and Y two different heating rates respectively.

From another viewpoint, Anderson and Alarie(35) have developed a newer method of assessing the acute lethal hazard index (ALH)* of plastics, but this requires thermal conductivity and other data which are not presently available for the majority of the polyphosphazenes examined here. However, for those samples where complete data is available(36,37) (see Table II) the ALH rating is listed. Values for APN polyphosphazenes are superior to most other polymers assessed using this procedure. For comparison purposes, numbers for some commercial polymers are also given in this table.

$$* \ ALH = \left(\frac{K.D}{T.LC_{50}}\right) 10^{-5}$$

where K is the thermal conductivity and D is the density of the original polymer, T is the temperature (K) corresponding to 1% weight loss and LC_{50} has its usual definition.

Based upon the measured carbon monoxide concentration in the animal chamber, no direct correlation between CO concentration and toxicity can be found for different polyphosphazene materials (see Table IV). This suggests that other possible decomposition products such as phenolics, cyanide or halogen compounds may contribute significantly to the animal mortality ratings in our dynamic test procedure. The CO concentration is usually peaks at the end of the animal exposure period when the autoignition temperature is surpassed in constant heating rate experiments. The CO level is naturally affected by the air supply to the furnace and is related amongst other things, to the carbon centent in the sample. In our experimental procedure the oxygen level at 20 liters air per minute is more than adequate.

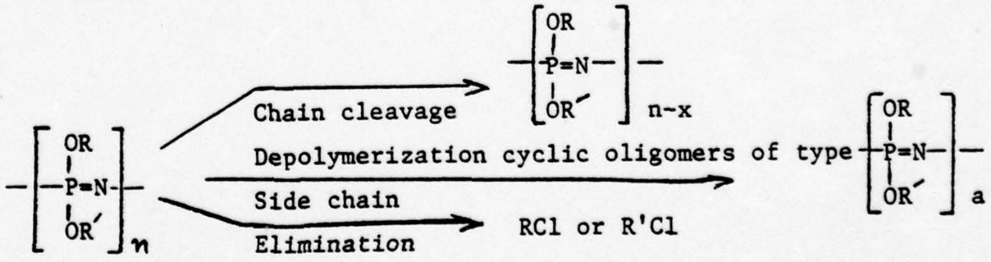
The observed differences in toxicity must depend upon the type of side group and on the mechanism of polymer degradation. In substituted polyphosphazenes, the relative order of this hazard is fluroalkoxy > aryloxy polymers. The latter materials according to a convention used by Alarie and co-workers(27) may be classified as being "as toxic as wood".

ISOTHERMAL VS. NON-ISOTHERMAL TESTING

Toxicity effects for isothermal vs. gradual heating conditions are shown in Figure 4. Animal response for identical sample starting weights for the same material are provided. As previously shown for other polymers, the animal response is very closely associated with the sample weight loss (see also Figures 4). The more rapid rate of heat release into the animal test chamber during isothermal testing still does not influence the test results adversely since the chamber temperature never reaches $45^{\circ}C$(28). In all tests, the animal respiratory response reaches a maximum depression rate within 10 to 15 minutes after the beginning of the exposure. Following this drop in respiration, a recovery trend is always evident if the animal(s) survive the test conditions. Frequently, the respiration rate of the animal does not return to the initial pretest rate within the 10 minute post exposure period. More detailed testing at longer recovery times is suggested by these experiments. Such experiments are in progress.

LC_{50} values for the same polyphosphazene sample under isothermal and non-isothermal heating modes are to be found in Figure 4. It is clear from this graph that the respiratory depression is more severe under isothermal heating conditions (500°C) than in the programmed heating process where a ceiling of 700°C is reached. Note that the polymer ignition temperatures is 600°C approximately. Presumably, the overall difference in animal response is directly attributed to the fact that the concentration of toxic products generated per unit of exposure time is greater during isothermal testing (at least for the earlier part of the exposure period). At present it is not possible to comment meaningfully on the mechanism of thermal decomposition but G.C./M.S. and other analytical procedures are being used to probe this aspect of the degradation chemistry.

Thermal degradation mechanisms of polyphosphazene that have been postulated by Allcock,[32] are illustrated below:



Note that R may not equal to R' and that "a" can be 3, 4, 5 . . .

For these inorganic polymers, the reaction mechanism is likely to more complicated at higher than it is at lower temperatures. Random rupture of primary bonds, chain fragmentation and rearrangement of polymer chain groups/ atoms plus reaction between the products of decomposition may well give rise to other toxic substances, but no clear-cut mechanism has been determined so far.

For instance, release of cyanide has been reported for polyphosphazenes.[15] Preliminary qualitative analysis performed in the present work, using a gas chromatographic apparatus (GC) equipped with a special nitrogen-phosphorus detector indicates that one of the decomposition products has the same retention time as HCN, but so far it has not been confirmed by other techniques. At this stage in the screening program, it is more important to assess the overall toxic hazard with little regard for the detailed chemistry and complexity of the degradation products. More extensive chemical analysis are being undertaken in order to determine the type and extent of decomposition products as well as how they may be modified and/or controlled.

In Table II, a general comparison of the performance of several polymeric materials assessed by their LOI, toxicity index and smoke density are listed. From the results it can be concluded that the polyphosphazenes in most cases have higher L.O.I.'s, lower smoke density and relatively lower toxicity indices when compared with many other polymers. Accordingly they compare favorably with other commercial plastics in overall behavior. From the results of Table II, it is clear that higher thermal stability in a polymer and/or low smoke density does not necessarily guarantee a lower toxicity hazard. For instance, polymers such as polytetrafluoroethylene and fluoralkoxy-polyphosphazene (in the series studied here) which possess the highest thermal stability also exhibit a higher toxicity hazard when thermally decomposed in air (teflon > fluorophosphazene). Whenever the highest thermal stability is required of a polymer in some practical applications it must always be weighted in respect to its toxiological hazard, for in these two important screening parameters a delicate balance exists and valued judgements must be made in the materials selection. Fire-proofing techniques always demand compromises to be made in the choice of plastics where optimization of various factors dependent upon the end-use of the material (in film or foam form) and the likelihood of its encountering hostile environmental conditions. So far, an acceptable protocol in regard to fire hazard rating is still moot although valued test data are being accumulated.

CONCLUSIONS

1. Polyphosphazenes with halogen-free groups generally exhibit relatively high thermal stability and comparatively low toxicity.
2. Limiting oxygen index values decrease as the ambient temperature surrounding the test sample is raised. Sample configuration filler content and type usually affect L.O.I. - an indicator of flammability.
3. There is no direct correlation between CO level and toxicity implying that degradation product(s) other than CO are important.

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TABLE LEGENDS

Table I	Description of polyphosphazene samples
Table II	Limiting oxygen index (LOI), relative toxicity and smoke density values for polyphosphazenes and other commercial samples.
Table III	RD_{50} values for polyphosphazenes and other commercial plastics. Data includes 95% confidence (test) limits.
Table IV	Relative toxicity of polyphosphazene (with respect to Douglas Fir) and CO concentration during test.

TABLE I

POLYPHOSPHAZENE SAMPLES

Sample	Type	Side Group	Filler
Naphthoxy	gum	R = phenoxy- R' = 2-naphthoxy-	none
Dichloro	gum	R = phenoxy- R' = 2,4-dichlorophenoxy	none
210877 (D)	film	CH_2CF_3 with other fluoroalkoxy groups	30 phr silica
210878 (B)	film	CH_2CF_3 with other fluoroalkoxy groups	30 phr carbon black
212728 (C)	film	R = phenoxy - R' = p-ethylphenoxy-	144 phr of 3:1 of Aluminum trihydrate and Magnesium Hydroxide
208896 (E)	foam	same as 212728	144 phr of 1:1 of the same filler as 212728
208897 (G)	foam	same as 212728	192 phr of 1:1 of the same filler as 212728
208898 (F)	foam	same as 21728	192 phr of 1;1 of the same filler as 212728
Navy	foam	R = phenoxy - R' = p-ethylphenoxy	Unknown
PTFE (A)	film	R = R' = F	none
Polyethylene (H)	film	R = R' - H	none

TABLE II

Polymer[a]	O.I.	LC$_{50}$ (gms)		relative[b] toxicity	D_M (non-flaming)	ALH
D. Fir	19	37.0	63.8[c]	1	380	200
208896	32	24.8	--	1.5	---	0.64
208898	37	24.6	--	1.5	---	0.65
Navy (foam)	37	20.9	--	2	54	0.56
naphthoxy	--	18.2	--	2	187[e]	---
dichloro	--	10.4	--	3.5	89[e]	---
PUF (flexible)	17[d]	---	10.4[c]	6	156[d]	83
PVC	47[d]	---	7.0[c]	10	300[d]	---
Polystyrene	18[d]	---	5.8[c]	10	395[d]	---
210877	52	2.1	---	18	---	---
210878	67	2.6	---	15	---	---
PTFE	92	---	0.6[4]	100	0	100,727

a. refer to Table I for sample descriptions.

b. as compared to Douglas fir.

c. data obtained from ref. 27, heating rate 20°C/min; other data 35°C/min. (present work).

d. reference #38.

e. Robert L. Hinricks (private communication)

TABLE III

RD_{50} values

sample [a]	RD_{50} (mg/1)*
208896	0.19
208897	0.10
208898	0.30
Navy (foam)	0.09
D. Fir	0.20
PUF (flexible)	0.06
Polystyrene	0.18
Polytetrafluoroethylene	0.25

a. refer to Table I for sample descriptions.

* total weight loss (mg) / total air flow (ℓ)

TABLE IV

CORRELATION BETWEEN CO CONCENTRATION AND RELATIVE TOXICITY

sample[a]	CO (%)[b]	Relative toxicity[c]
208896	5.9	1.5
208898	5.8	1.5
Navy foam	7.0	2.0
phenoxy -2, 4-dichlorophenoxy-	2.7	3.5
phenoxy-2-naphthoxy-	4.2	2.0
210877	3.0	18
210878	3.2	15

a. refer to Table I for sample description.

b. based on original sample loading.

c. relative as compared to Douglas Fir.

FIGURES LEGENDS

Figure I. Effect of environmental temperature on the oxygen index of polyphosphazenes and other reference polymers. (Sample details Table II).

Figure 2. Thermogravimetric analysis of polyphosphazenes. (See Table 1 for sample descriptions). Heating rate 40° min^{-1} in air. Sample weights 5-10 mg. approximately.

Figure 3. Graphic representation of LC$_{50}$ value of percent mortality vs. log sample weight (original loading) polyphosphazenes. (See Table 1 for sample descriptions).

Figure 4. Weight loss expressed as Weight fraction as a function of time for APN polyphosphazene (R208898) under (a) isothermal, 500°C (i.e. below ignition),(b) non-isothermal conditions at 35° min^{-1}. The corresponding respiratory response behavior for these two conditions is given by curves (a') and b') respectively.

Figure 5. LC$_{50}$ dose response curves (on logrithmetic scale) for (a) isothermal heating at 500°C and (b) gradual heating at 35°C min.$^{-1}$. (sample 208896 was used for this experiment.)

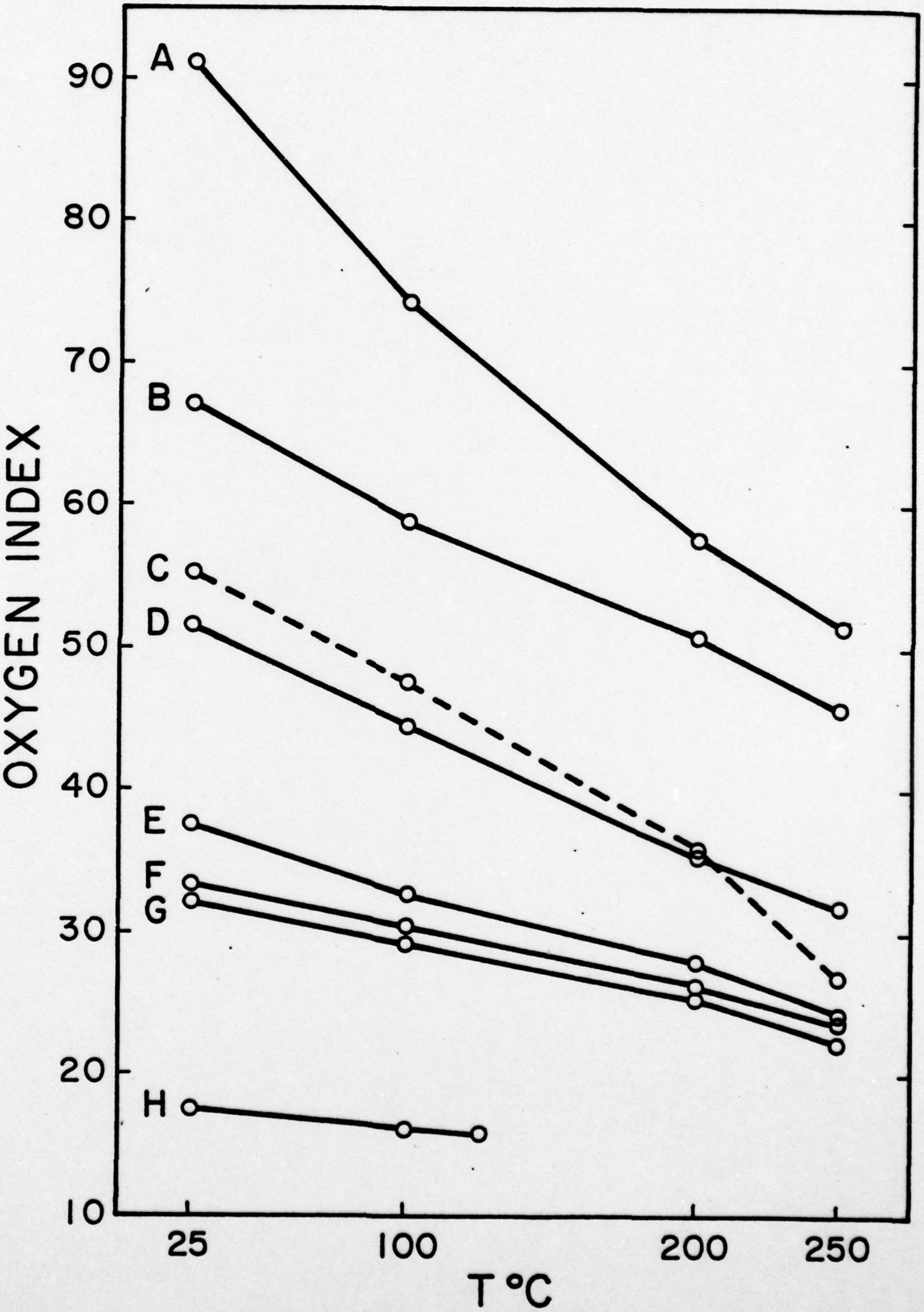
OXYGEN INDEX
90
80
70
60
50
40
30
20
10
A
B
C
D
E
F
G
H
25
100
200
250
T °C

FIGURE 1

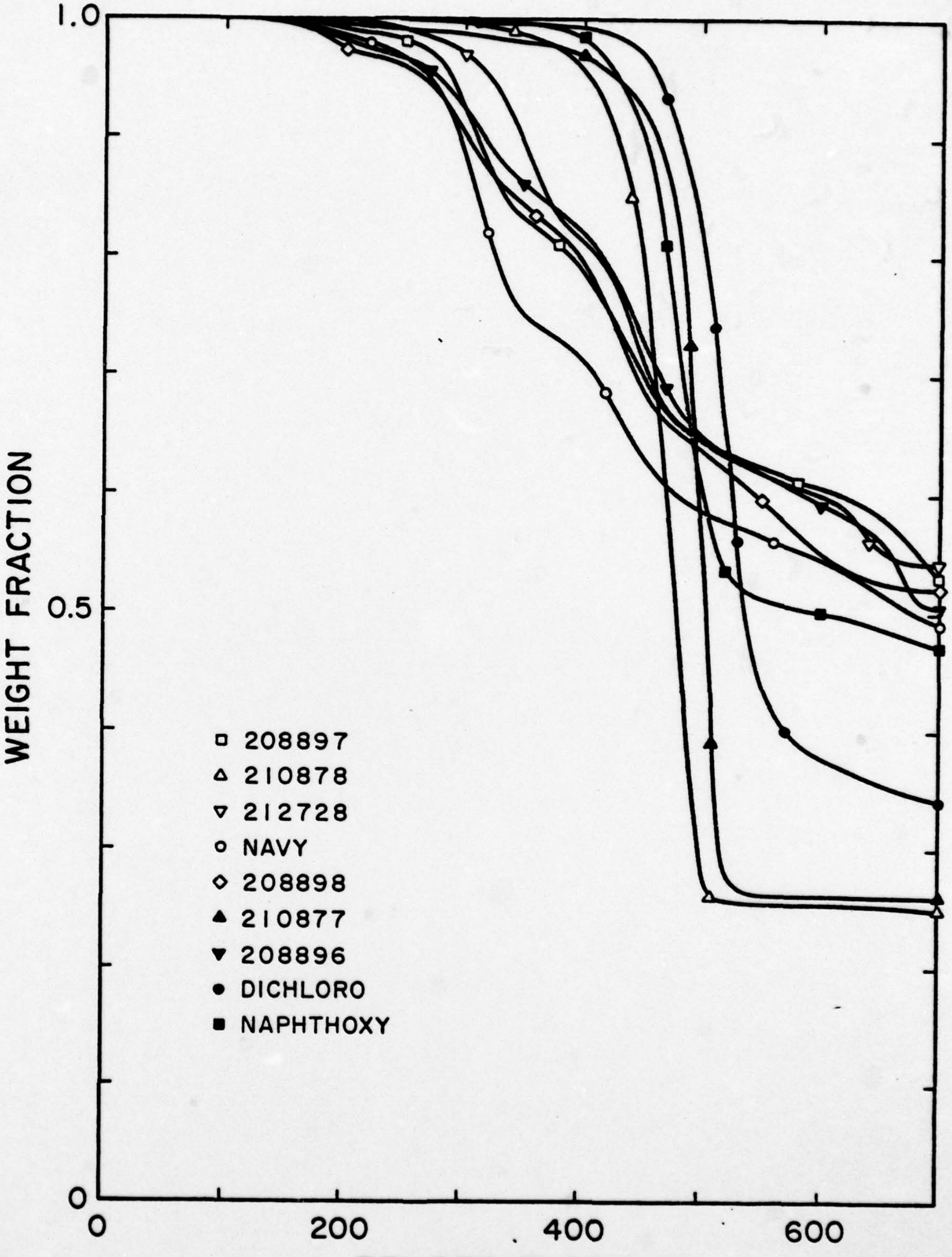
1.0
0.5
0
0
200
400
600
WEIGHT FRACTION
TEMPERATURE (°C)
□ 208897
△ 210878
▽ 212728
○ NAVY
◇ 208898
▲ 210877
▼ 208896
● DICHLORO
■ NAPHTHOXY

FIGURE 2

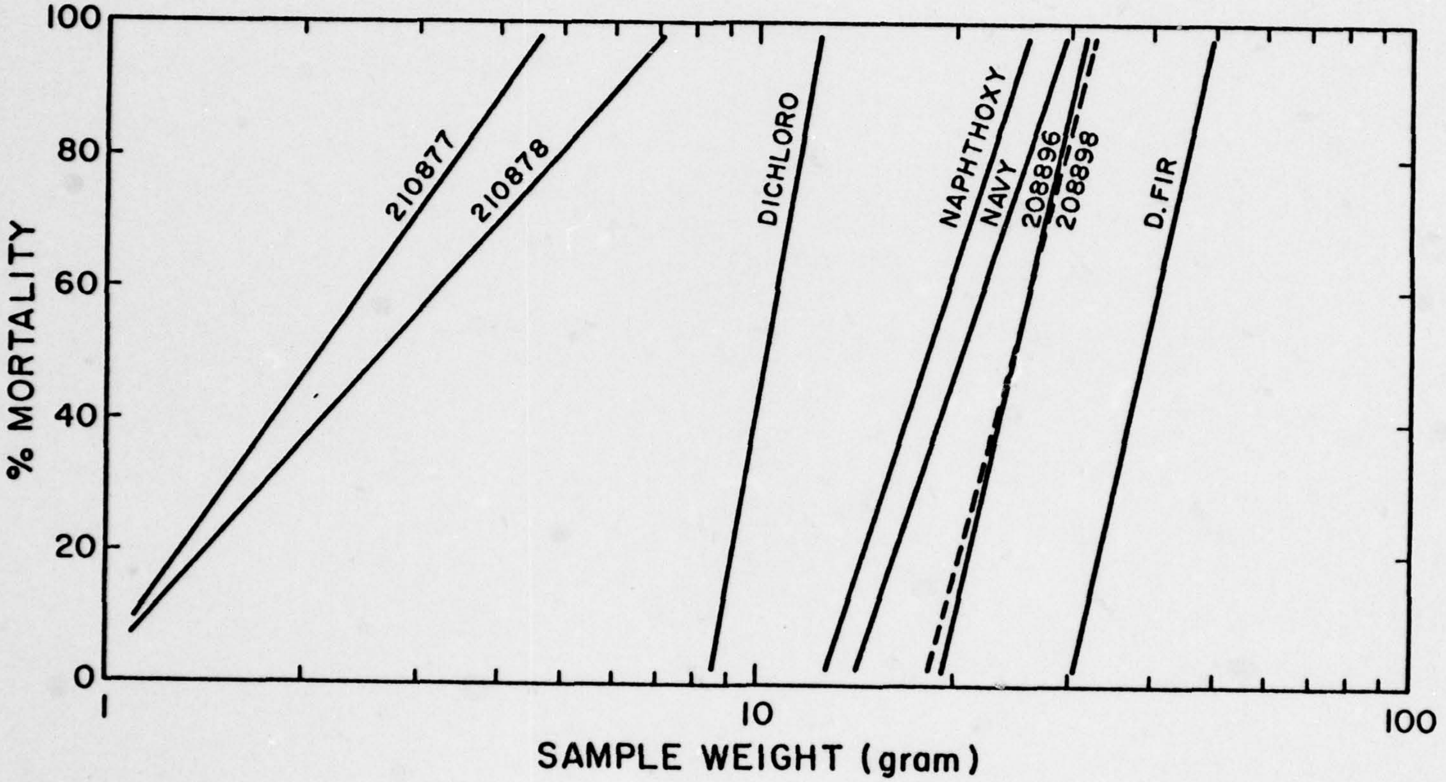
% MORTALITY
100
80
60
40
20
0
1
10
100
SAMPLE WEIGHT (gram)
210877
210878
DICHLORO
NAPHTHOXY
NAVY
208896
208898
D. FIR

FIGURE 3

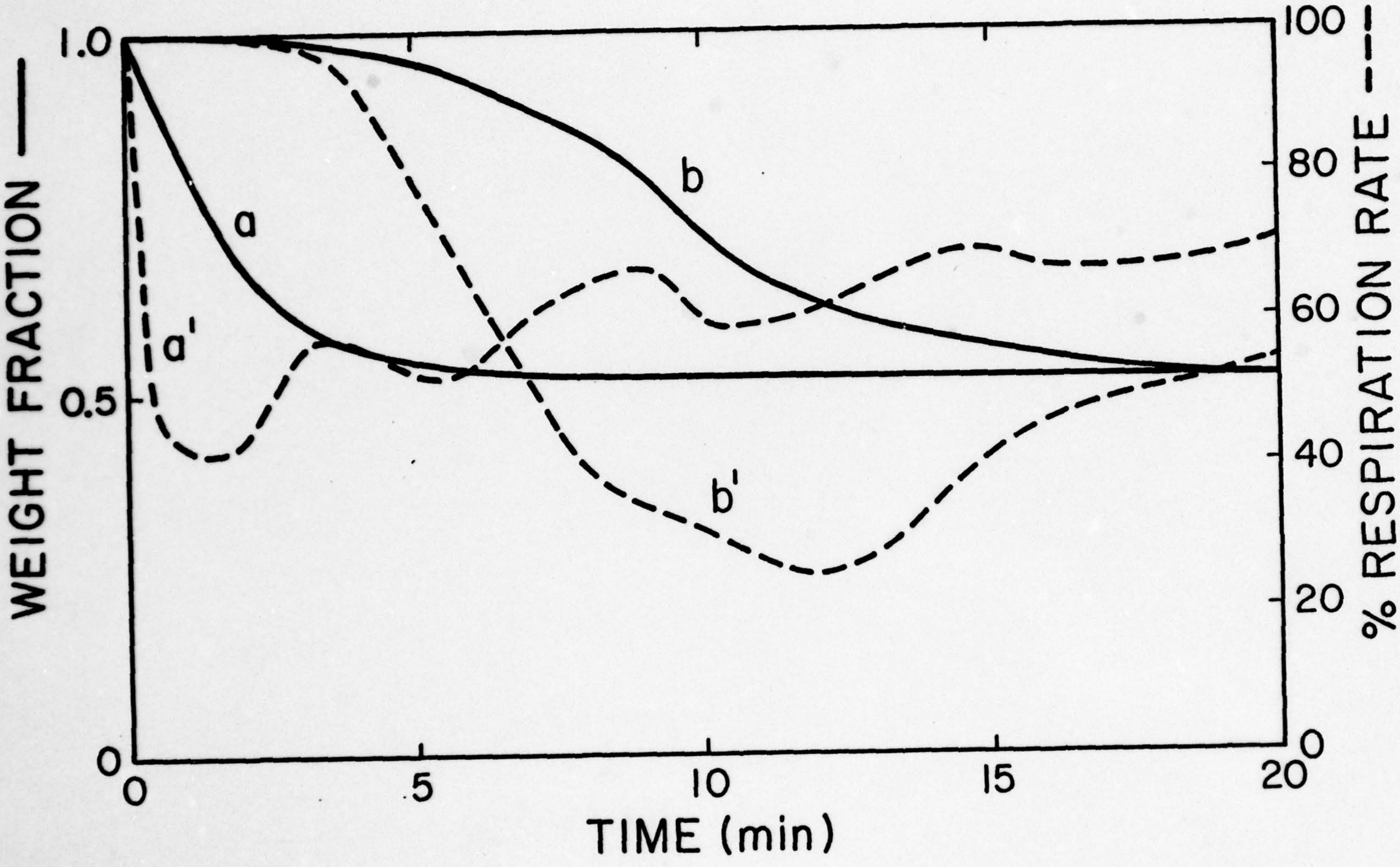
WEIGHT FRACTION ——
1.0
0.5
0
% RESPIRATION RATE - - -
100
80
60
40
20
0
0
5
10
15
20
TIME (min)
a
a'
b
b'

FIGURE 4

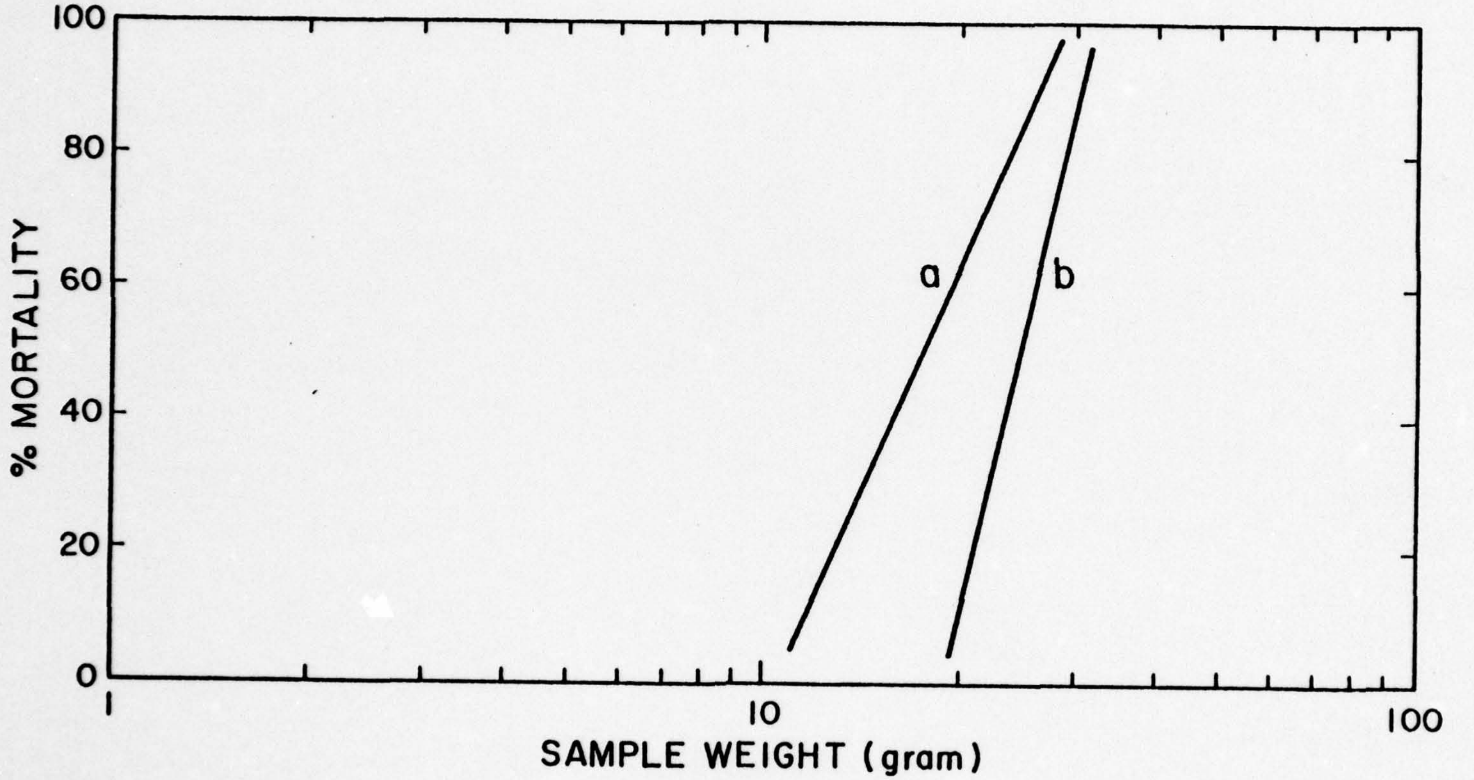

FIGURE 5

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