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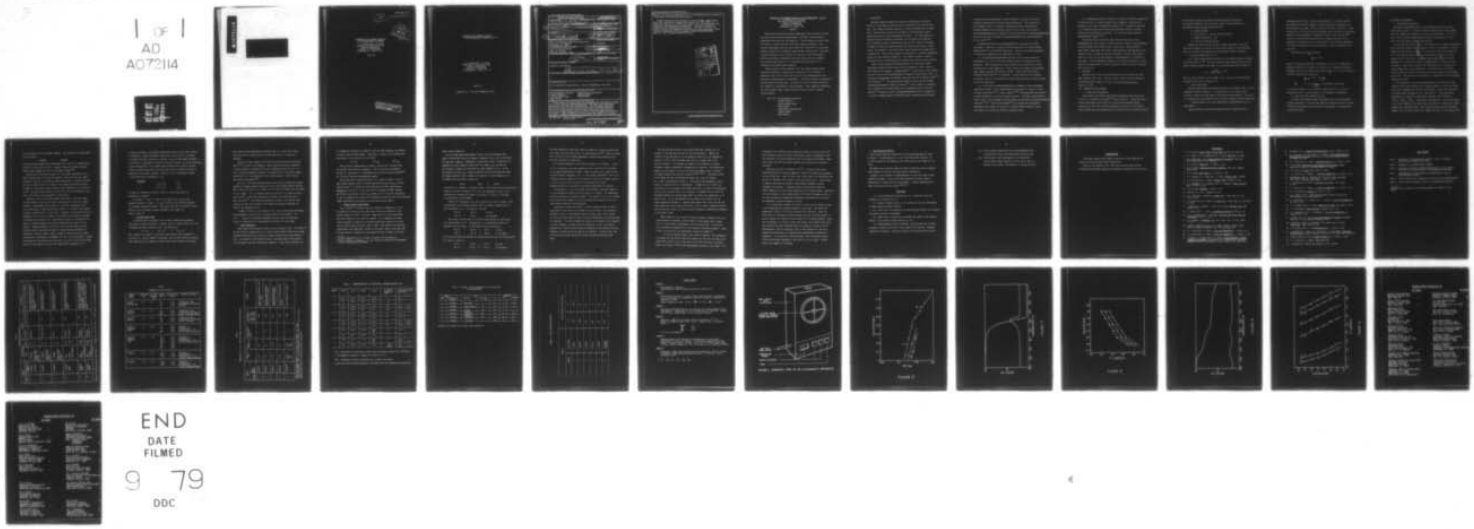

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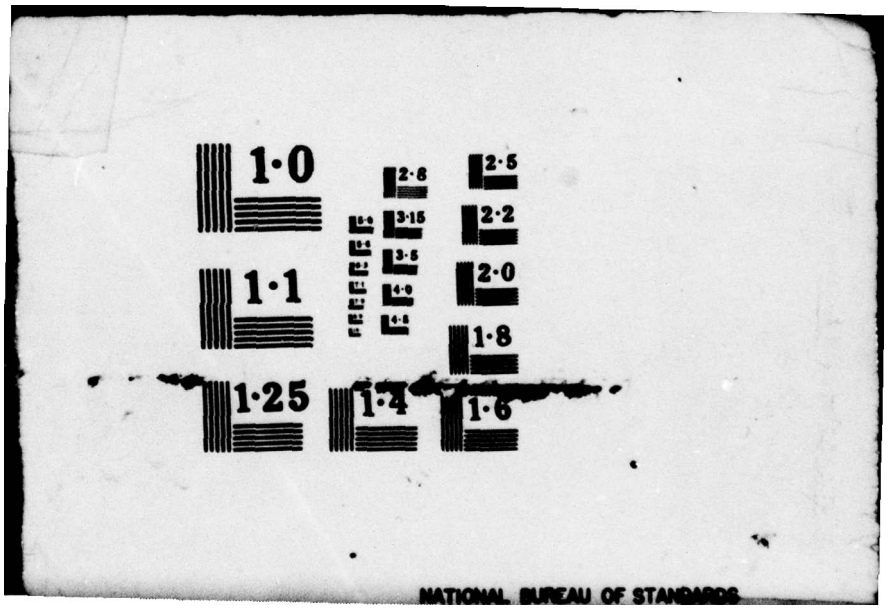
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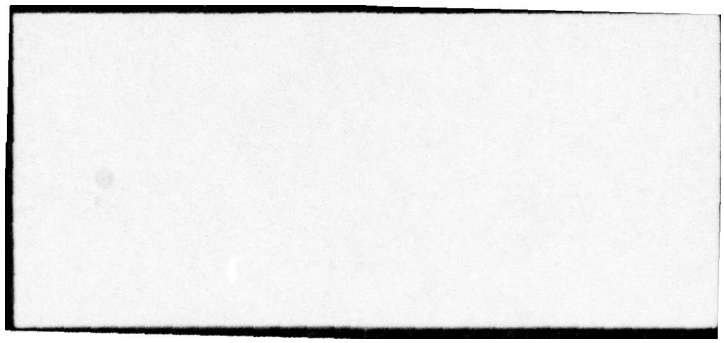

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FLAMMABILITY AND THERMAL STABILITY OF POLYPHOSPHAZENES COPOLYMERS

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June 1979

FLAMMABILITY AND THERMAL STABILITY OF POLYPHOSPHAZENES COPOLYMERS-Part II

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Flame spread and thermal stability measurements have been made on filled and unfilled poly(fluoroalkoxyphosphazenes) (PNF sheet) and poly(aryloxy-phosphazene) (APN sheet and foam materials). The PNF samples were also filled with silica or carbon black and the APN with aluminum trihydrate. Burn velocity measurements were made under steady state conditions in a vertically downward burning mode at different oxygen/nitrogen concentrations. The effect of sample thickness on burn rate was also studied for the foam speciments. Relative smoke density measurements were made using a photocell.

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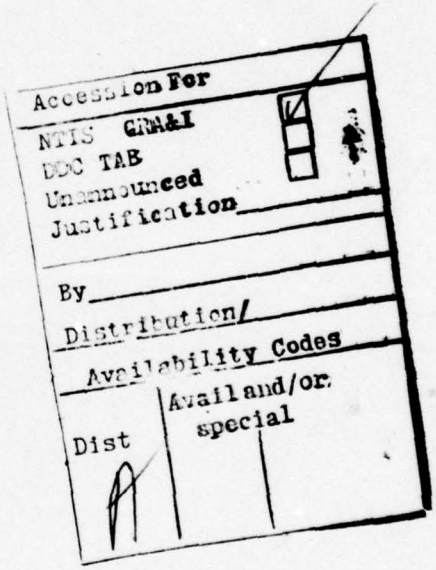
assembly, and limiting oxygen index (L.O.I.) determinations were carried out in accordance with standard ASTM procedures.

Thermal stabilities were measured in air and nitrogen using a Perkin Elmer TGS-2 apparatus at heating rates varying from 2.5° to 80°C min. A temperature span of 50° to 650°C was covered in both thermogravimetric and differential thermogravimetric measurements. Activation energies for degradation were determined from these data. The effect of fillers on thermal stability and flammability characteristics were determined. Glass transition temperatures were also measured ~~using a Perkin-Elmer DSC-2 unit~~ as an aid to polymer characterization.



FLAMMABILITY AND THERMAL STABILITY OF POLYPHOSPHAZENES - Part II

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ABSTRACT

Flame spread and thermal stability measurements have been made on filled and unfilled poly(fluoroalkoxyphosphazenes) (PNF sheet) and poly(aryloxyphosphazene) (APN sheet and foam materials). The PNF samples were also filled with silica or carbon black and the APN with aluminum trihydrate. Burn velocity measurements were made under steady state conditions in a vertically downward burning mode at different oxygen/nitrogen concentrations. The effect of sample thickness on burn rate was also studied for the foam specimens. Relative smoke density measurements were made using a photocell assembly, and limiting oxygen index (L.O.I.) determinations were carried out in accordance with standard ASTM procedures.

Thermal stabilities were measured in air and nitrogen using a Perkin Elmer TGS-2 apparatus at heating rates varying from 2.5° to 80°C min. A temperature span of 50° to 650°C was covered in both thermogravimetric and differential thermogravimetric measurements. Activation energies for degradation were determined from these data. The effect of fillers on thermal stability and flammability characteristics were determined. Glass transition temperature were also measured using a Perkin-Elmer DSC-2 unit as an aid to polymer characterization.

Key words: Polyphosphazene copolymers
Thermal Stability
Limiting Oxygen Index
Flame Spread
Filler/Filler concentration
Polymer Residue
Smoke density

I. INTRODUCTION

Synthetic organic polymers are the basic raw materials for the manufacture of a vast range of articles used in technology and in ordinary daily life. Even though the polymer industry is a rapidly expanding one, in recent years there has been a decline in the number of new economically viable polymer systems with strong technological potential. To a large degree this situation has arisen because new materials are now needed with properties that conventional organic polymers just cannot provide. Nearly all polymers in common use today are organic materials that contain long chains of carbon atoms in the backbone or have carbon atoms linked together with oxygen and/or nitrogen atoms. Many of these systems are susceptibile to oxidative degradation, exhibit low chain backbone flexibility. Some readily dissolve or swell in hydrocarbon fuels and lubricants which restricts their end-use in many markets.

Some of these problems have prompted chemists to synthesize polymers containing inorganic elements such as silicon, phosphorus, sulfur, boron or metal atoms in the backbone. Polyphosphazenes[1] which belong to this category, are one of the more interesting classes of inorganic polymers made to date. In the area new developments and research activities have been reviewed by Shaw[2,3] and by Allcock.[4,5] The earliest known example initially was the unstable polydichlorophosphazene, reported by Stokes.[6] Later attempts to synthesize and to stabilize this polymer failed, but a breakthrough came in 1966 when Allcock[7,8] showed that quality polyorganophosphazenes could be prepared by a two-step synthesis sequence involving the melt ring-opening polymerization

of hexachlorocyclotriphosphazene (trimer) followed by a reaction of soluble polydichlorophosphazene with various organo-nucleophiles. The versatility of this synthesis route, in contrast to conventional polymer synthesis where different monomers must be employed, lies in the fact that a wide variety of polyorganophosphazenes may be prepared from one polymer source, polydiclorophosphazene. Until now, well over 50 different polyorganophosphazenes have been synthesized by this route.[9-14]

In general applications of polyphosphazenes can be grouped into three broad areas. These are: (a) special service applications, (b) flame retardant applications and (c) bio-medical applications. Some of the end-uses highlighted in the various categories may be summarized as follows:

(a) Polyfluoroalkoxyphosphazenes frequently have low glass transition temperatures ($T_g \sim -50^\circ$ to -70°), good thermal stability and excellent solvent resistance. Useful properties are often retained even in contact with various fluids and after thermal aging tests. Their potential as cryogenic fuel handling hoses, gasket materials,[15] fabrics coatings, o-rings seals and speciality elastomer applications[1,18] is impressive. Because they are little affected by moisture, they are also desirable in outdoor applications such as metal coating and for wire insulation.

(b) In this area polyorganophosphazenes are expected to have the greatest technological impact. Cyclic phosphazenes have been used in a variety of flame retardant applications[16] as recent research[17-22] and development has established their versatility and utility in several end uses. Low smoke, flame retardant foams as well as wire coverings have been prepared using several polyorganophosphazene copolymers.[23,24] Other recent studies[25] have revealed that polyaryloxyphosphazene (APN) rubbers are suitable in expanded thermal insulation lining particularly for the interior surface of submarine hulls.

(c) Polphosphazenes exhibit considerable promise as biological substitutes to fabricate and/or to replace defective body components. They also show potential in the field of biodegradable polymers.[26] Progress has been made too in biomedical applications where polyphosphazenes function as carrier molecules for biologically active units for the controllable release of chemotherapeutic drugs.[1,10]

The present study focuses upon other important properties of polyphosphazenes which are currently of great interest in regard to the performance of these polymers under thermal stress. Specifically, thermal stability, flame spread, oxygen index and relative smoke generation upon degradation are needed in order to screen and optimize performance in end-use applications. Results for both foam and sheet samples of polyphosphazenes are described in this paper. From an engineering viewpoint, their mechanical behavior, at both high and low temperatures, is also an attractive feature that will be reported upon in later work.

II. MATERIALS

Materials used in this work were obtained from the Firestone Tire and Rubber Company, Akron, Ohio. They are listed in Table 1 and are referred to as polyfluoroalkoxy, samples #1-3 (PNF), and polyaryloxyphosphazenes, samples #4-6 (APN.

III. APPARATUS AND TEST METHODS

1. Flame Spread Measurements

Burn velocity and relative smoke density measurements were carried out in the T.R.I. Flammability Analyzer[27] shown in Figure 1. Steady state burn velocity measurements were conducted in the vertically downward burning configuration. This simply involved adjusting the velocity of the rotating wheel carrying the burning sample until the relative velocity between the wheel

and the flame front was zero under selected experimental conditions. The variable parameters used in our burn velocity and smoke density investigations (using the above apparatus) were:

a) sample thickness,

b) inert gas type - used to dilute the oxygen,

c) oxygen concentration, and

d) flow rate of gaseous mixture.

Nitrogen was used as the gas diluent in these experiments. Most tests were made on samples as received from the supplier except for APN foams which were cut to provide test materials at three different sample thicknesses.

2. Limiting Oxygen Index (L.O.I.)

L.O.I. values were determined according to the standard procedure prescribed by ASTM, D2863-74.[28] The lowest measured oxygen concentration that would support flaming combustion was taken as the Limiting Oxygen Index defined as:

$$\text{L.O.I.} = \frac{[O_2]}{[O_2] + [N_2]} \times 100$$

Here O_2 is the volumetric flow of oxygen, cm^3/s, and N_2 is the corresponding volumetric flow rate of nitrogen, cm^3/s.

3. Smoke measurements

Relative smoke density measurements were made in the exhaust tract of T.R.I. Flammability Analyzer (Figure 1). A photoelectric cell in the gas outlet was used to measure the smoke density from various burning samples. The output of a photoelectric cell monitored with a recorder to measure the smoke obscuration.

4. Thermogravimetric (T.G.) and differential thermogravimetric (D.T.G.) measurements.

Thermal stability studies were conducted using a Perkin-Elmer TGS-2

Thermogravimetric System. From the non-isothermal T. G. analysis between room temperature and 650°C changes in sample weights were monitored in air and nitrogen over a range of heating rates from 2.5°C/min to 80°C/min. Lower heating rates (1.25°C/min) were often employed in the calculation of activation energies (E) for degradation, following the method of Flynn and Wall.[29] Values for E were obtained from these data by making cross plots of the logarithm of the heating rate vs. the reciprocal of the absolute temperature at a selected concentration of residual polymer. Various conversion levels were used.

The conversion rate $\frac{dC}{dt}$ is given by:

$$\frac{dC}{dt} = k.\ f(C),$$

where k is temperature dependent rate constant and f(C) is a temperature independent function of the degree of conversion (C). Assuming an Arrhenius dependency for the rate constant and noting that $\frac{dT}{dt} = \beta$, the rate of heating in the above equation may be written as:

$$\frac{dC}{dT} = \frac{A}{\beta} \cdot f(C) \cdot \exp\ \frac{(-E)}{RT},$$

where $E = -4.35\ \frac{d \log \beta}{d\ (1/T)}$, is the energy of activation

R is the gas constant, T is the absolute temperature and A is the "pre-exponential factor", usually assumed to be independent of temperature.

5. Glass Transition Temperatures (Tg)

Tg values were measured using a Perkin-Elmer Model DSC-2 Differential Scanning Calorimeter. Tg values were measured at heating rates of 10, 20 and 40°C/min and the sample Tg was obtained by extrapolation to a heating rate approaching 0°C/min.

IV. RESULTS AND DISCUSSION

1. Flame Spread Measurements

Burn velocity measurements made on polyphosphazene materials in Table I are listed in Table II. Except for sample #1 (unfilled) the filler loading (parts per hundred) was constant for a particular polymer type. It is noteworthy that the unfilled sample dripped profusely during testing, but that none of the other samples exhibited such behavior.

The burn velocity listed in Table 3 are tabulated at 75% oxygen concentration. These values were deduced from the results of Table 2 for comparison. For PNF samples the burn velocity of sample #1 is much faster than that for sample #2 or 3. The reason for this difference in performance lies in the fact that samples #2 and #3 both leave a residue on burning whereas sample #1 drips. Consequently, the residue functions as a thermal shield or barrier to reduce the amount of radiant heat available from the flame front so protecting the virgin polymer below it from degradation. Considerable heat is available from the combustion process occurring above the surface ahead of the advancing flame front. This description and explanation is consistent with many published observations (30-34).

It is interesting to note that although samples #2 and #3 have the same chemical structure and the same filler loading, samples #2, filled with carbon black, has a negligible burn velocity (0.05 mm/sec). More will be said about this result after reviewing the T.G.S. data (Table 4). From flame spread measurements the comparative flame spread resistance (FSR) is given by $(FSR)_{\#2} >> (FSR)_{\#3} > (FSR)_{\#1}$. Comparison of PNF samples #2, 3 and the APN sample #4 (all tested samples in the sheet form), (see Table 3), indicate that the PNF samples have a marginally better flame spread resistance than the APN sample. Remember that the aryloxy sample #4 is loaded with 150 phr of ATH compared with

a 30 phr loading of the fluoroalkoxy samples. The resistance to burning (FSR) is in the order:

$$(FSR)PNF > (FSR)APN$$

for polymer sheet because the alkoxy samples have a "built-in" halogen flame inhibitor in the form of fluorine. Polymers containing fluorine invariably exhibit lower flammability than if the halogen is absent[35].

Typical data of log (burn velocity) vs. log (oxygen concentration) from Table 2 indicate that in the PNF type samples, the burn velocity for sample #2 tends to level off at the higher oxygen concentrations. Similarly the burn velocity of sample #1 tends to plateau at 75% oxygen concentration, whereas in sample #3, the velocity shows an almost linear dependence up to Cox levels of 80%. Once again these results show that silica in the PNF samples does not prove to be effective in suppressing the flame spread.

Similarly, data for the aryloxy samples (from Table 2) show that sample #4 sheet exhibits a burn velocity that is decreasing as the level of oxygen increases. Measurements made on sample #5, the aryloxy phosphazene foam, over a wide range of oxygen concentration (Figure 2), illustrate that between an oxygen concentration of 49.5 and 54.4%, a change in the burning rate occurs. Presumably, this is due to a change in the mechanism of burning as the oxygen concentration falls below 49.5%. Substantiative answers to the question of a change in burning mechanism with oxygen concentration must await G.C./M.S. analysis. Thicker specimens, 3.8 mm and 5.1 mm, were only tested at three different oxygen concentrations because of limited material available for examination. However, Figure 2 shows a change in burn velocity with oxygen concentration corresponding to mechanism 1 for the 2.5 mm thick sample. Perhaps this change may stem from the fact that below a C_{ox} level of 49.5% the burning surface of the polymer can utilize more oxygen than is available to it,

so that any increase in the oxygen concentration results in more rapid burning. In mechanism 2, oxygen "saturation" exists above a C_{ox} of 49.5%. An attempt to formulate the burn velocity as a function of C_{ox} for fixed sample thickness, in the form $V = A\, C_{ox}^{m}$ where V is the burn velocity in mm/sec, C_{ox} is the percentage oxygen concentration, A is a constant which includes factors such as the heat capacity, thermal conductivity of the gas phase as well as density and heat of combustion of the polymer specimen. Values of A and m, pertaining to Figure 2, have been found for Mechanisms 1 and 2.

Mechanism	A	m
1	1.80×10^{-6}	3.63
2	2.8×10^{-2}	1.184

The power law dependence involving a factor of three times higher for mechanism 1 is obtained.

In columns 2, 4, and 5 of Table 2 the change in burn velocity with specimen thickness is listed. At a C_{ox} of 49.5% the burn velocity decreases as the sample thickness increases. The results show that the decrease in burn velocity with an increase in sample thickness is not-linear, but tends to level off.

2. Limiting Oxygen Index

It has been noted that sample #3 has a better flame spread resistance than sample #1 which was unfilled. However, the L.O.I. values (Table 3) for the two samples are nearly identical (~48). The results are:

L.O.I. #2 > L.O.I. #3 = L.O.I. #1

Note, however, that sample #3 is one and a half times as thick as sample #1. The high L.O.I. value of sample #2, which has a very low burn velocity, indicates that carbon black at a loading of 30 phr in PNF is very efficient in reducing

burn velocity while simultaneously elevating the L.O.I. More will be said about the action of carbon black as a filler when the T.G.S. results are discussed.

Silica as a filler (sample #3) follows the pattern outlined by Quinn and Dieck [19] for silica in APN samples. These workers found that the addition of various amounts of hydrated silica had a negligible effect on L.O.I. In fact, if anything meaningful happened, this adulteration of the sample slightly lowered the L.O.I. value compared to the unfilled samples. Similar results were found by Wittenwyler[35].

The L.O.I. of the unfilled APN material was 26.5 and it showed poor thermal stability in thermal analysis studies in air only (see Thermal Analysis Section). Table 3 shows that the L.O.I. of sample #4 is 44 and the corresponding foam sample #5 has a value ~48.6. Aluminum trihydrate loses 35% of its weight as water vapor at 250°C. Under these conditions it absorbs 470 calories per gram of water envolved[38]. The competitive absorption of heat by the hydrate, thus detracts from the heat available to the polymer and strongly influences the shape of the degradation curve.

In sample 5 (Table 2), the variation of O.I. with varying sample thicknesses was investigated, and was found to increase linearly with thickness. The L.O.I. values of the samples investigated are well above the borderline values for combustion in air when samples are exposed to an open flame.

3. Smoke Measurement

Smoke density figures given in Table 3 are in arbitarary units. For Sample #5, the APN foam has a higher value of (7) than the other samples because the specimen undergoes decomposition most rapidly as already discussed under flame spread results. For sample #3, PNF filled with silica, the smoke density value appears to be abnormally high when compared with sample #2. These results indicate that

the flammability properties of sample #3, with the same chemistry, are inferior to those of the other PNF samples. From Table 3, column 5, it is evident that smoke density (S.D. values) are in the order:

$$(S.D.)_{\#3} > (S.D.)_{\#2} > (S.D.)_{\#1}$$

The low value of smoke density of sample #1 may be due to the fact that the material drys during the combustion. There is no obvious correlation between S.D. values and O.I. in agreement with the work of Quinn and Dieck[20] for filled and unfilled polyphosphazene samples.

Converting from the smoke obscuration T.R.I. values in Table 3 to N.B.S. Smoke chamber numbers using a corrected smoke density value of $D_{m,c}$ of 50 for sample R-210147*, if follows that APN foam material R-210107 would have an inferred value about 350. On the other hand, the sheets: K-19298, R-209152 and R-209153 are expected to have $D_{m,c}$ numbers of 50, 125 and 350 respectively. It must be remembered that these are only guideline values and that actual NBS smoke chamber measurements are required to provide more precise numbers.

4. Thermal Analysis Measurements

Data in Table 4** illustrate that with reference to samples #1, 2, and 3 the addition of fillers such as carbon black and silica contributes to the residue formation at 550°C. The level ranges from 5% to 27.5% there being more char formation in the latter two samples. As a consequence the flame spread resistance is expected to be better because heat transfer to the fuel front is reduced when the residue level is high. This result has already been established in the flame spread section of this paper, where it was found that the burn velocity of Sample #1 is much higher than that of Sample #2 but about

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* Private communication, Dr. D. Lawson, Firestone Tire and Rubber Co.

** Values in Table 4, Columns 3, 4, 5, and 6 have been obtained from thermograms run at a heating rate of 10°C/min.

double that for Sample #3.

From the flame spread measurements of Part 1 we have established that Sample #3 filled with Silica is inferior to Samples #1 and 2, all of which have the same basic chemistry. Examination of TGS results (Table 4) shows that the temperature at which Sample #3 loses 10% of its weight, T_{10}, (in both air and nitrogen) is higher than that found for either Samples #1 or 2. At the 50% weight loss level, T_{50}, a similar conclusion follows indicating that again the Thermal Stability (TS) of Sample #3 is superior to either Samples #1 or 2. In summary form, the relative values are:

$$(TS)\#3 > (TS)\#2 \text{ or } (TS)\#1$$

in either air or nitrogen. The general nature of the weight loss and differential weight loss curves for Samples #1, 2, and 3 are comparable in Figure 3 the thermogram was obtained when Sample #1 was heated at $10^{\circ}C$/min. in nitrogen is characteristic of PNF samples.

Weight loss thermograms at T_{10} and T_{50} when carbon black is present, show no improvement in the thermal stability (TS) in nitrogen, although there is some improvement in air. The relative TS values:

$$(TS)\ \#2 > (TS)\ \#1 \quad \text{(in air)}$$

$$(TS)\ \#2 \gtrsim (TS)\ \#1 \quad \text{(in nitrogen)}$$

The success of carbon black as a filler arises through its functioning as a reducing agent in air. Consequently, it is ineffective in inert atmospheres such as nitrogen. At this stage, we can conclude that:

$$(TS)\ \#3 > (TS)\ \#2 > (TS)\ \#1 \quad \text{(in air)}$$

$$(TS)\ \#3 > (TS)\ \#2 \gtrsim (TS)\ \#1 \quad \text{(in nitrogen)}$$

The calculated activation energies for thermal decomposition of the PNF materials are (Table 4, Column 7):

$$(E)\ \#3 > (E)\ \#2 > (E)\ \#1 \quad \text{(in air)}$$

$$(E)\ \#3 > (E)\ \#2 \gtrsim (E)\ \#1 \quad \text{(in nitrogen)}$$

(The high temperature values were chosen for Sample #2.) From our results here it is clear that silica which acts as a reinforcing filler[19], helps to improve the TS in both air and nitrogen atmospheres. Besides being thermally inert, the filler functions as a heat sink.

Two activation energies (E) are found for sample #2 in nitrogen. A value of 14.5 k.cal/mole at the lower temperature, and a value of 33.9 k.cal/mole at the higher temperatures is formed. Figure 6 presents the E plots for ATH filled APN Sample 6 degraded in air. At low polymer conversions C =0.1 to 0.3 a single activation energy of 27.2 k.cal/mole is found, but at higher values of c, viz 0.4 and 0.45, two E values of 37.3k cal/mole at the lower temperatures and 50.2 k.cal/mole at the higher temperatures are obtained.

For samples #1, 2, and 3 the weight loss occurred in one step (Figure 3) but the differential weight loss curve (Figure 3) is skewed. Two degradation reaction mechanisms are therefore implied. For Samples #1 and 3 it is presumed that the activation energies for the two mechanisms are similar and for the three samples competitive reactions occur.

According to Allcock and Cook[39], a chain cleavage process is firstly responsible for the sharp loss in weight in the TGA curves. The cleavage is presumed to occur at "weak points" along the polymer chain, where residual P-Cl units and other possible defects have been inadvertently introduced during the synthesis). The second competitive reaction is attributed to the formation of cyclic oligomers. The TGA curves for Samples #1, 2, and 3 are found to superpose when laterally shifted along the temperature axis implying that the mechanism of weight loss is the same in all instances. In other words, both silica and carbon black improved TS without introducing additional weak links.

TGS work performed recently on an unfilled APN sheet revealed that its stability in nitrogen was less than for the filled material. However the stability of this APN sheet in air was impaired especially in the temperature interval. 400°C to 490°C the sample lost 60% of its weight (30% of this was lost abruptly). At the moment the reason for this behavior is unknown although a change in mechanism of decomposition is suspected. This deleterious behavior is not observed in air for ATH filled APN samples, where in general, the higher stability has been well documented[19,24,36,37]. The general nature of the weight loss and the differential weight loss curves for Samples #4, 5, and 6 are displayed in Figure 5. This weight loss-temperature curve is found to be typical for all the APN samples. In Sample #4, up to 400°C, the TS curves in air and nitrogen, were almost equivalent, but above this temperature the TS in air is better than it is in nitrogen. In samples #5 and 6 the TS is marginally improved in nitrogen below 440°C, but beyond this temperature, it is better in air. In all three samples a third weight loss is noted in air at higher temperatures (Figure 5). Because these samples were filled with ATH, the first weight loss, which begins about 240°C, is due to water of hydration evolved from the filler as vapor; the other two steps correspond to degradation mechanisms of the polymer itself.

Again, Samples #4 and 6 exhibit activation energies consistent with a two stage degradation mechanisms, whereas Sample #5 surprisingly shows a single value of E even though the degradation curve has three steps. In this case the two mechanisms presumably occur with equivalent activation energies. Figure 6 shows a plot used for the determination E values for Sample #6.

For the APN samples, again a clear trend is observed. The thermograms in nitrogen have two distinct weight loss steps, the first one occurring in the range 240°C to 265°C is due to the loss of water from the filler, the second step in the interval 275°C to 550°C approximately pertains to the polymer. The

thermogram in air indicates that an additional weight loss occurs above 575°C. The differential weight loss (DTG) curves exhibit peaks corresponding to each loss mechanism, the second degradation peak (in nitrogen) being skewed. These result again show that the polymer degrades by two mechanisms occurring in succession.

Based upon the work of Goldfarb et al.[40], a scission rather than a depolymerization model has been suggested to explain the thermolytic breakdown in the APN materials. Again the first step is most likely to be associated with fracture of inherently weak regions in the chain backbone (e.g., branch points or impurity locations) and possibly random thermal breakages at points throughout the molecules. Cyclization which is entropically favored at higher temperatures is most likely connected with the second process. Essentially, the real difference in the thermal analysis for PNF and APN samples is that in the former polymers the degradation mechanisms overlap whereas in the latter the degradation reactions takeplace in series.

It is interesting to examine the effect of filler type and amount on some of the polyphosphazene copolymers examined in this paper. The results are summarized in Table 5 for PNF (#1-3) and APN (#4-6) materials. While the filler generally enhances the Limiting Oxygen Index over unfilled polymer, it does not improve the residue of actual polymer for the systems examined. Somewhat surprisingly it is found to lower this residue (total sample minus filler duly corrected for loss of hydrated water and alumina) by as much as 50% in APN materials. With the exception of SiO_2 in PNF polymers too, the LOI is enhanced on adding filler thus improving the polyphosphazene resistance to combustion. It is also worth noting from Table 5 that the polymer residue level in an nitrogen atmosphere is less than it is in air itself. Further work in this regard is in progress.

5. Glass Transition Results

Typical glass transition temperature for the polyphosphazenes are listed in Table 6. The PNF Samples #1, 2, and 3 have values close together, -62 to -64°C, whereas the APN Samples #4 and 5 have values in the range of -9 to -16°C.

APN samples have relatively hight Tg values (as expected) from the impaired chain flexibility caused by the bulky aromatic substituents.

In general, the Tg values of polyphosphazenes are lower than those of many commercial polymers, a feature which helps extend their useful range of applicability to temperature well below ambient. Possible explanations for these low Tg values are now obvious [5,41,42].

CONCLUSIONS

(i) All polyphosphazenes measured had L.O.I. values well above the borderline for combustion in air.

(ii) Alumina trihydrate proved to be in effective filler for APN samples in flame spread and thermal stability.

(iii) Silica filler is ineffective for improving flame spread, but increases the thermal stability of PNF samples.

(iv) Carbon black is excellent in retarding flame spread in PNF polymers. However it only improves thermal stability in air.

(v) Polyphosphazenes behave differently in flame spread and in thermogravimetry; property corelations in this regard are not obvious. Different mechanisms are expected. Analytical results will help establish this point.

(vi) Filler additions improve the LOI of polyphosphazenes with the exception of SiO_2 in PNF (fluoralkoxy) type polymers.

(vii) Fillers used in this investigation do not enhance the actual polymer residue formed, but in the case of APN (i.e. phenoxy) type polymers a 50% reduction in residue was noted.

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TABLE LEGENDS*

Table 1. Description of Polyphosphazene Materials. Source: Firestone Tire and Rubber Company, Akron, Ohio.

Table 2. Flammability of Polyphosphazene Polymers.

Table 3. Comparison of Results of Limiting Oxygen Index (L.O.I.), Relative Burn Velocity, and Smoke Density for Polyphosphazene Materials.

Table 4. Thermogravimetric and Differential Thermogravimetric Data for Polyphosphazene Polymers.

Table 5. Polymer residue-filler comparisons for film and foam polyphosphazenes.

Table 6. Glass Transition Temperature Data for Polyphosphazene Materials.

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*Manufacture code numbers and corresponding sample test numbers 1-6 are given.

Table 1

Materials Description

Sample		Substituents		Filler		Description
Number	Manufacturer Number	Type	Mole %	Material	Parts Per 100	Sample Type and Other Remarks
1	K-19298 PNF-200[R]	CF_3CH_2O Other fluoro-alkoxy side groups	65 35	Unfilled	---	Sheet form-gum stock, radiation vulcanized no filler or anti-oxidant added to Samples 1 through 3.
2	R-209152	CF_3CH_2O Other fluoro-alkoxy side groups	65 35	Carbon Black	30	Sheet form-filled stock, peroxide vulcanized.
3	R-209153	CF_3CH_2O Other fluoro-alkoxy side groups	65 35	Silica	30	Sheet form-filled stock, peroxide vulcanized.
4*	R-210147 APN[TM]	PhO p-EtPhO o-CH_2=CHC_6H_4O	49.1 41.3 9.6	Alumina Trihydrate	150	Filled sheet material samples 4 through 6 characteristics (sulfur cured)
5*	R-210107 APN[TM]	PhO p-EtPhO o-CH_2=CHC_6H_4O	49.1 41.3 9.6	Alumina Trihydrate	150	Closed cell sponge blowing agent present Samples 5 & 6 are same except Sample 6 was heated at $110^oC/10^{-3}$ Torr for 20 hours to remove excess solvent. Sulfur cured
6*	R-210107 APN[TM]	PhO p-EtPhO o-CH_2=CHC_6H_4O	49.1 41.3 9.6	Alumina Trihydrate	150	

*Details of unfilled stock: DSV (THF) = 1.77 dl/g; Tg = ~18.5° C; Mw = 1.3 X10^6, Mw/Mn = 50; 49% High Mw Polymer.

Table 2

Flammability Characteristics

Sample Number	Thickness mm	Flow Rate of Gases ℓ/m	Oxygen Conc. %	Burn Velocity mm/sec	Chemical Structure
K-19298 PNF-unfilled	0.7	9.4	55 65 75	1.10 1.49 1.64	$-OCH_2CF_3$ and other fluoroalkoxy side groups No filler
R-209152 PNF-(CB)	1.4	9.3	86 95.5 100	0.10 0.21 0.24	$-OCH_2CF_3$ and other fluoroalkoxy side groups 30 phr. of carbon black
R-209153 PNF-(Si)	1.1	9.4	60 70 80	0.49 0.61 0.77	$-OCH_2CF_3$ and other fluoroalkoxy side groups 30 phr. of silica
R-210147 APN-Sheet (ATH)	1.2	11.48	68 73 78 100	0.32 0.39 0.41 0.42	PhO-49.1% p-EtPhO-41.3% o-CH_2=CHC_6H_4O- 9.6% 150 phr. alumina hydrate
R-210107 APN-Foam (ATH)	2.5	9.5	40 44.7 49.5 54.5 65 75 100	1.15 1.77 2.45 3.11 3.67 4.60 6.61	PhO-49.1% p-EtPhO-41.3% o-CH_2=CHC_6H_4O - 9.6% 150 phr. alumina hydrate
R-210107	3.8	9.5	44.7 49.5 54.5	1.13 1.55 1.89	PhO-49.1% p-Et-PhO-41.3% o-CH_2=CHC_6H_4O - 9.6% 150 phr. alumina hydrate
R-210107	5.1	9.5	49.5 52.5 54.5	1.11 1.31 1.77	PhO-49.1% p-EtPhO-41.3% o-CH_2=CHC_6H_4O 9.6% 150 phr. alumina hydrate

Table 3

Comparison of L.O.I., Relative Burn Velocity and Smoke Density

Sample		Thickness mm	L.O.I. (Ambient)	Smoke Density Arbitrary Units	Burn Velocity at 75% O_2 Conc. and Const. Flow Rate mm/sec	Remarks
Number	Mfg.* Number					
1	K-19298	0.71	48	1	1.64	Sample drips profusely, very little smoke.
2	R-209152	1.35	65	2.5	0.05	Dripping absent-moderate, smoke-brittle residue.
3	R-209153	1.07	47.5	7	0.71	Dripping absent-dense, smoke-brittle residue.
4	R-210147	1.24	44	1	0.40	Very little smoke-brittle residue.
5	R-210107≠	0.15 ≠ 2.5 3.8 5.1	36 ≠ 34 38 48.6	7	4.60	Dense smoke-soft residue.

*Note that Samples Number 1-4 are sheets and Number 5 is a foam.
Raw APN, R-218584, LOI = 26 (our measurement) which agrees with refs. 20 and 43.

≠Oxygen index values for different sample thicknesses.

TABLE 4. THERMOGRAVIMETRIC AND DIFFERENTIAL THERMOGRAVIMETRIC DATA

Number	Amount	T_{10} °C	T_{50} °C	T_{max} °C	% Average Residue at 550°C	Activation Energy Kcal/mole E_1	E_2
1	Air	377.1	428.1	440.9	4	30.5	
	N_2	385.6	437.4	443.3	6.5	31.5	
2	Air	396.2	443.8	443.8	26*	35.4	23.3
	N_2	385.6	439	443	28.5	33.9	14.5
3	Air	420	462.2	463.3	26	41.6	
	N_2	417	461.5	466.6	29	47.4	
4	Air	317.8	-----	321.8	52	52.2	26.50
	N_2	310.3	-----	414.4	51.5	53.50	26.10
5	Air	266.2	654.6	269 & 400	49	23.9	
	N_2	256.7	469.8	437.4	45	34.8	
6	Air	276.7	------	272 & 393	52	35.3 56.3	35.3
	N_2	280.2	524.3	447.5	49 at 585°C	37.3 50.2	27.2

T_x °C - Temperature at which sample reaches fixed percentage decomposition, (10°C/min)

* - Decomposition residue of a sample with filler in #s 2-6.

T_{max} - Temperature at which the maximum rate of weight loss occurs.

E_1 and E_2 are the activation energies at the higher and lower temperatures respectively.

Table 5. Residue - filler comparison for film and foam polyphosphazenes*

Sample		Filler			RESIDUE*	
Number	Manufacturer Number	Material	Parts Per 100	L.O.I.	AIR	NITROGEN
1	K-19298	Unfilled	-	48	4	6.5
2	R-209152	Carbon Black	30	65	3	5.5
3	R-209153	Silica	30	47.5	3	6
4	R-210147	Alumina Trihydrate	150	44	13	12.5
5	R-210107	Alumina Trihydrate	150	48.6	10	16
6	R-218584	Unfilled	-	26.5	20	34

*Residue from polymer only (filler level subtracted)

TABLE 6. GLASS TRANSITION VALUES*

Sample		Glass Transition (Tg) Values	
Number	Mfg. Number	^{o}K	^{o}C
1	K-19298	211.1	-61.9
2	R-209152	208.9	-64
3	R-209153	210	-63
4	R-210147	264	-9
5	R-210107	257	-16
6	R-210107 (Treated)	259	-14

FIGURE LEGENDS

Figure 1.

TRI Flammability Analyser
(manufactured by Textile Research Institute, Princeton, NJ)

Figure 2.

Logarithm Burn Velocity (V, mm/sec) versus logarithm oxygen concentration (C_{ox}) for different film thickness of Sample #5 (phenoxy- p-Ethoxyphenoxy phosphazene polymer)

Sample thickness are: ⊖, 0.26 cm; ◐, 0.38 cm; ●, 0.51 cm.

Figure 3.

Representative Thermogravimetric and Differential Thermogravimetric weight loss curves vs. temperature (^{o}C) for unfilled Sample #1, PNF-200^{R}. Heating rate 20^{o}C/min., sample weight 4.71 mg, nitrogen atmosphere.

Figure 4.

Logarithm β ($=\frac{dT}{dt}$ versus reciprocal absolute temperature (K^{-1}) for Sample #2 containing Carbon black, 30 phr. Symbols refer to conversion rates, C:

Symbol	C
⊖	=0.1
◐	=0.2
●	=0.4

in nitrogen atmospheres.

Figure 5.

Thermogravimetric and differential thermogravimetric curves versus temperature (^{o}C) Sample #6 (Phenoxy - p-ethylphenoxy phosphazene polymer (alumina trihydrate content 150 phr). Run in air at 20^{o}/min; sample weight 2.215 mg. Sample preheated at 110^{o}C for 20 hours at 10-3 Torr before testing.

Figure 6

Logarithm β ($= \frac{dT}{dt}$) versus reciprocal absolute temperature (K^{-1}) for sample #5 (phenoxy: p-ethyl-phenoxyphosphazene polymer). Conversions listed according to plot

#	1	2	3	4	5	6
C	0.1	0.15	0.2	0.3	0.40	0.45

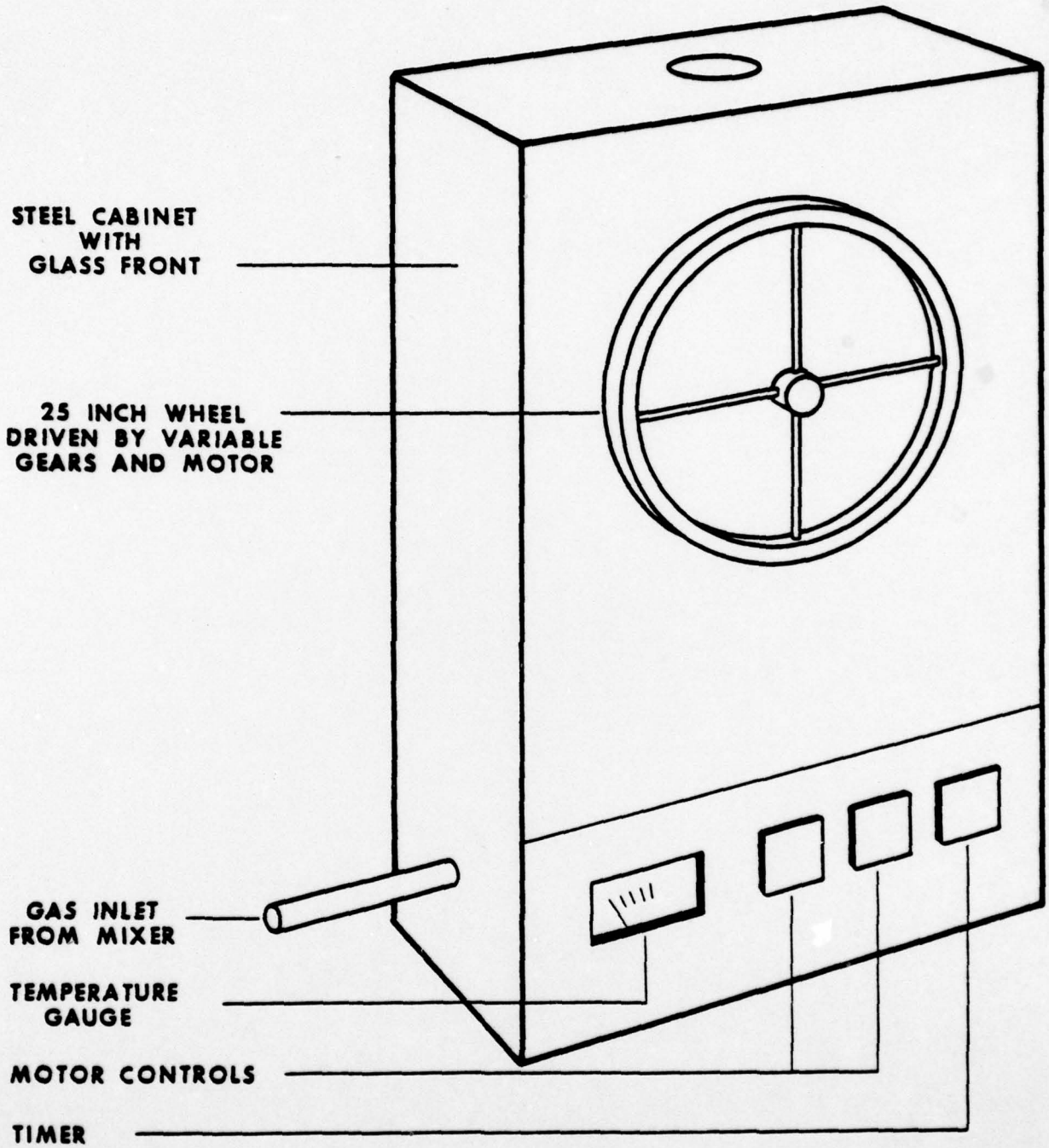

FIGURE 1 SCHEMATIC VIEW OF TRI FLAMMABILITY APPARATUS

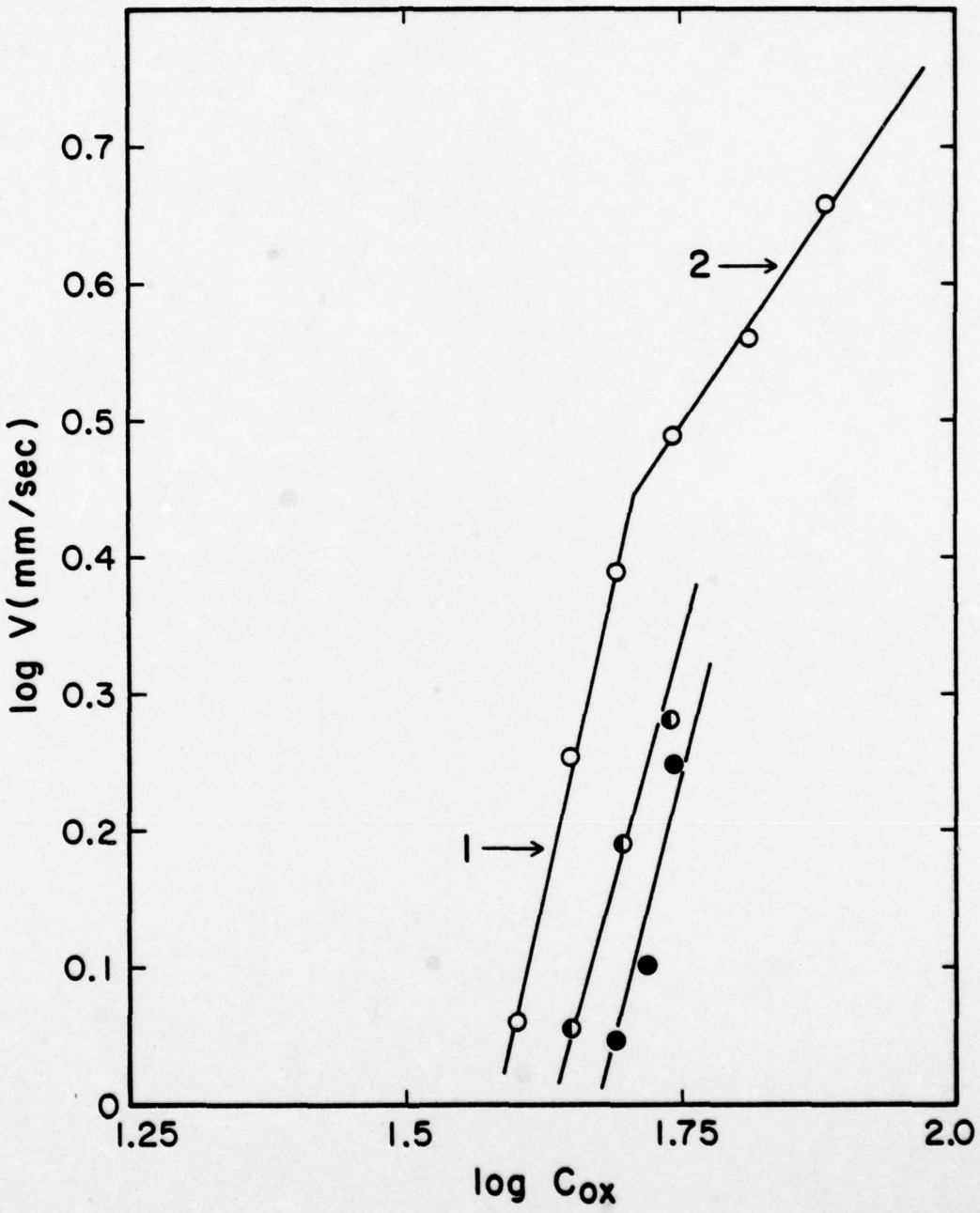

FIGURE 2

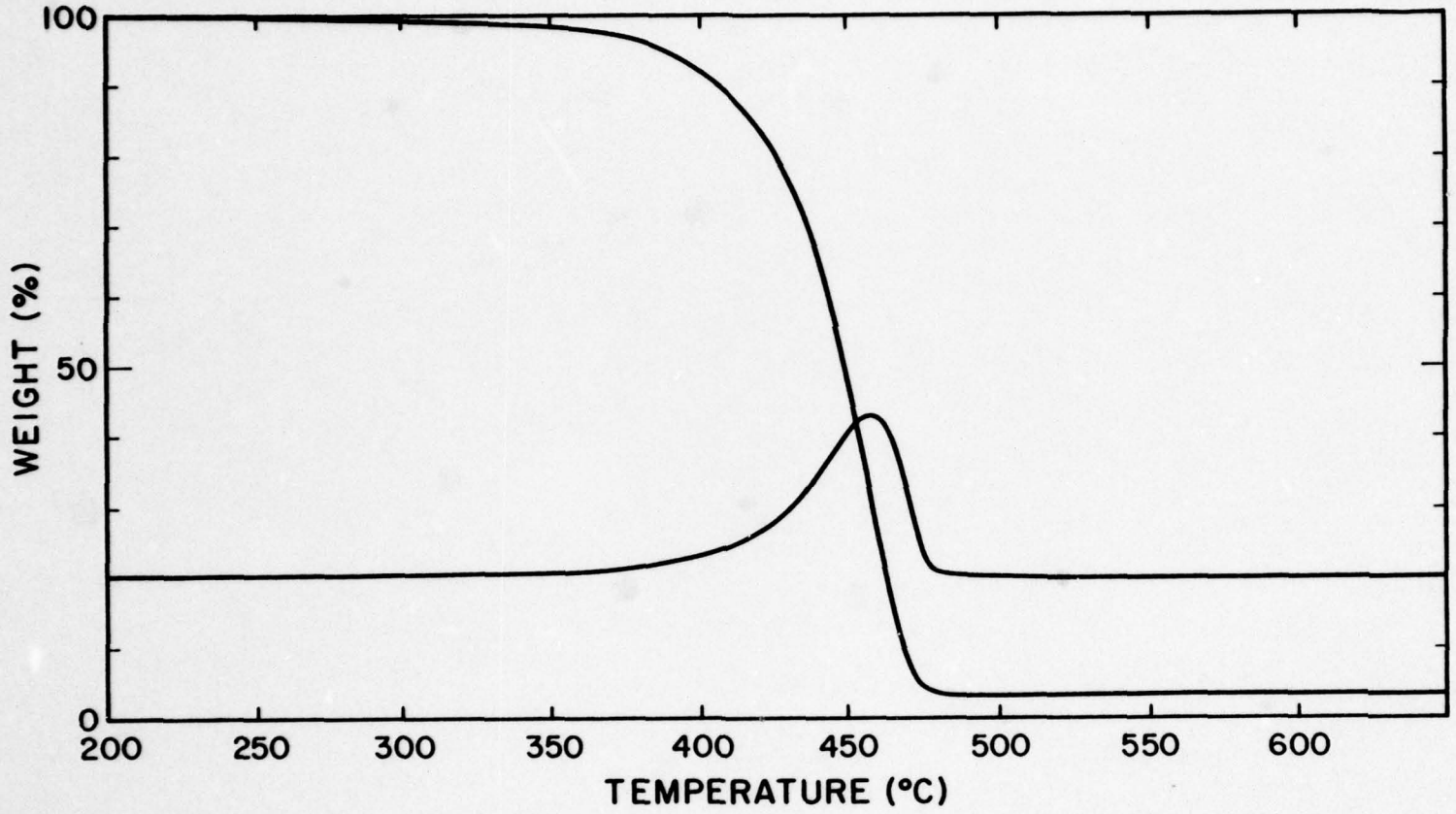
100
50
0
WEIGHT (%)
200
250
300
350
400
450
500
550
600
TEMPERATURE (°C)

FIGURE 3

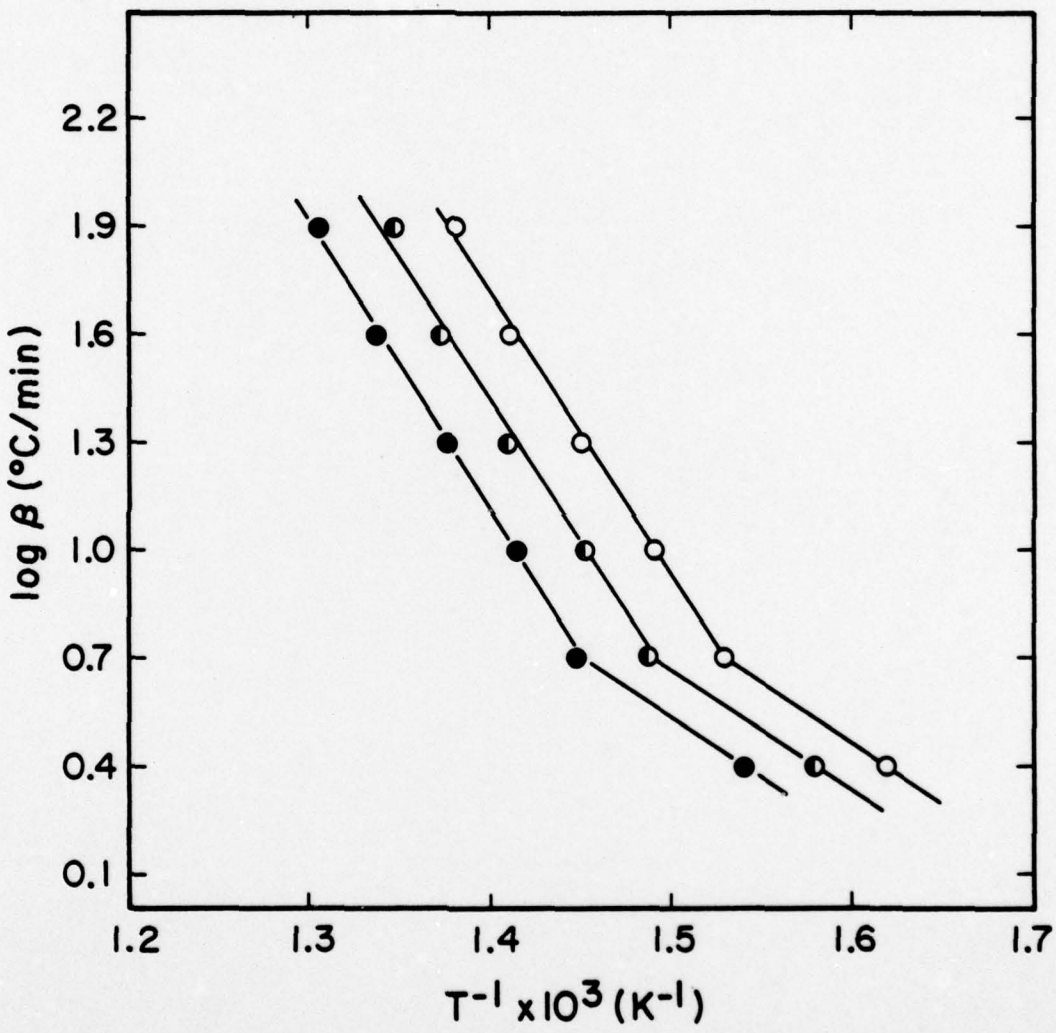

FIGURE 4

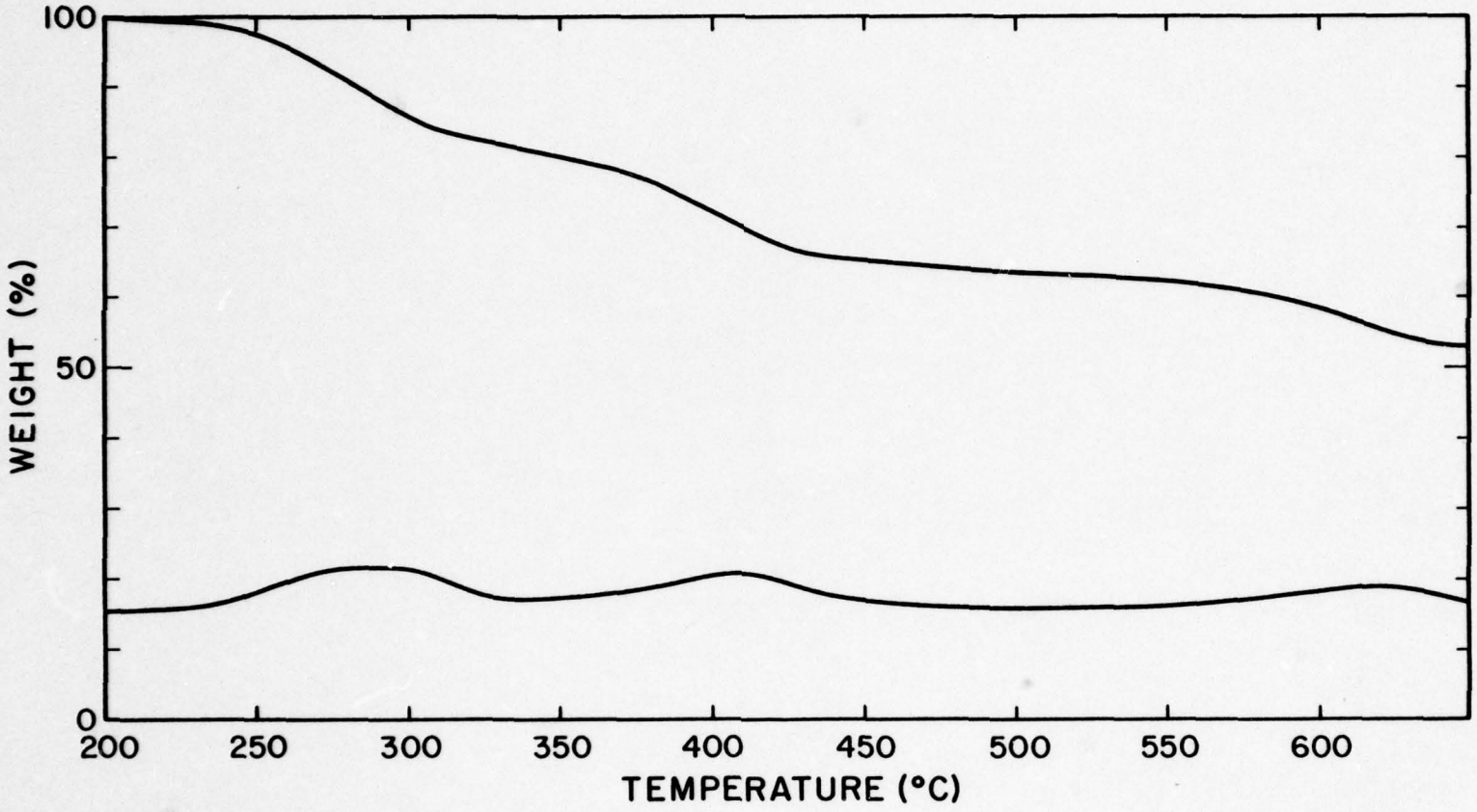
100
50
0
WEIGHT (%)
200
250
300
350
400
450
500
550
600
TEMPERATURE (°C)

FIGURE 5

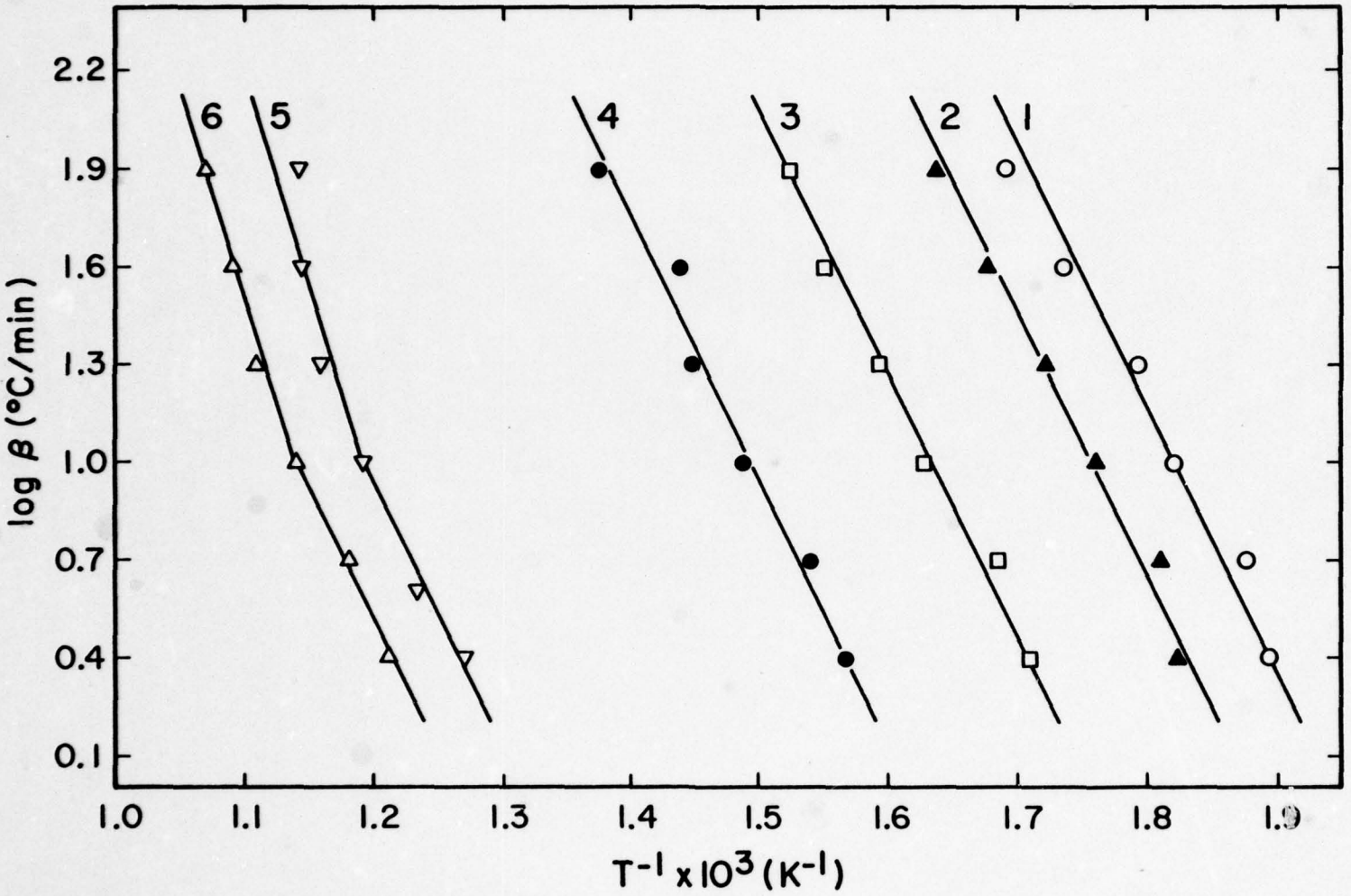
2.2
1.9
1.6
1.3
1.0
0.7
0.4
0.1
log β (°C/min)
6
5
4
3
2
1
1.0
1.1
1.2
1.3
1.4
1.5
1.6
1.7
1.8
1.9
T⁻¹ x 10³ (K⁻¹)

FIGURE 6

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