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Part III

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STRUCTURE-STABILITY RELATIONSHIPS OF POLYMERS BASED ON THERMOGRAVIMETRIC ANALYSIS DATA

Part III. Semiorganic Polymers

POLYMER BRANCH
NONMETALLIC MATERIALS DIVISION

NOVEMBER 1975

TECHNICAL REPORT AFML-TR-74-177, Part III
FINAL REPORT FOR PERIOD 1960 — 1974

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AIR FORCE MATERIALS LABORATORY
AIR FORCE WRIGHT AERONAUTICAL LABORATORIES
Air Force Systems Command
Wright-Patterson Air Force Base, Ohio 45433

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Project Monitor

FOR THE COMMANDER

R. L. VAN DEUSEN, Chief
Polymer Branch
Nonmetallic Materials Division

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Thermogravimetric Analysis	

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To provide guidance for research in polymer synthesis for high temperature non-metallic materials, two previous reports were issued (AFML-TR-74-177, Parts I and II) in which the structures of aliphatic, aromatic and heterocyclic polymers were correlated with their thermal stabilities based on TGA data. Additional stabilities of repeat units and moieties were determined, and the effect of ortho, meta and para substitution, crosslinking, molecular weight, pendant groups and other factors were discussed. The present report concludes this structure-stability correlation with the discussion of semiorganic polymers.

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FOREWORD

The report covers thermogravimetric analysis data on polymers from inhouse synthesis work, contractual or commercial sources. The data were determined between 1960 and 1974. Results from the literature were also used.

Polymer samples with AFML given as a source were synthesized by one of the following: E. W. Choe, R. F. Kovar, H. Rosenberg and T. T. Tsai. The TGA determinations were made by personnel and students of the University of Dayton Research Institute.

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SECTION I

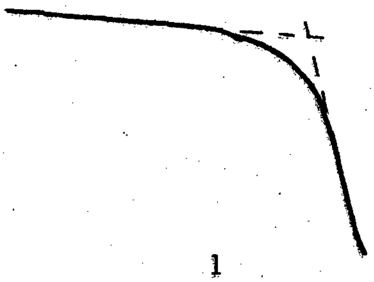
INTRODUCTION

To provide guidance for various research programs dealing with synthesis of high temperature polymers for Air Force applications, an attempt was made to derive structure-stability relationships from thermogravimetric analysis (TGA) data. This investigation is based on about 1300 experimental polymers, obtained between 1960 and 1973. In two previous reports (AFML-TR-74-177, Parts I and II) results on polyaliphatics, polyalicyclics, spiro polymers, phenylene-R-polymers, and polyheterocyclics were discussed. This final report covers semiorganic polymers.

The majority of the polymers under investigation have been synthesized by Air Force contractors or were the result of inhouse work; a few were from other sources or commercially available. Of the large amount of data, that obtained from polymers which could not be compared readily with others, those with insufficient information about the structure, and polymers with ill-defined structure were omitted.

The TGA data were obtained using a modified Chevenard thermobalance at a heating rate of about 180°C/hr. Most of the runs were performed in nitrogen, some in air at a flow rate of 98 cc/min. The sample size was 200 mg in the earliest runs, then 100 mg. After some modifications of the balance had been made to increase sensitivity, a sample size of 50 mg was used. These runs were carried out in porcelain crucibles (Coors 0000).

The criterion for thermal stability was the extrapolated onset of decomposition, i.e., the intersection of the tangent of the steepest part of the curve of the first major weight loss step with the tangent of the weight loss curve immediately before the actual onset of the above weight loss step, as shown below:



Discretion was used to disregard early weight losses which obviously were caused by impurities, water, solvent, etc. The extrapolated onsets thus determined were designated $T_{dec}(N_2)_2$ or T_{dec}(Air), and listed in centigrade.

The results are discussed and compared by groups of related polymer structures. At the end of each group, the sources of the polymers are listed with the exception of those which are covered by the references. The Section "Conclusions" summarizes the most important findings of general validity.

Literature results were used if they were available as sets of data and could be compared among themselves. Different instrumentation and experimental conditions normally do not allow comparison of results obtained by different authors. The T_{dec}'s obtained from TGA curves in literature figures can at best only be approximate values.

SECTION II

DISCUSSION

The polymers which were investigated and discussed in this report can be divided into the following groups:

Polysiloxanes and arylene bridged polysiloxanes
Polyarylene (alkylene) siloxanes
Polyarylene (alkylene) oxysiloxanes
Polyarylenesilanes
Polysilazanes
Ferrocene polymers
P-O and P-N polymers

Several other semiorganic polymers which are studied, such as polymers containing borine, copper, aluminum and germanium, some metal-containing siloxanes and some polychelates, were either ill defined, or the results could not be used for valid comparisons for other reasons.

The results of the individual polymer groups are discussed below.

1. POLYSILOXANES

Data collected on polysiloxanes are shown in Tables 1 and 2.

TGA curves of some representative polysiloxanes and arylene bridged polysiloxanes are shown in Figures 1-4.

The two tables show maximum T_{dec}'s in the 500 to 550°C range. Table 1 clearly indicates the order of stability

$$\underline{C_6H_5 > CH_3 > CH_2CH_2CF_3 > (CH_2)_3NH_2}$$

for the substituents on the silicon atom, while in the arylene bridged polysiloxanes the arylene bridge seems to have a prominent effect on the stability. The order

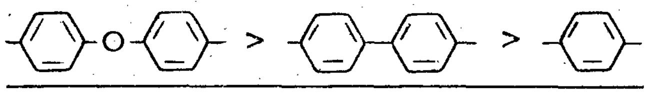
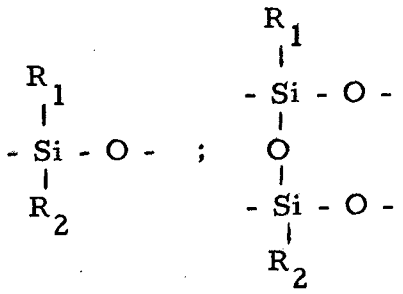


TABLE 1

Decomposition Temperatures of Polysiloxanes



$$-\overset{R_1}{\underset{R_2}{\mathrm{Si}}}-\mathrm{O}- \quad ; \quad \begin{array}{c} R_1 \\ | \\ -\mathrm{Si}-\mathrm{O}- \\ | \\ \mathrm{O} \\ | \\ -\mathrm{Si}-\mathrm{O}- \\ | \\ R_2 \end{array}$$

R_1	R_2	$T_{dec}(N_2)$(°C)	T_{dec}(Air)(°C)
C_6H_5	C_6H_5	500 1)	550 1)
CH_3	C_6H_5	480	
CH_3	CH_3	465	
CH_3	$CH_2CH_2CF_3$	365 2)	
CH_3	$CH_2CH_2CF_3$	330 3)	310 3)
CH_3	$CH_2CH_2CF_3$	480 4)	430 4)
CH_3	$(CH_2)_3O\ CF(CF_3)_2$	180, 380	
CH_2NH_2	$(CH_2)_3NH_2$	320	
C_6H_5	$(CH_2)_3NH_2$	280	

1) "Phenyl-T" polymer

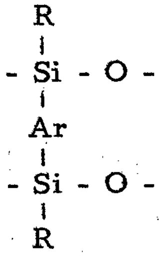
2) Copolymer with dimethylsiloxane

3) LS 422 gum stock (assumed structure)

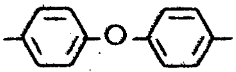
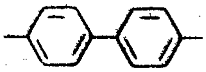
4) LS 53, filled and cured (assumed structure)

TABLE 2

Decomposition Temperatures of Arylene Bridged Polysiloxanes



$$\begin{array}{c} R \\ | \\ -Si-O- \\ | \\ Ar \\ | \\ -Si-O- \\ | \\ R \end{array}$$

R	Ar	$T_{dec}(N_2)$(°C)
CH_3		515
CH_3		490
C_6H_5		460
CH_3		460
$-OCH_3$		410
$-Cl$		400
$-N(CH_3)_2$		160

seems to suggest that the bulkiness of the group is of importance. As far as the substituents on the silicon are concerned, no apparent difference exists between methyl and phenyl; however, substituents with functional groups reduce the stability considerably.

The limited data in air (Table 1) when compared to the data in nitrogen, show a stability increase for the all-phenyl substituted Phenyl-T polymer and a decrease in stability for the alkyl substituted polymers. In the first case, crosslinking between the phenyl groups increases the stability, and only very little weight loss is involved. In the second case, the alkyl groups are oxidized under evolution of carbon monoxide and dioxide.

Sources of samples:

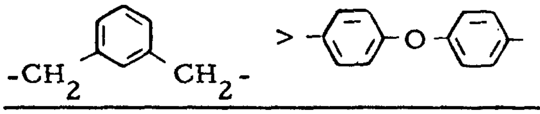
Dow Corning
GEC
Midwest Research Institute
Wackerchemie
AFML

2. POLYARYLENE (ALKYLENE) SILOXANES

The data in Table 3 led to the following conclusions:

Substituents on Si: $C_6H_5 > CH_3 > CH_2CH_2CF_3$

Moieties in the chain (R_3):



$- (CH_2)_2(CF_2)_8(CH_2)_2 -$

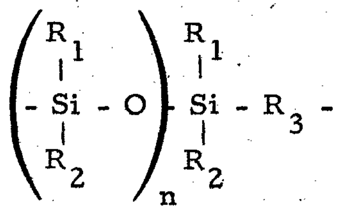
TGA curves of two of the polymers from Table 3 are shown in Figures 5 and 6.

Sources of Polymers:

Dow Corning
Midwest Research Institute
AFML

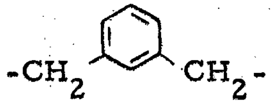
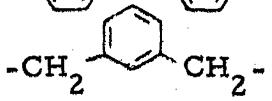
TABLE 3

Decomposition Temperatures of Polyarylene (Alkylene) Siloxanes



$$\left(-\underset{R_2}{\overset{R_1}{Si}}-O\right)_n-\underset{R_2}{\overset{R_1}{Si}}-R_3-$$

n = 1-3

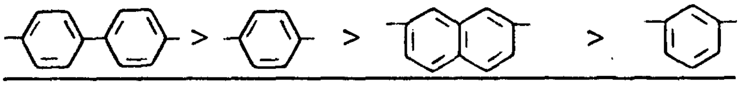
R_1	R_2	R_3	$T_{dec}(N_2)$(°C)	T_{dec}(Air)(°C)	Reference
C_6H_5	C_6H_5		540		1
$\underline{C_6H_5}$ + CH_3	$\underline{C_6H_5}$ + CH_3		530		1
$\underline{CH_3}$ + C_6H_5	$\underline{CH_3}$ + C_6H_5		465		1
CH_3	CH_3		535	340	
CH_3	CH_3		515		
CH_3	$CH_2CH_2CF_3$		490		
CH_3	$CH_2CH_2CF_3$	$-(CH_2)_2(CF_2)_8(CH_2)_2-$	450	370	

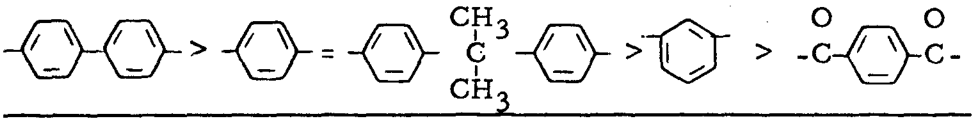
3. POLYARYLENE (ALKYLENE) OXYSILOXANES

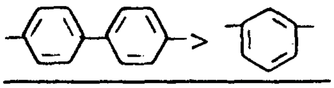
The following orders of stability can be derived from Table 4:

Substituents on Si: $C_6H_5 > CH_3$

Moiety (R_2) in the chain:







The few decomposition temperatures in air are of the same magnitude or higher than those in nitrogen. This is to be expected for polymers with phenyl substituents on the silicon; it is, however, difficult to explain for a polymer with methyl substituents.

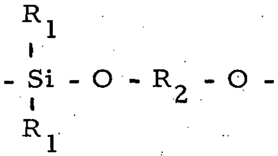
TGA curves of a polyaryloxysiloxane are shown in Figure 7.

Sources of samples:

American Potash
Koppers
Monsanto

TABLE 4

Decomposition Temperatures of Polyarylene (Alkylene) Oxysiloxanes



$$-\underset{\underset{R_1}{|}}{\overset{\overset{R_1}{|}}{Si}}-O-R_2-O-$$

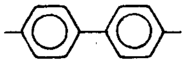
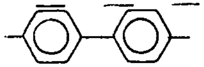
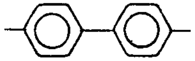
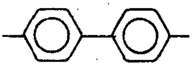
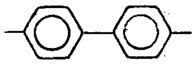
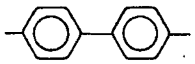
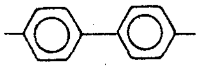
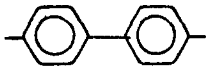
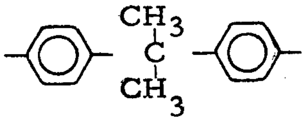
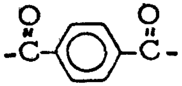
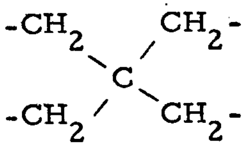
R_1	R_2	$T_{dec}(N_2)$(°C)	T_{dec}(Air)(°C)	Reference
C_6H_5		600		2($\Delta T=4$°C/min)
C_6H_5		580		
C_6H_5		570		
C_6H_5		500		
C_6H_5		~600		
$C_6H_5 + CH_3$		~470		
CH_3		~450		
C_6H_5		525	525	3(Heating rate unknown)
CH_3		450	510	
C_6H_5		515		4(Helium, $\Delta T=3$°C/min)
C_6H_5		515		

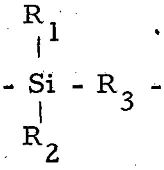
TABLE 4 (Concluded)

R_1	R_2	$T_{dec}(N_2)(°C)$	$T_{dec}(Air)(°C)$
C_6H_5		510	510
C_6H_5		460	520
C_6H_5		460	
C_6H_5		440	510
C_6H_5		350	
CH_3		210-230	

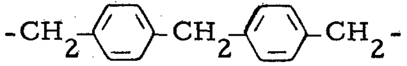
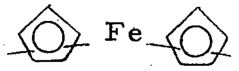
4. POLYARYLENESILANES

TABLE 5

Decomposition Temperatures of Polyarylenesilanes



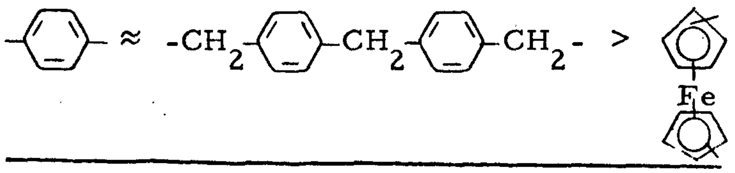
$$-\overset{R_1}{\underset{R_2}{Si}}-R_3-$$

R_1	R_2	R_3	$T_{dec}(N_2)$(°C)	T_{dec}(Air)(°C)
$C_6H_5+CH_3$	$C_6H_5+CH_3$		505	
↓ increasing CH_3	↓		495	
			480	
CH_3	CH_3		465-495	
CH_3	CH_3		485	
C_6H_5	C_6H_5		455	450
C_6H_5	C_6H_5		380	
CH_3	CH_3		340	

The first four results suggest, as expected, that increased numbers of methyl groups in phenyl and methyl substituted silanes decrease the stability, thus

$$\underline{C_6H_5 > CH_3.}$$

However, the sixth polymer does not fall into line. Somewhat questionable too, is the result of the comparison of the in-chain moieties:



A TGA curve of a polyarylenesiloxane is shown in Figure 8.

Sources of samples:

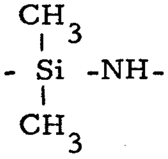
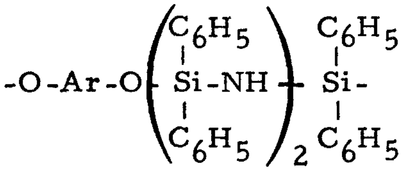
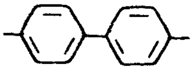
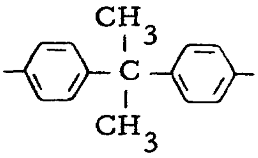
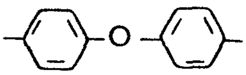
T.N.O. Utrecht (Netherlands)
Ford Motor Co.

5. POLYSILAZANES

Several different types of Si-N polymers were investigated, as shown in Table 6.

TABLE 6

Decomposition Temperatures of Polysilazanes

	$T_{dec}(N_2)$(°C)	T_{dec}(Air)(°C)
 $-\overset{CH_3}{\underset{CH_3}{Si}}-NH-$	~450	~450
 $-O-Ar-O\left(\overset{C_6H_5}{\underset{C_6H_5}{Si}}-NH\right)_2\overset{C_6H_5}{\underset{C_6H_5}{Si}}-$		
Ar:		
	~530*)	
	~520*)	
	~510*)	

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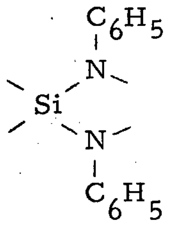
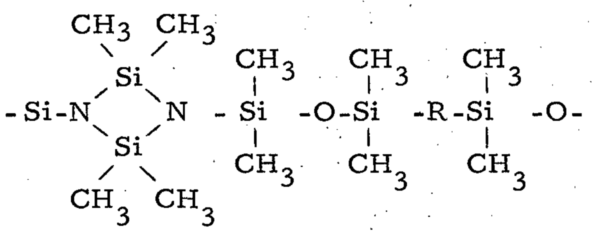
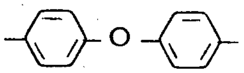
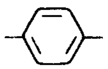
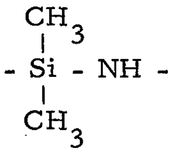
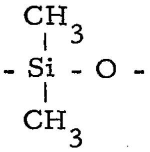
*) Reference 5; data presumably obtained in nitrogen; heating rate not known.

TABLE 6 (Concluded)

	$T_{dec}(N_2)$(°C)	T_{dec}(Air)(°C)
	~490	
		
R:		
	550	
	520	

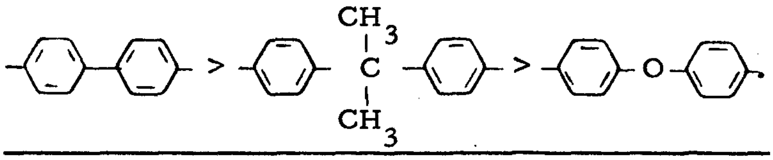
A comparison of the stability of the dimethylsilazane (first polymer in Table 6) with the one of the dimethyl-siloxane suggests:

	$T_{dec}(N_2)$
 $$-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{Si}}-NH-$$	~450
 $$-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{Si}}-O-$$	465

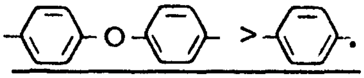
However, valid conclusions cannot be drawn from these data for the following reasons: First, both structures are idealized. The silazane polymer is actually crosslinked through every third N-atom, while the dimethylsiloxane polymer was a cured and filled rubber. Both materials had a 2- or 3-step breakdown, and it was difficult to assign a major breakdown step, as the TGA curves show (Figures 1 and 9). The early and the high overall weight loss of the silazane polymer make it appear less stable than the polysiloxane; but the stability of the latter may be enhanced by intensive crosslinking and the filler.

The TGA curves of the polydimethylsilazane in nitrogen and in air are quite different, yet they give the same T_{dec}. The run in air does not show the early weight loss steps of the nitrogen run, apparently because in the presence of air crosslinking through the NH-groups occurs, which prevents early weight loss. A similar observation has been made in the case of the polyiminoazoles (Reference 6).

The second polymer in Table 6, with its three different moieties for Ar, shows a slight difference in stabilities as follows:



Finally, the last polymer in above table suggests:



Sources of samples:

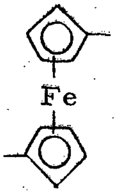
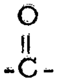
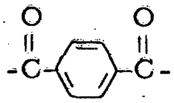
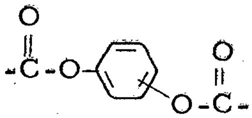
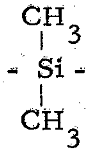
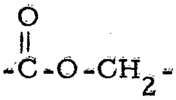
AFML
GEC
Midwest Research Institute

6. FERROCENE POLYMERS

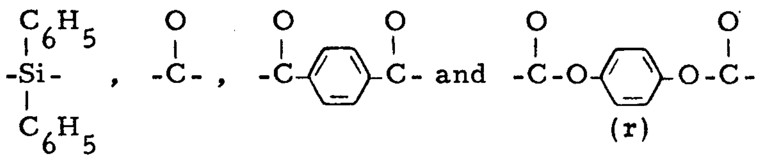
The following Table 7 lists the decomposition temperatures of a number of Ferrocene polymers.

TABLE 7

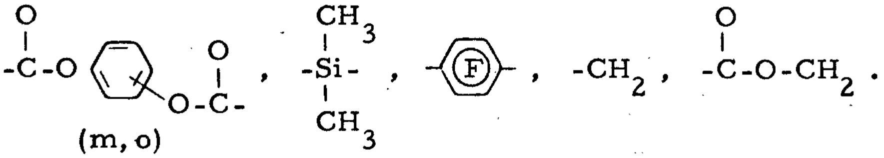
Decomposition Temperatures of Ferrocene Polymers (Ferrocene molecule and linking units are listed separately for convenience)

		$T_{dec}(N_2)(°C)$
	 $-Si(C_6H_5)_2-$	410
"	 $-C(=O)-$	410
"		400
"		370(p) 300(m) 250(o)
"	--	350
"	 $-Si(CH_3)_2-$	340
"		340
"	$-CH_2-$	330
"	 $-C(=O)-O-CH_2-$	280

The table indicates a $T_{dec}(N_2)$ of 350°C for polyferrocene. Its stability seems to be enhanced by some in-chain moieties, such as



and decreased by others, such as



A TGA curve of a polyferrocene is shown in Figure 10.

Source of samples:

AFML

7. P-O AND P-N POLYMERS

A limited number of polymers containing P-O and P-N linkages have been investigated. The results are shown in Table 8.

While the P-O system seems to be very stable (see first polymer in Table 8), the spiro unit reduces the stability considerably. This is in agreement with earlier findings (Reference 7). The cycloaliphatic moiety further reduces the stability.

The P-N polymers are distinctly lower in stability than the P-O polymers. This became quite apparent when comparing the following two polymers from Table 8.

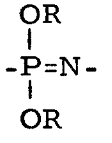
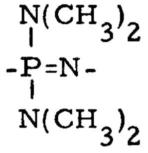
	$T_{dec}(N_2)(°C)$
 $-\overset{OR}{\underset{OR}{P}}=N-$	370-420
 $-\overset{N(CH_3)_2}{\underset{N(CH_3)_2}{P}}=N-$	190

TABLE 8

Decomposition Temperatures of P-O and P-N Polymers

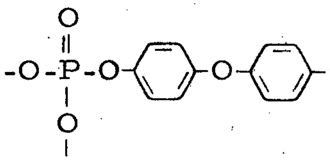
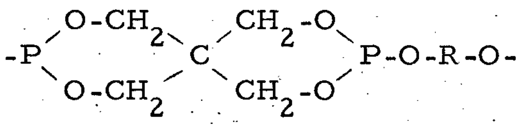
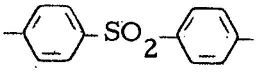
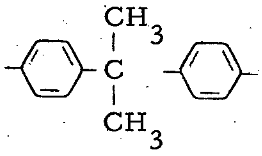
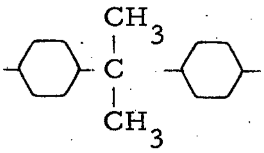
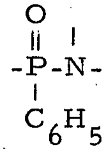
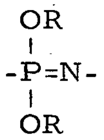
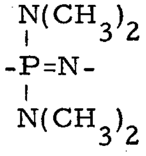
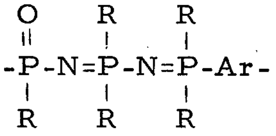
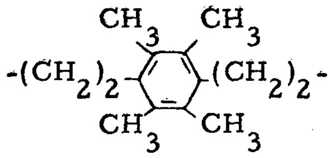
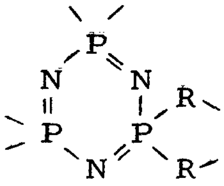
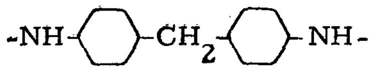
	$T_{dec}(N_2)$(°C)
probably 	510
	
R:	
	350
	350
	215
 $-\underset{C_6H_5}{\overset{O}{\overset{\parallel}{P}}}-\overset{\vert}{N}-$	270-340
 $-\underset{OR}{\overset{OR}{P}}=N-$	370-420
 $-\underset{N(CH_3)_2}{\overset{N(CH_3)_2}{P}}=N-$	190
 $-\underset{R}{\overset{O}{\overset{\parallel}{P}}}-N=\underset{R}{\overset{R}{P}}-N=\underset{R}{\overset{R}{P}}-Ar-$	400-460

TABLE 8 (Concluded)

	$T_{dec}(N_2)(°C)$
R = alkyl, fluoroalkyl or aryl	
Ar = phenylene, biphenylene, diphenylene-methane	
or 	
	
R: $-NH(CH_2)_6NH-$	180
	220

The last system in Table 8, also with P linked exclusively to N, has the same low order of stability.

The majority of the P-N polymers have a second breakdown step between 790 and 890°C, possibly caused by the breakdown of the P-N ring system (which, in the linear P-N polymers, may have formed by a secondary reaction).

TGA curves of a P-O polymer and a P-N polymer can be seen in Figures 11 and 12.

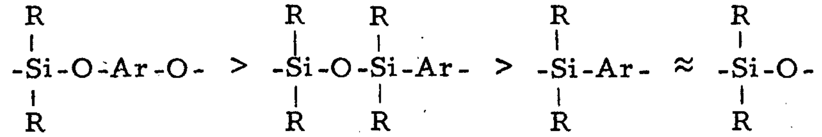
Sources of samples:

American Potash
Eastman Kodak
Monsanto
Pennsylvania State University
Shell
University of Heidelberg (Germany)
Western Chemical

SECTION III

CONCLUSIONS

The silicon-containing polymers discussed previously can be rated in the following order of stability:

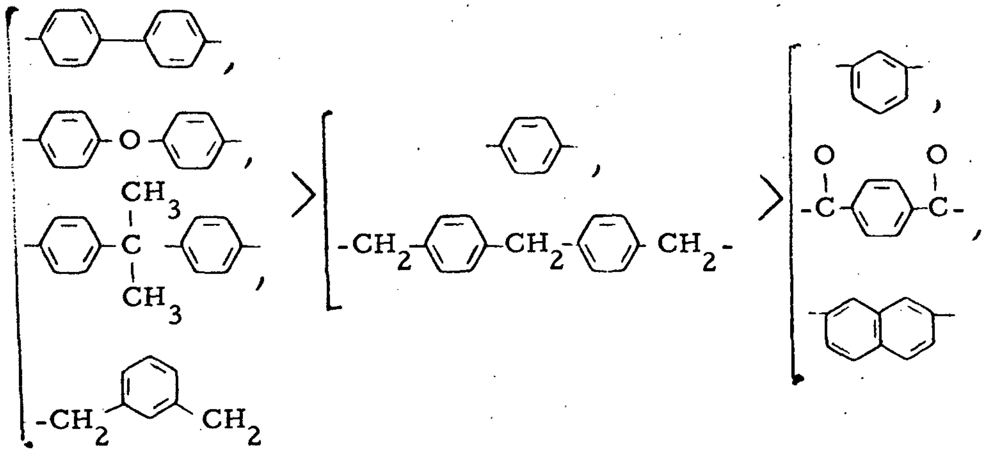


$$-\underset{R}{\overset{R}{Si}}-O-Ar-O- > -\underset{R}{\overset{R}{Si}}-O-\underset{R}{\overset{R}{Si}}-Ar- > -\underset{R}{\overset{R}{Si}}-Ar- \approx -\underset{R}{\overset{R}{Si}}-O-$$

Substituents on the silicon clearly fall into the order:

$$C_6H_5 > CH_3 > CH_2CH_2CF_3 > (CH_2)_3\,NH_2$$

while the effect of aromatic in-chain moieties on the thermal stability is less consistent. These moieties can be roughly divided into the following groups in order of decreasing stability:



In the presence of air, improved stability may be obtained with phenyl substituents on the silicon as a result of crosslinking through the phenyl groups. Polymers with methyl groups on the silicon show decreased stability in air, as these groups are oxidatively removed at higher temperatures. From the available data, it is not possible to decide whether the dimethylsiloxane or the dimethylsilazane unit is the more stable moiety.

The T_{dec} of polyferrocene was found to be 350°C. Some improvement in stability is being obtained by introducing certain aromatic moieties or the phenylsilane group into the chain.

Data on phosphorus-containing polymers show that the P-N bonds are considerably less stable than the P-O bonds.

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3. George C. Marshall Space Flight Center (NASA), Annual Summary Report NAS 8-11837 (1966).

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5. R. E. Burks, J. D. Byrd and J. E. Curry, Insulation Materials 115 (1966).

6. G. F. L. Ehlers, AFML-TR-74-177, Pt. II (1974).

7. G. F. L. Ehlers, AFML-TR-74-177, Pt. I (1974).

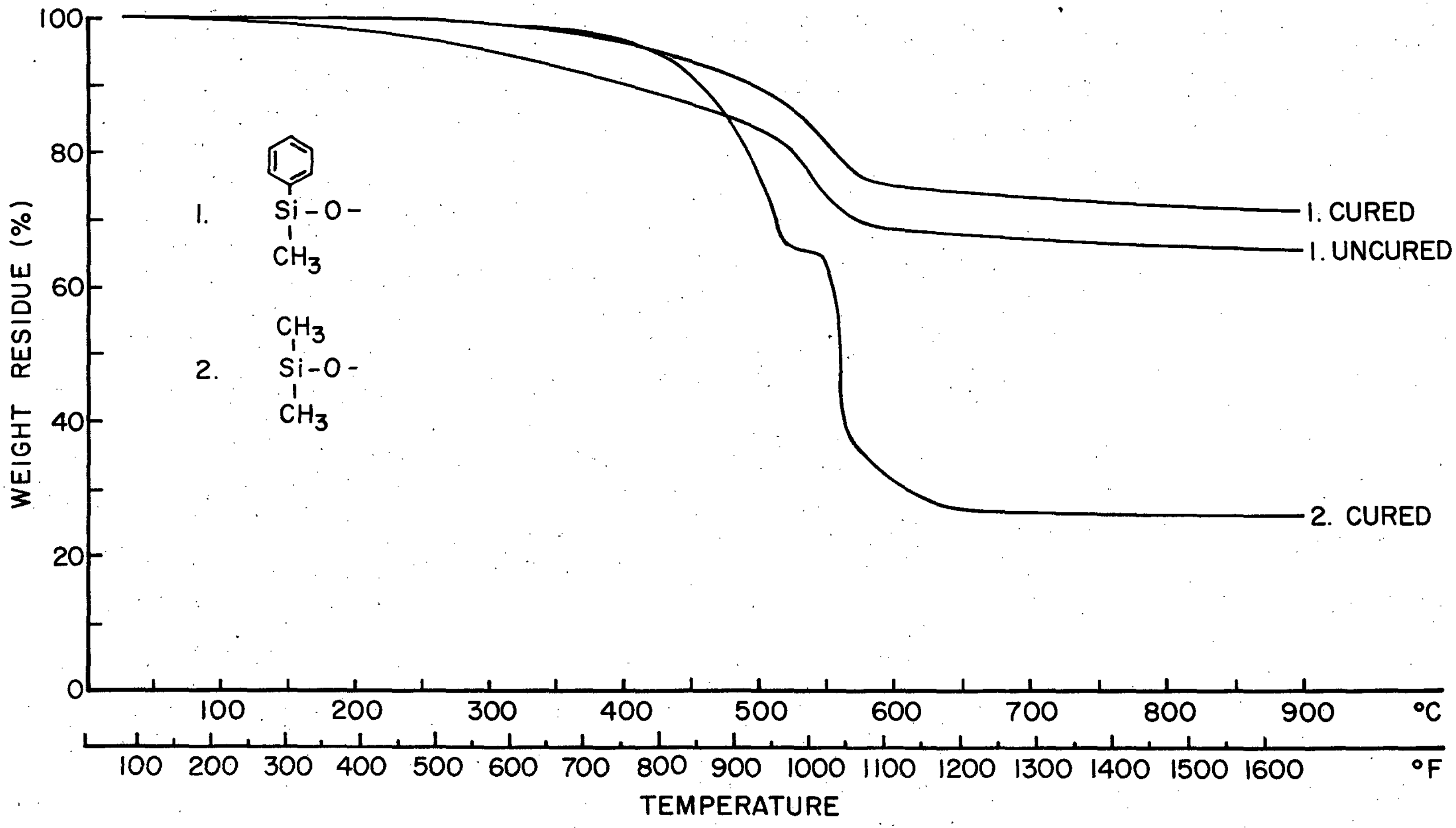

Figure 1. TGA Curves of Siloxane Elastomers

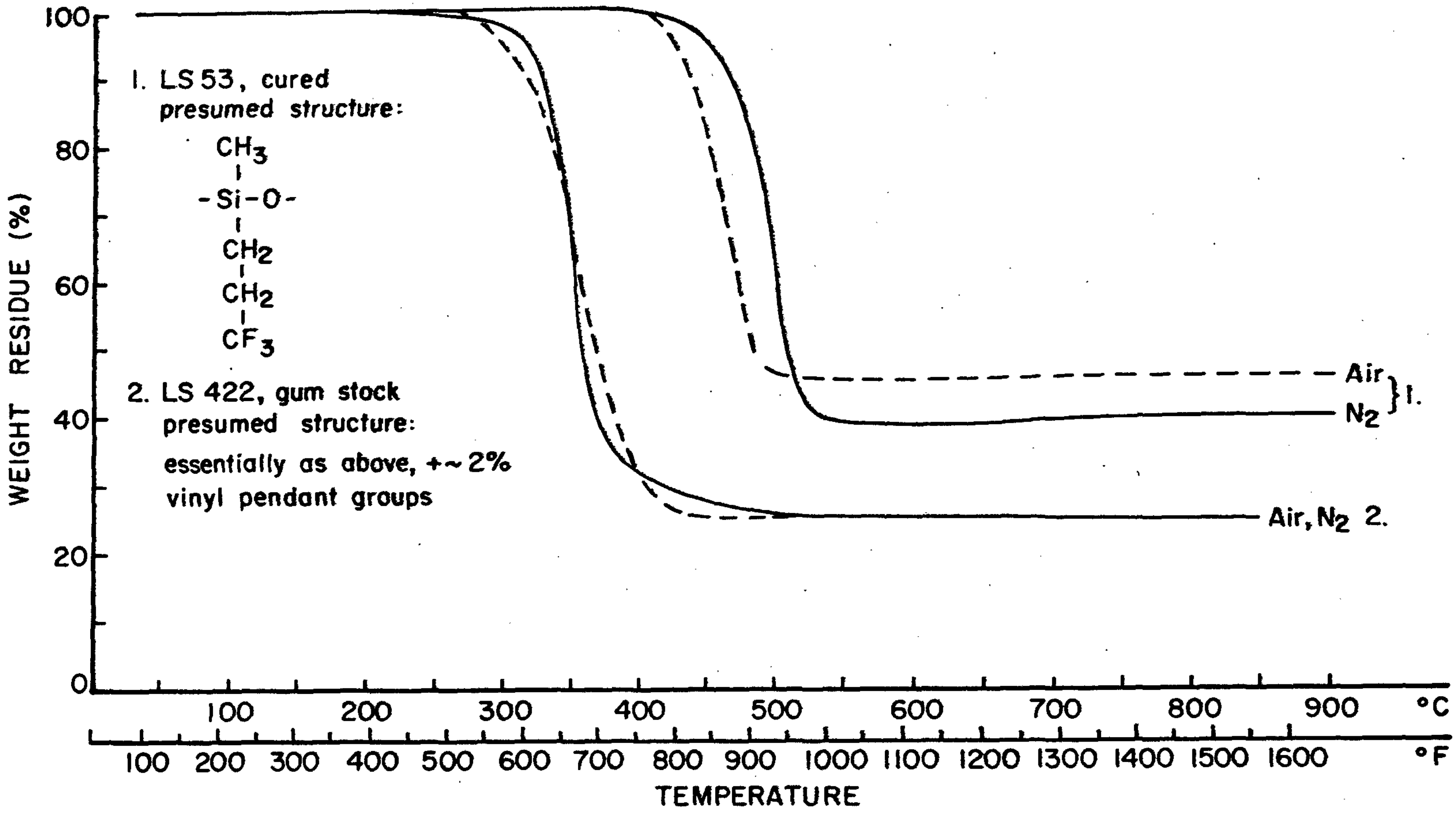

Figure 2. TGA Curves of LS-53 and LS-422

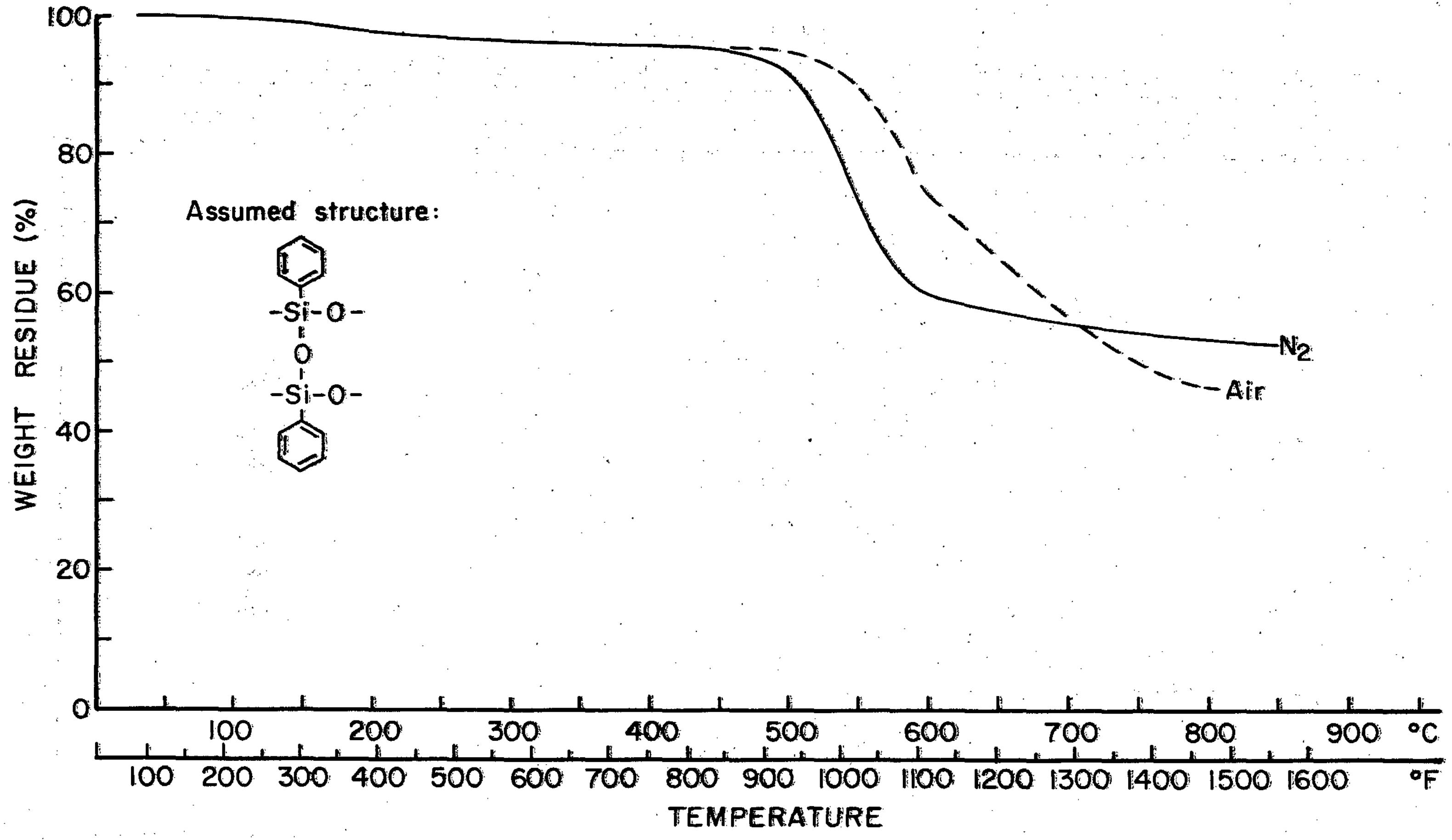

Figure 3. TGA Curves of "Phenyl-T" Polymer

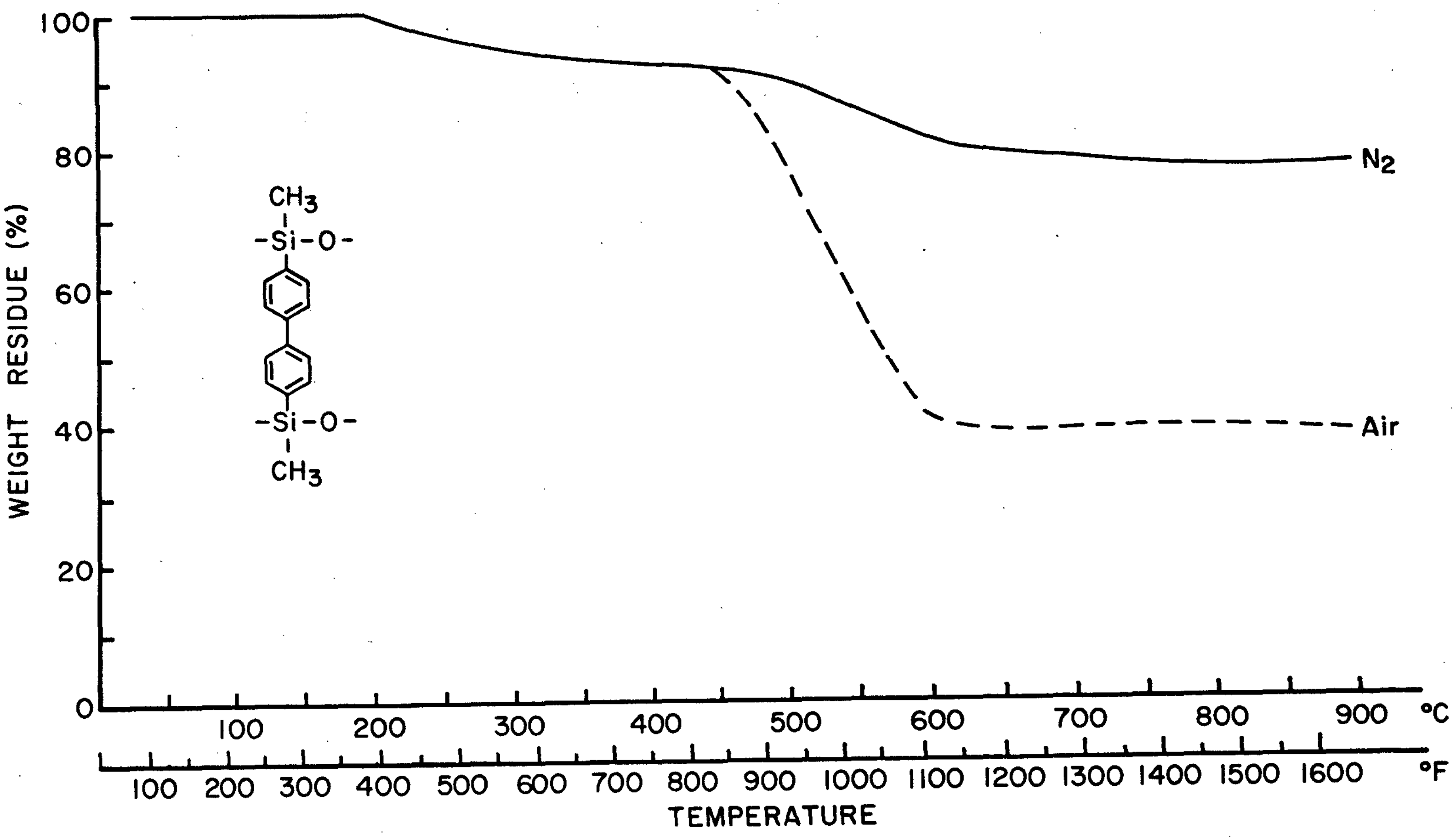

Figure 4. TGA Curves of an Arylene Bridged Polysiloxane

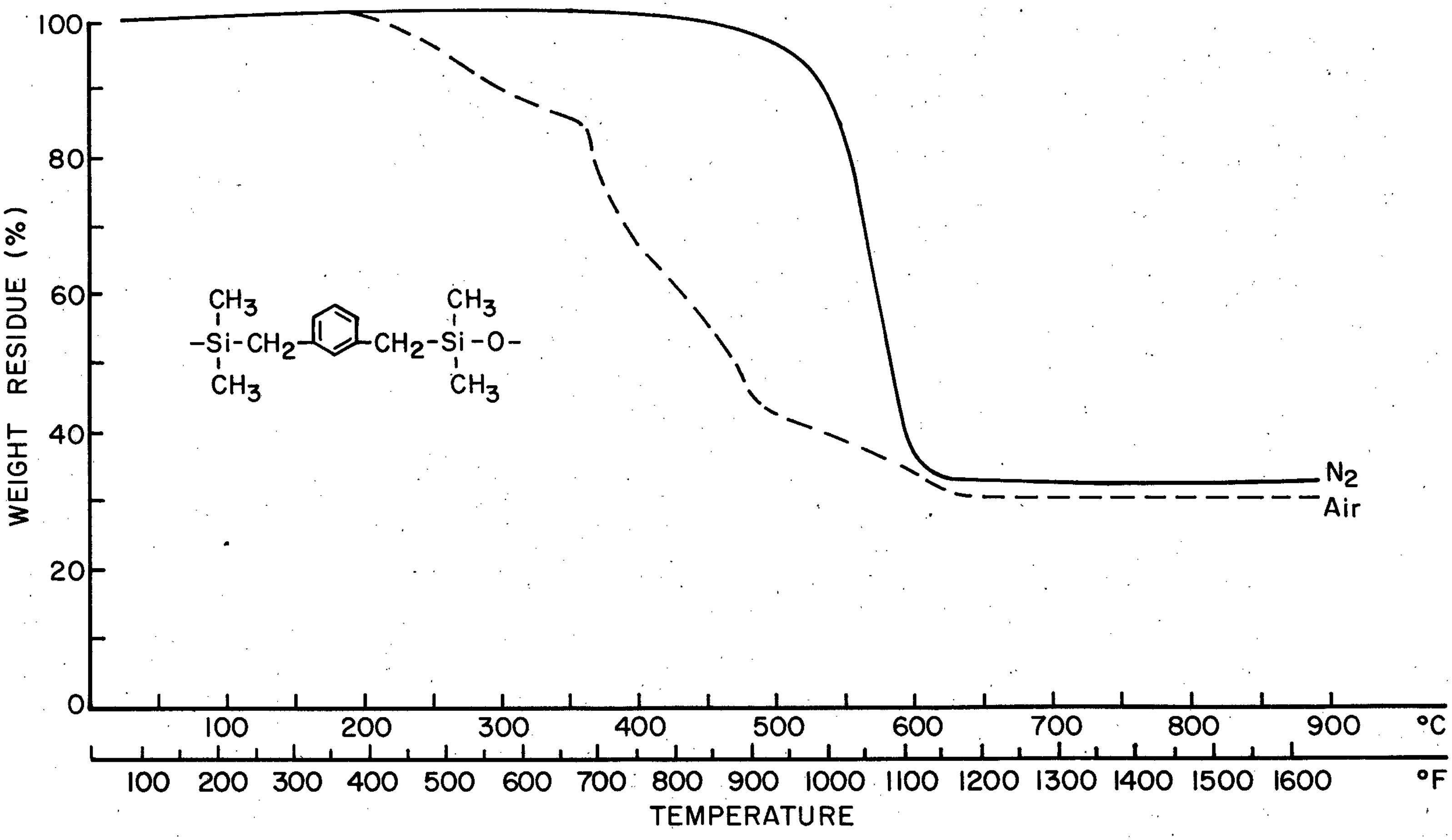

Figure 5. TGA Curves of a Polyxylylenesiloxane

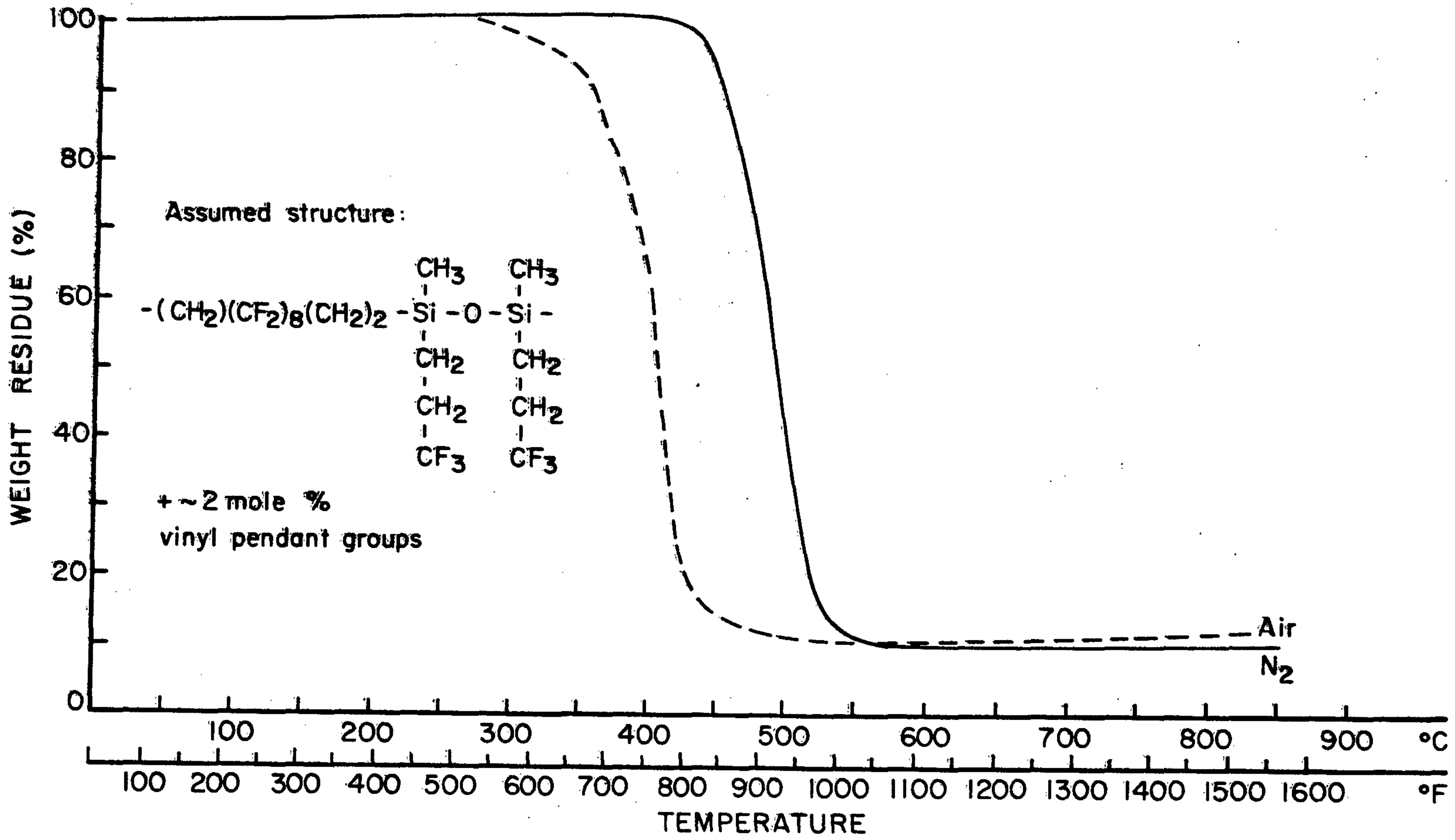

Figure 6. TGA Curves of FCS 810 Polymer

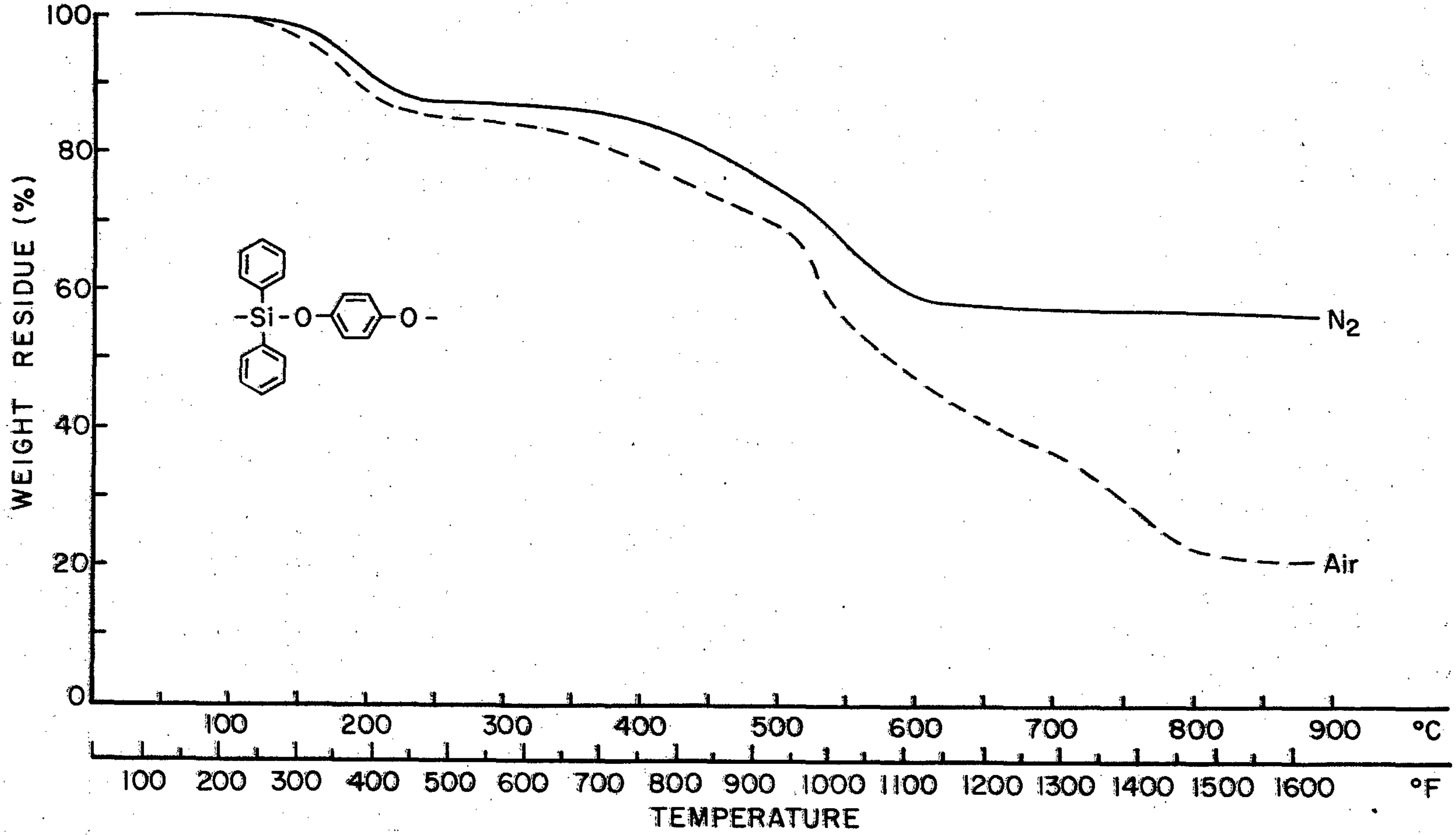

Figure 7. TGA Curves of a Polyaryloxysiloxane

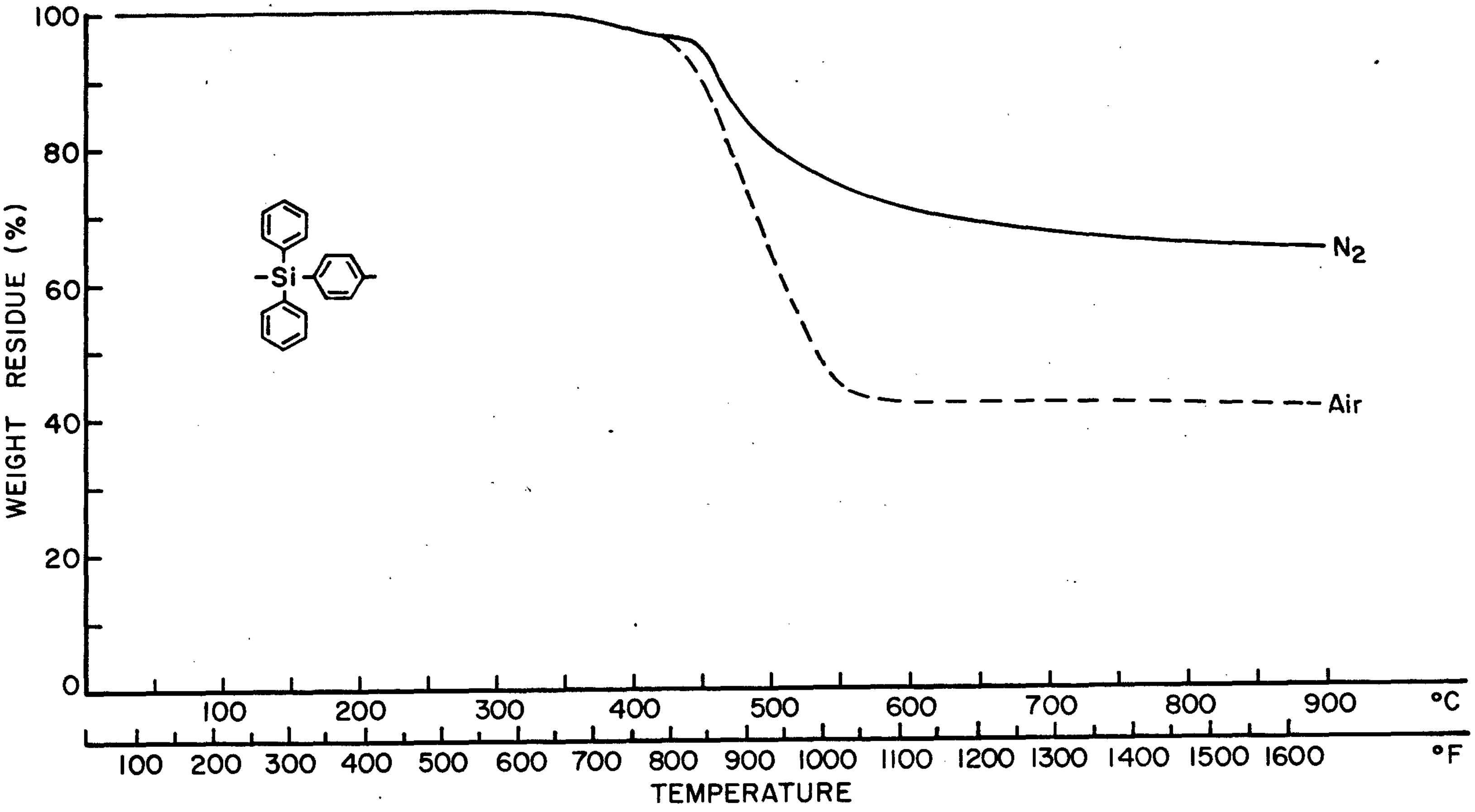

Figure 8. TGA Curves of a Polyarylenesilane

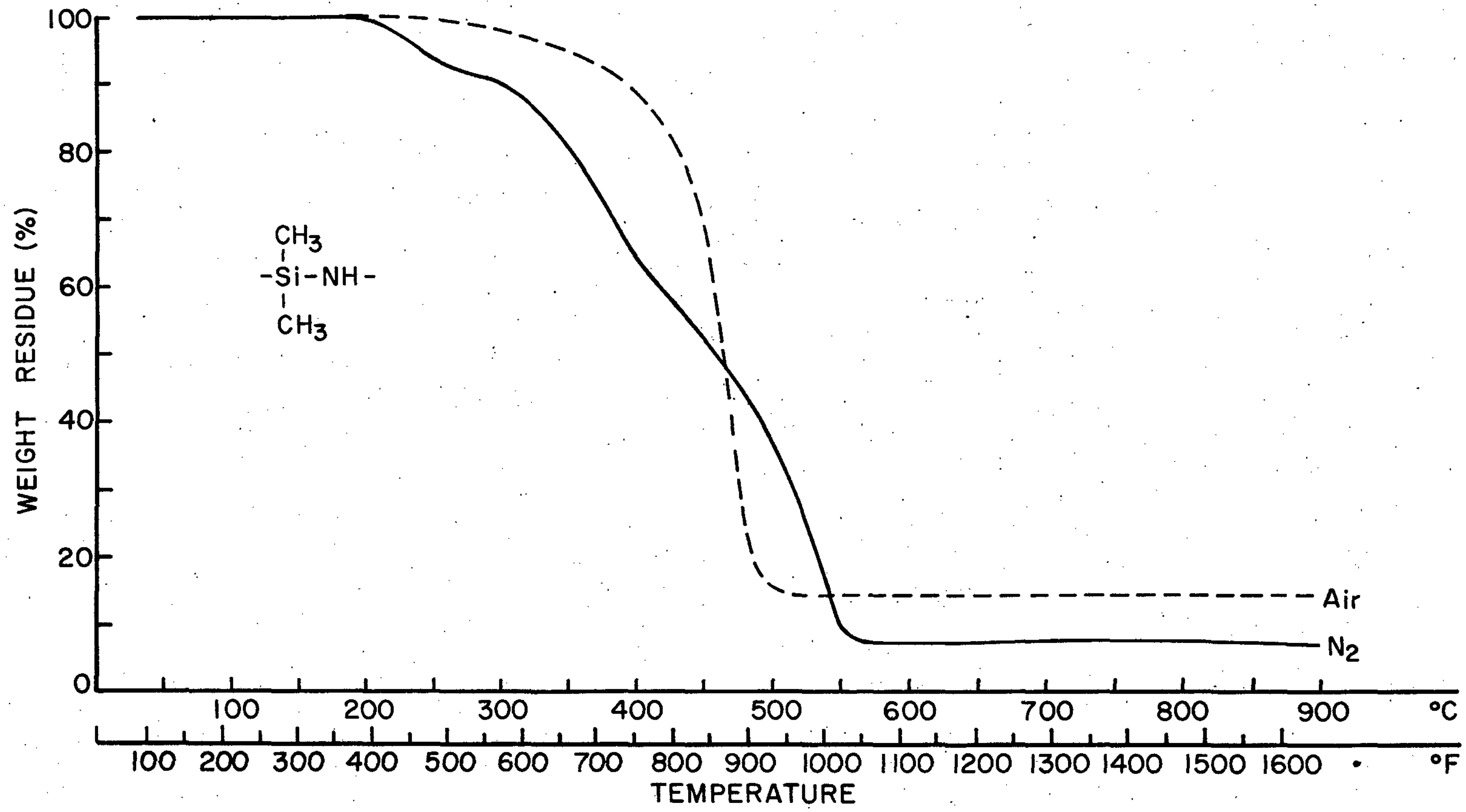

Figure 9. TGA Curves of a Polysilazane

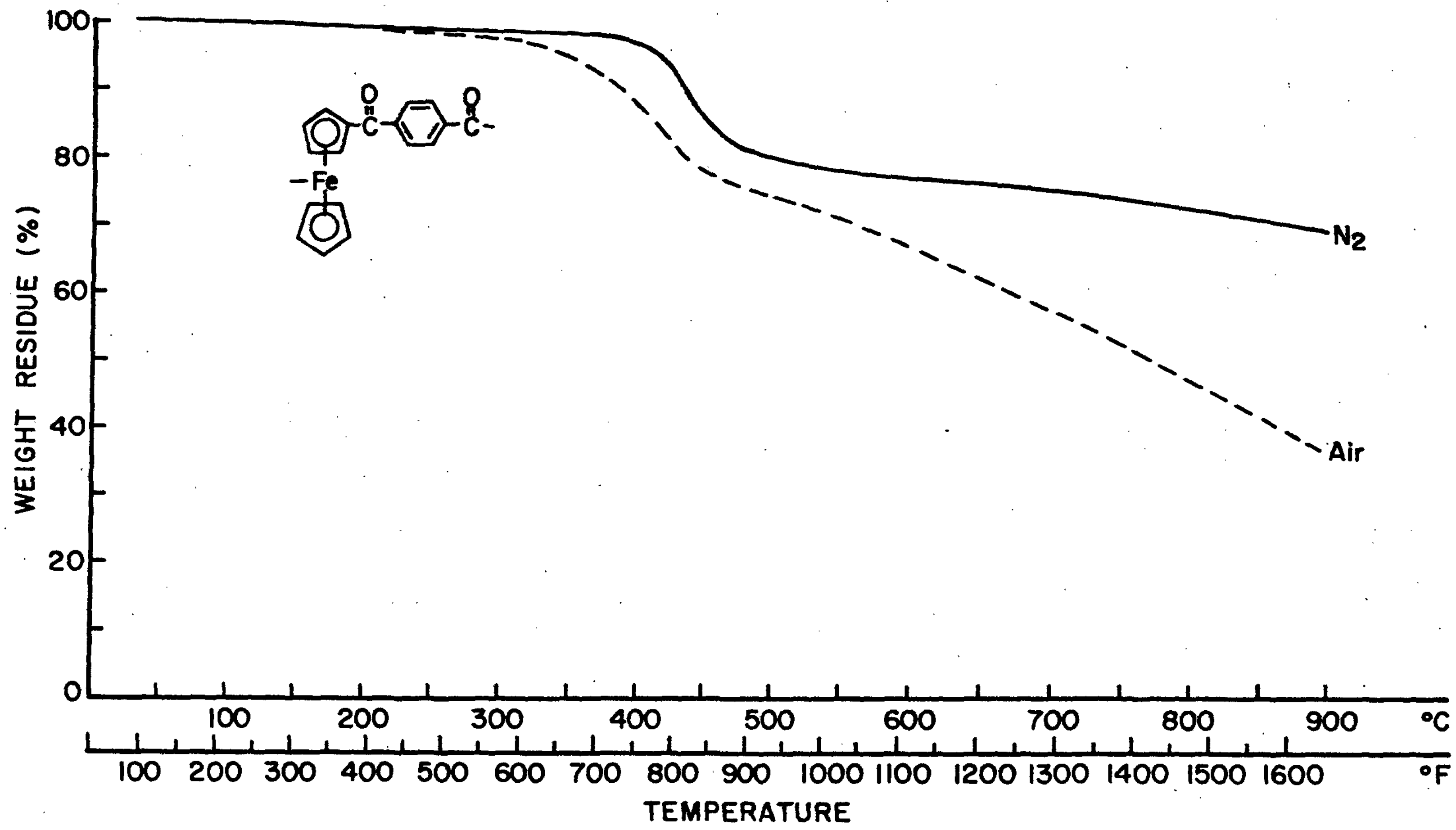

Figure 10. TGA Curves of a Ferrocene Polymer

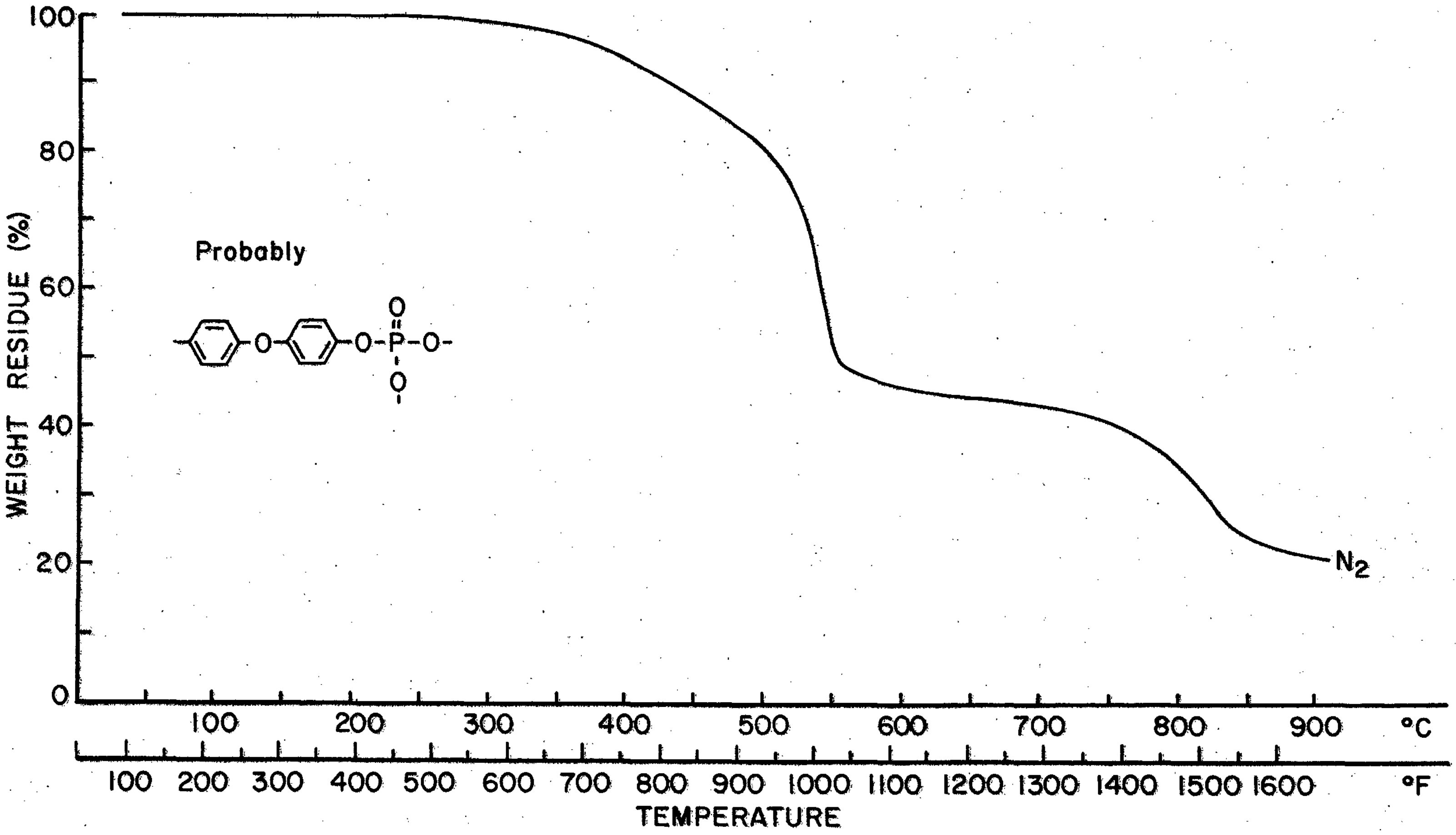

Figure 11. TGA Curve of a P-O-Polymer

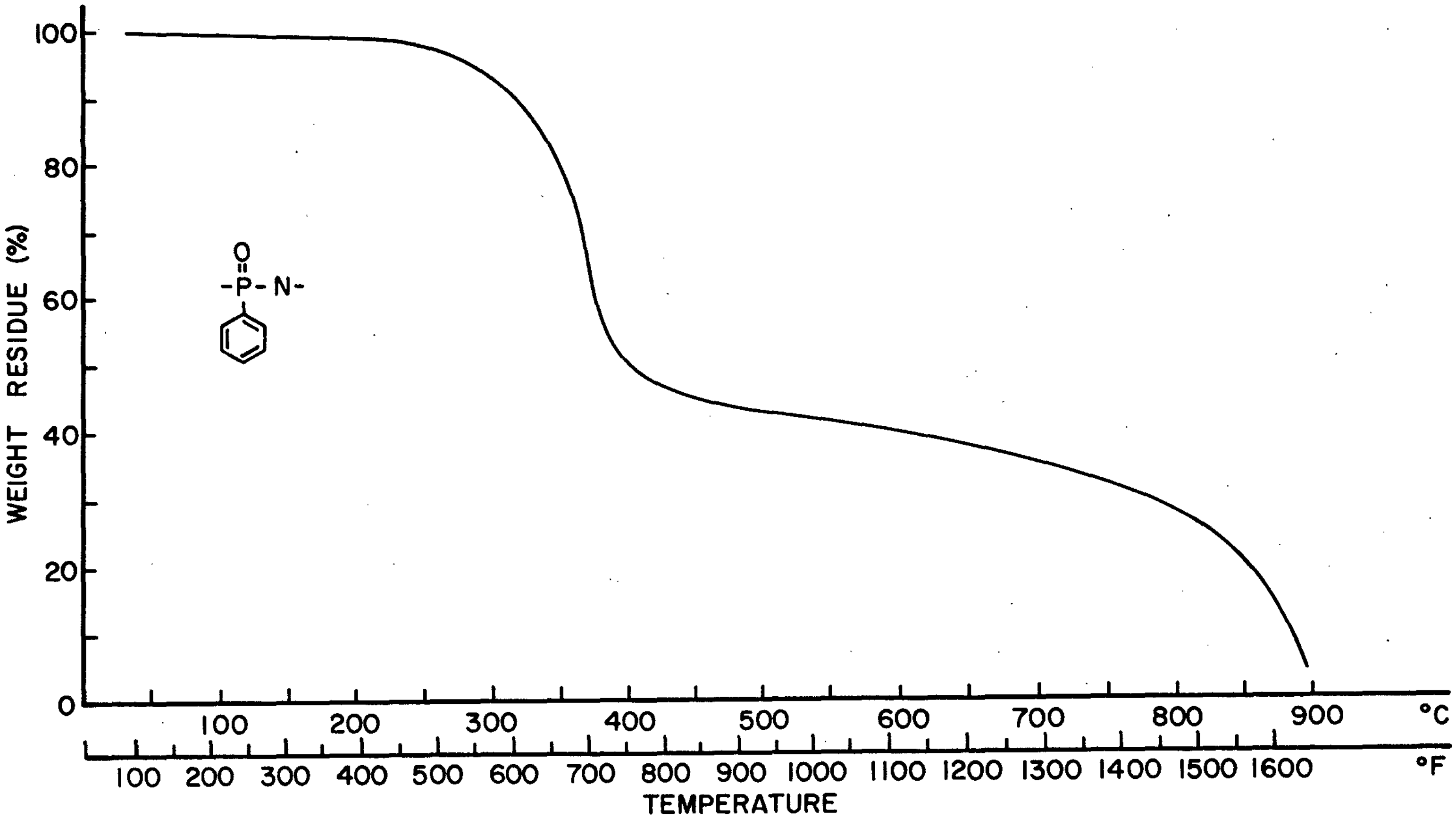

Figure 12. TGA Curve of a P-N-Polymer

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