MAR 15 1967

PROJECT U6046-7
PROGRESS REPORT

RESISTANCE OF POLYMERIC MATERIALS TO NITROGEN TETROXIDE

CALIFORNIA INSTITUTE OF TECHNOLOGY
Jet Propulsion Laboratory
Pasadena, California 91103

This work was performed for the Jet Propulsion Laboratory, California Institute of Technology, sponsored by the National Aeronautics and Space Administration under Contract NAS7-100.

IIT RESEARCH INSTITUTE

PROJECT U6046

PROGRESS REPORT

RESISTANCE OF POLYMERIC MATERIALS TO NITROGEN TETROXIDE

California Institute of Technology
Jet Propulsion Laboratory
4800 Oak Grove Drive
Pasadena, California 91103

Attn: D. D. Lawson

I. INTRODUCTION

The resistance of polymeric elastomers to nitrogen tetroxide has been examined and literature is available. (Ref. Green). This data (Table A) can be utilized in the project being conducted at IITRI. The literature, however, fails to provide an answer to the mechanism and cause of the nitrogen tetroxide attack.

It has been presumed that unsaturation provides a sight for N_2O_4 addition and consequent degradation. Saturated hydrocarbons resist degradation for some length of time. This evidence implies that there is a certain time dependent interaction of N_2O_4 with the unsaturated hydrocarbons. Also, high density polyethylene becomes embrittled after exposure to N_2O_4, while isotactic polypropylene loses its tensile strength. It is, therefore, necessary to determine whether the interaction causes:

a) Polymer chain scission or crosslinking,
b) Solvation of chains reducing interchain cohesion and crystallinity, and/or
c) New chemical entities.

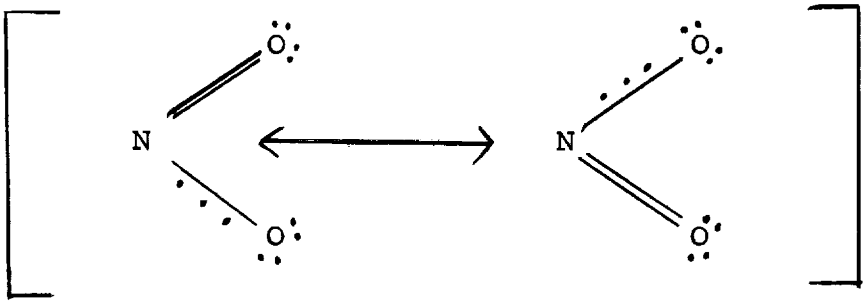
TABLE A

(Ref. J. Green)

RESISTANCE TO NITROGEN TETROXIDE
(Strong Oxidizer)

A. **EXCELLENT** Fluorinated	(Teflon TFE (Teflon FEP (Kynar (Some Nitroso rubbers
B. **SHORT TERM RESISTANCE** Saturation	(Saturated hydrocarbon elastomers (Some). (Polypropylene, Polyethylene
C. **SWELL OR DISSOLVE** Functional Groups: Amide Chlorine Groups	(Nylon (Acrylonitrile-butadiene-copolymers (Polychloroprene (Chlorosulfonated polyethylene (Hypalon) (Viton A (Kel-F
D. **HARDEN, EMBRITTLE** Unsaturation Silicone Aromatic esters	(Polyethylene teraphthalate (Mylar) (Polyethylene (irradiated) (Polypropylene (long exposure) (Silicone elastomers
E. **DEGRADE** Unsaturation Silicone	(Unsaturated Hydrocarbon (Silicone elastomers

The structure of NO_2 and N_2O_4 depends on the resonance configuration in which one oxygen is held by a double bond and the other is held by a single bond plus a three-electron bond. (Ref. Sneed p. 85).



This structure implies that the unpaired electron induces the characteristics of a radical. The charge distribution, on the other hand, produces polarity and ionic interactions. Thus, it can be expected that N_2O_4 will act as a radical and as an ion source.

The N_2O_4 can dissociate heterolytically as well as homolytically.

(heterolytic) $N_2O_4 \rightleftarrows NO_2^{\oplus} + NO_2^{\ominus}$

(heterolytic) $N_2O_4 \rightleftarrows NO^+ + NO_3^-$

(nitrosium ion)

(homolytic) $N_2O_4 \rightleftarrows 2NO_2 \rightleftarrows 2NO + O_2$

<u>Addition</u> to double bonds occurs homolytically.

The dimer N_2O_4 is in equilibrium with the components NO and NO_2. These latter species are oxidizing free radicals which can add to double bonds (Sneed p. 113), even though the monomeric oxide of nitrogen, NO_2, exist mainly as the dimer N_2O_4.

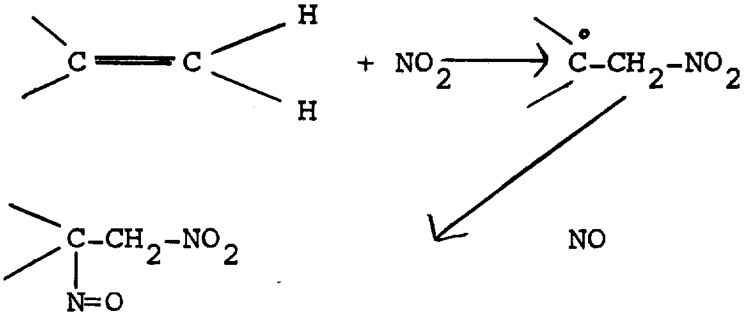
At temperatures above 150°C nitrogen dioxide begins to dissociate into nitrogen oxide and oxygen

$$2NO_2 \rightleftharpoons 2NO + O_2$$

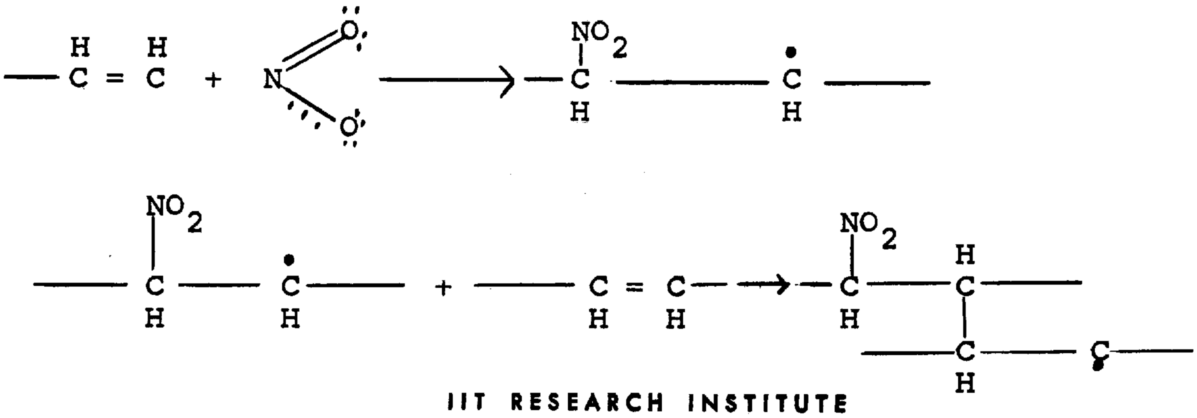
and

$$NO + NO_2 \rightleftharpoons N_2O_3$$

The NO (nitrous oxide) does not add to olefinic double bonds unless NO_2 is also present. (Waters)



<u>Crosslinking</u> of unsaturated molecules is due to radical attack. The radicals are formed from the dissociation of N_2O_4 into NO_2.



It can be seen that crosslinks are formed by carbon bonds. But there is also a chemical compound formation by the addition of NO_2. Both of these factors contribute to embrittle and harden the material with exposure to N_2O_4.

<u>Heterolytic</u> dissociation of N_2O_4 produces ions.

It is known that N_2O_4 exists in the following equilibrium (Ref. Gould).

$$N_2O_4 \rightleftharpoons NO^+ + NO_3^-$$

(nitrosium ion)

The nitrosium ion is the active species involved in nitrosation of aromatic rings.

The nitrosium ion attack would require ionic medium. This is not usually present in the exposure of fuel bladders to N_2O_4. However, traces of water and hydrazine may be sufficient to induce nitrosation of aromatic structures.

It has been found (Table B) that ethylene-propylene and butyl rubbers cured with phenolic resins resist N_2O_4 degradation better than those cured with sulfur. This might tend to indicate that nitrosium attack on the phenolic component does not cause degradation, while oxidation of sulfur linkages induce chain breakage.

An even more interesting observation involves the resistance of butyl rubber which has been postcured, i.e. heated 16 hrs. at 300°F. It is to be presumed that heat treatment induces structural orientation (possibly crystallization) of the chains rather than chemical changes.

In this project we intend to examine these possibilities of interaction, crosslinking and structural variations, in order to establish the mechanism which determines the resistance

TABLE B

EFFECT OF CURING MATERIAL
(Ref. Green)

ETHYLENE -- PROPYLENE RUBBERS,

Curing Agent	Resistance to N_2O_4
Peroxide	3 days at 70°C
Phenolic Resin	Greater resistance
Sulfur	Worse

BUTYL RUBBERS

Curing Agent	Resistance to N_2O_4
Phenolic Resin	30 days at 70°F
Sulfur or) p-Quinone Dioxime)	Degrades fast
Postcured 16 hrs. at 300°F	Superior (7 days at 100°F)

and susceptibility of polymeric materials to N_2O_4.

Three methods will be employed. First, the mechanical changes in strength are being determined by creep measurements. Second, permeability (as a function of temperature) of materials to N_2O_4 will be determined in order to establish the thermodynamic parameters of permeation mechanism. Third, infrared and other spectroscopic methods will be utilized to determine the chemical changes under the N_2O_4 exposure.

II. MATERIALS

It has been proposed to examine a variety of commercially available materials with emphasis on correlating the results with the structure. The determination of which structures are susceptible and which resist N_2O_4 attack will be utilized in establishing the mechanism of the attack.

The material groups to be studied are listed in Table C. Those which have been obtained are listed in Tables Cl and C2. The polymeric samples which have been requested from suppliers are listed in Table C3.

III. METHODS

A. Creep Measurements

The mechanical properties of polymeric materials depend on their molecular weight, morphology, crosslinking and other structural parameters. The polymeric structure is such that several mechanisms of stress accommodation can operate at any particular time during the test (Fig. 1). However, immediately after the application or release of stress the <u>covalent bonds respond</u> in anologous manner to that of a spring. That is, the stress induces an elongation proportional to the applied load. After a certain period of time, the visoelastic forces, or retarded elongation mechanism sets into operation. This mechanism involves the uncoiling and mobility of <u>chain segments</u>. Presence of crystallinity or

TABLE C

POLYMERIC STRUCTURES FOR PROPOSED STUDY
(December 28, 1966)

1. Natural Rubber
   - a) Cured with Sulfur (Goodyear)
   - b) Cured with peroxide (Goodyear)
2. Butyl Rubbers -- differing in their degree of unsaturation (Polymer Corporation)
3. Ethylene -- Propylene terpolymer rubbers differing in their degree of unsaturation (U. S. Rubber)
4. Butadiene -- Styrene Rubbers -- differing in certain yet unspecified molecular parameters, but also reflecting different curing times and/or recipes (Polymer Corporation)
5. Butadiene -- Acrylonitrile Rubbers
   - a) Commercial offerings will be from Polymer Corporation and U.S. Rubber Co.
   - b) Specimens differing in acryllonitrile content from 11 and 65% (B. F. Goodrich)
   - c) Cyanacryl -- (American Cyanamid)
   - d) Nitrile Rubbers with and without polyvinyl chloride (U.S. Rubber)
6. Polyurethane Rubbers
   - a) Commercial specimens from Goodyear
   - b) Commercial specimens peroxide cured (U.S. Rubber)
   - c) Commercial specimens sulfur cured (Thiokol)
7. Polyalkylene Sulfide Rubbers (Dunlop)
8. Polydisulfide Rubbers -- differing in their "rank" (Thiokol)

9. Rubbery Block Copolymeris -- differing in their molecular weights and segment size and frequency

10. Polyacrylate Rubbers -- (Thiokol)

11. Neoprenes -- commercial offerings of DuPont and American Cyanamid (not yet defined)

12. Fluorocarbons -- commercial offerings of Allied Chemical (not yet defined)

13. Hydrogenated Polybutadiene Rubbers -- differing in degree of unsaturation (Phillips Chemical)

TABLE C1

POLYMERS BEING TESTED

Material	Trade Name	Source
Polysiloxane		Delaware Res. & Dev. Corp.
Polyphenylene Oxide	PPO	G. E.
Poly(fluoroethylene-propylene)	FEP	DuPont
Polyurethane based on polyester	Elastothane 455 (E-70953)	Thiokol
Polysulfides		Thiokol
Polyimide	Kapton	General Motors
Polyfluorethylene	TFE	Allied

TABLE C2

POLYMERS TO BE TESTED

Material	Trade Name	Source
Polyethylene		Phillips
Polyethylene		
Ethylene-butene copolymer		Petroleum Co.
Ethylene-butadiene copolymer		
Terpolymer of ethylene, propylene, dicyclopentadiene	Royalene	U.S. Rubber
Polyurethane (sulfur cured)		
Polyurethane	Cyanoprene	American Cyanamid
Polyacrylic	Cyanocryl	American Cyanamid
Polyacrylonitrile (differing in content)	Hycar	B. F. Goodrich
Polyalkalene sulfide		Dunlop
Natural Rubber C-C crosslinks polysulfide crosslinks monosulfide crosslinks	) various) samples) differing in) cure times	The Goodyear Tire Company
Fluorinated polyalkalenes (double coated teflon tape)		Quantum Inc.
Chlorotrifluorethylene (Amorphous homopolymer)	Kel F-8112	3 M

Table C2 (contd.)

Material	Trade Name	Source
Copolymer (CTFE-VF) Chlorotrifluoroethylene and vinylidene fluoride (crystalline)	Kel F-8205	3 M
Copolymer of CTFE and VF in various ratios	Kel F	3 M
	Fluorel	

TABLE C3

SAMPLES REQUESTED

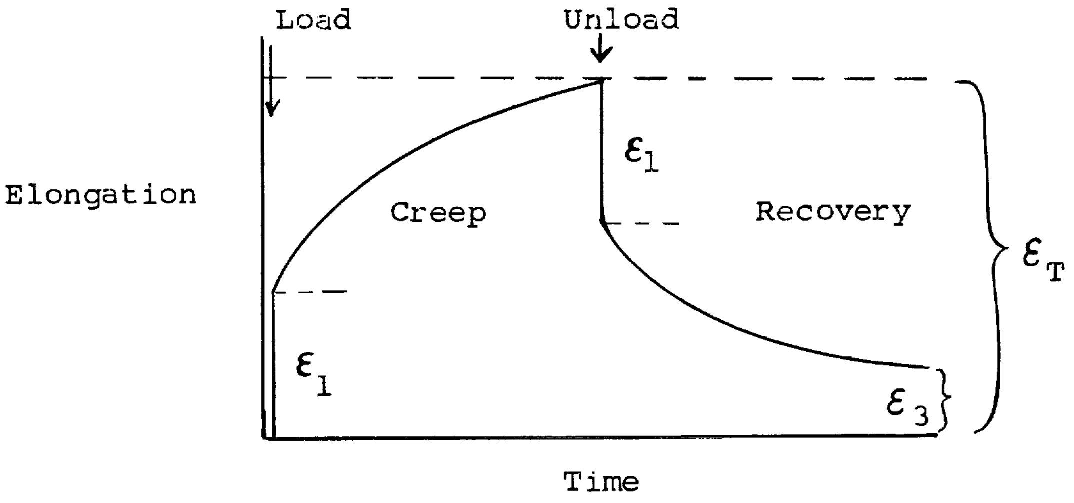
Material	Trade Name	Source
Butadiene-acrylonitrile (with various levels of co-polymerized acrylonitrile and various levels of crosslinking	--	Polymer Corporation
Butyl Rubber	--	Polymer Corporation
Butadiene-Styrene copolymer	--	Polymer Corporation
Modified polyphenylene oxide	Noryl	General Electric
Fluorinated	Viton	Industrial Fiber and Pump Mfg. Co.
Natural Rubber	--	Industrial Fiber and Pump Mfg. Co.
Neoprene	--	Industrial Fiber and Pump Mfg. Co.
--	Buna N	Industrial Fiber and Pump Mfg. Co.
Chlorosulfonated Polyethylene	Hypalon	Industrial Fiber and Pump Mfg. Co.
Neoprene	--	DuPont
Fluorinated	Viton A	DuPont
Fluorinated (vinylidene fluoride-hexafluoropropylene)	Viton B	DuPont
Polymer of ethylene-propylene terpolymer	Nordel	DuPont
Furane Polymer	--	Furane Plastic

Table C3 (cont.)

Material	Trade Name	Source
Polyurethanes	--	Goodyear
Chlorotrifluoro ethylene	Plascon	Allied
Fluorinated Polymer	Kynar	Penn Salt
Nitrile Rubbers	--	U.S. Rubber
Nitrile Rubber Polyblended with polyvinyl chloride	--	U.S. Rubber

chain orientation will control the extent of elongation in this second phase.

Finally, the chains begin to slide past each other inducing viscous flow. This is irreversible and can best be detected by the residual elongation after the stress has been released. This mechanism can be correlated with the chain scission and changes in crosslinking. Thus, a material which under exposure to N_2O_4 undergoes chain scission will exhibit a much larger irreversible elongation than before exposure. On the other hand, if crosslinking has been induced by any of the active species, the irreversible elongation will be smaller after exposure.



$$\varepsilon_{Total} = \varepsilon_1 + \varepsilon_2 + \varepsilon_3$$

ε_1 = instantaneous elongation; inversily proportional to elastic modulus

ε_2 = retarded viscoelastic elongation; dependent on time

ε_3 = irreversible elongation due to viscous flow

B. Permeation Measurements

Permeation of various materials is a useful tool in establishing structural characteristics. If the experiments are carried out with an interacting gas, such as N_2O_4, it becomes possible to determine the degree of chain scission, crosslinking or compound formation which occurs during the experiment.

For this purpose, we have built several permeation cells which would be useful, in that they are rather inexpensive and can be used while the permeation cells which have been ordered are obtained.

The permeation experiments will be conducted at several temperatures so that the thermodynamic properties, such as enthalpy and entropy of the permeation can be deduced. In this manner the resistance or susceptibility of materials to N_2O_4 will be determined in terms of universally meaningful parameters.

IV. APPARATUS

A. Creep Apparatus

Creep measurements are being carried out by means of an apparatus built at IITRI. (Fig. 2).

The creep-measurement apparatus is used to determine the extension of polymeric samples under load and recovery after release of the load. The extension or elongation is determined as a function of time. The polymer film specimens are attached to a rigid aluminum frame by means of clamps consisting of two pieces of aluminum with roughened inside surfaces to minimize slippage. The pulleys were attached to the frame by means of a ball-bearing axis to permit free rotation. Weights were placed on the wires extending through small holes in the bottom of the temperature control box.

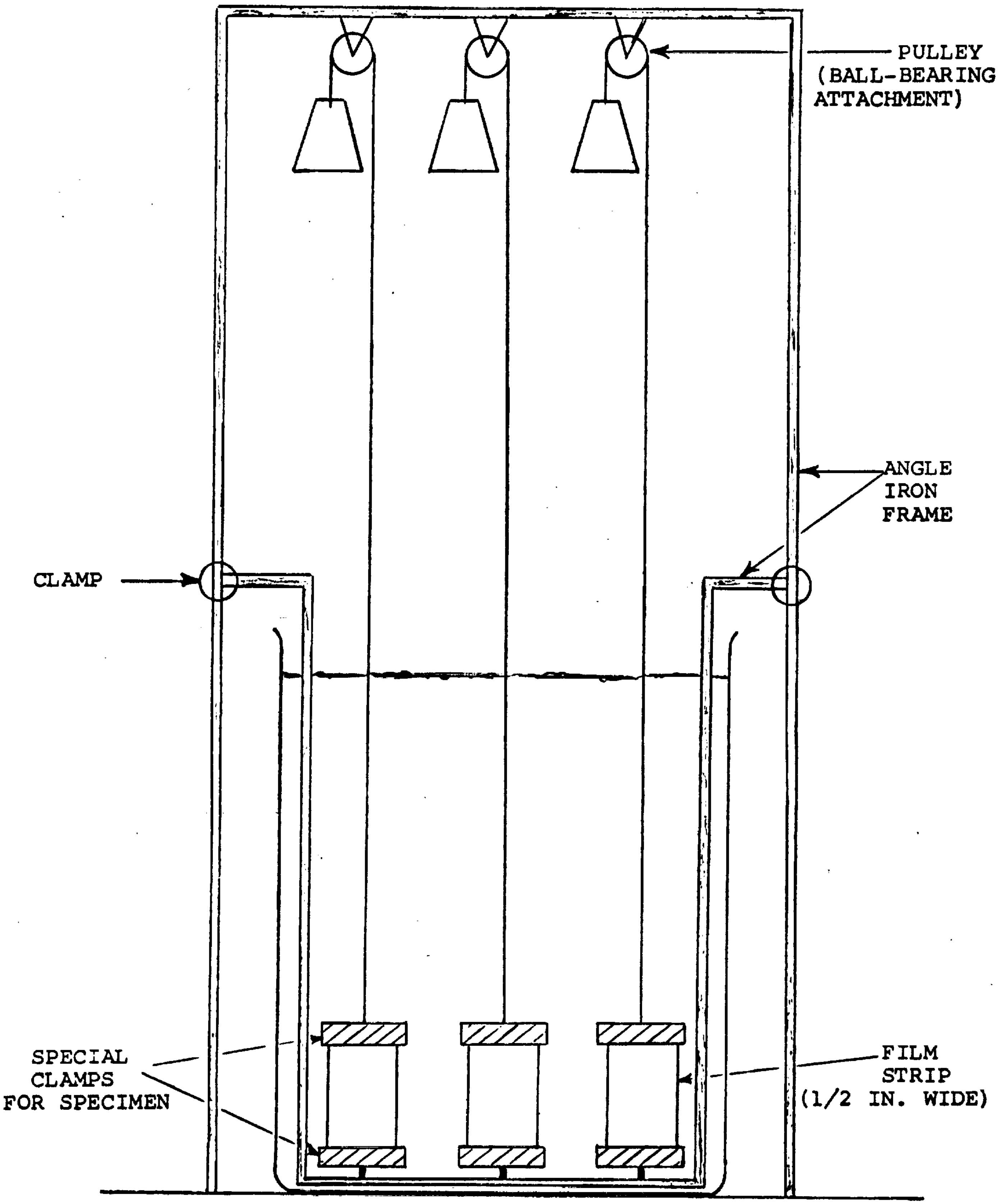


Figure 2

CREEP APPARATUS

A vertical aluminum pole cathetometer is equipped with telescopic lens. An eyepiece with a hairline marking is adjusted to coincide with the horizontal lines at the extremeties of the polymer samples. The cathetometer remains stationary for each measurement of the separation between specimen markings. It is then moved to stand directly in front of the next sample. The cathetometer vernier had 0.01-cm subdivisions. The polymer samples are about 10 cm long.

Percent elongation is calculated on the basis of the original unstressed separation between sample markings.

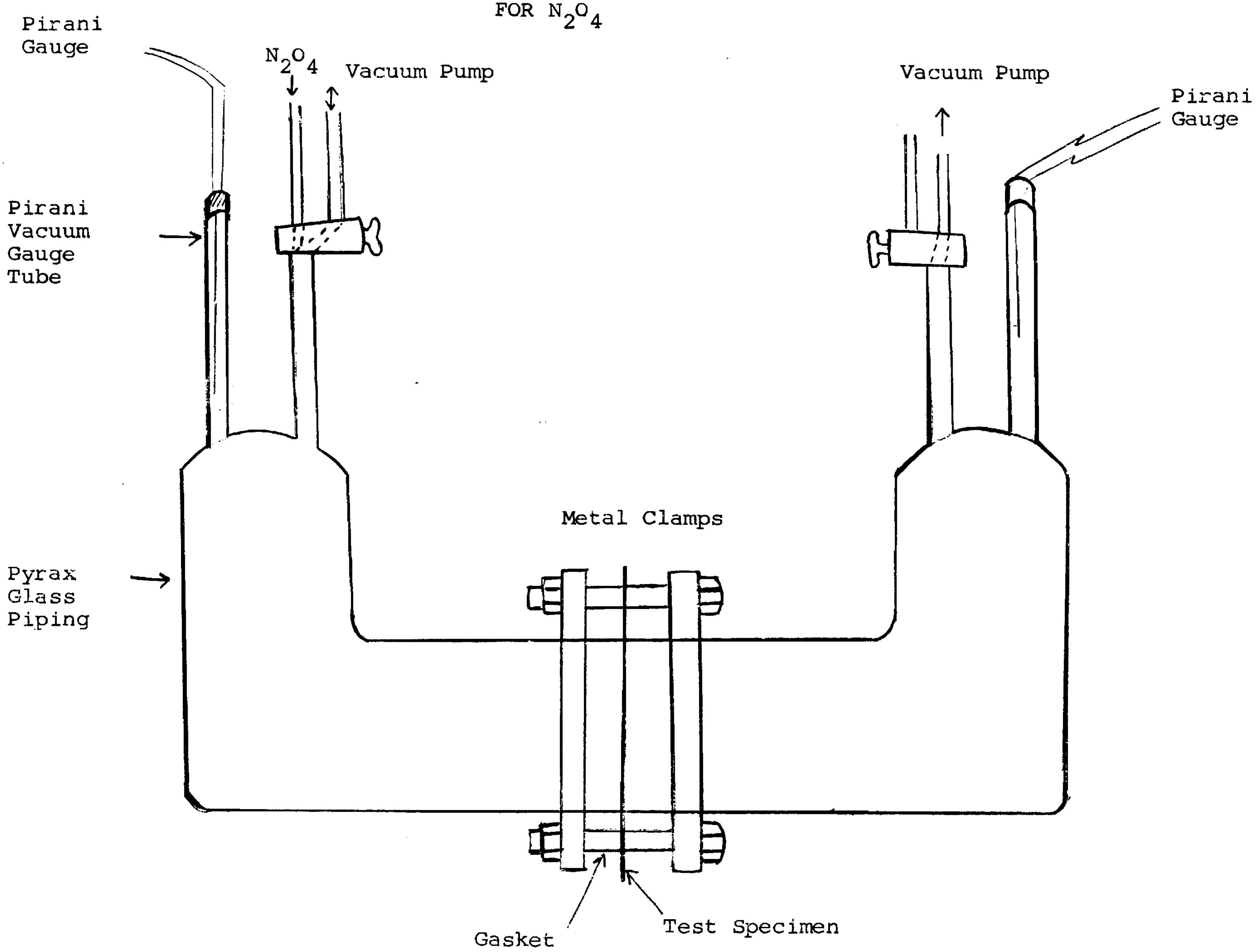
B. Permeation Cells

1. Two permeability cells have been ordered from Custom Scientific Instruments, Inc., Model CS-135. They will be delivered March 23.

2. Meanwhile several simple permeability cells have been constructed at IITRI. These consist of L-shaped pyrex glass piping joints, 1 inch in diameter, clamped by metal jaws, and equipped with vacuum, N_2O_4, and pressure gauge outlets. Both sides of the cell are evacuated and N_2O_4 is introduced into one chamber. The Pirani Autovac high vacuum gauge (range 10^{-3} to 10^{2} mm Hg) is used to detect changes in pressure as the N_2O_4 permeates through the test sample. The gauge is equipped with 4 channels, thus at least four detector tubes can be permanently in operation. (Fig. 3).

Figure 3

IITRI PERMEATION CELL
FOR N_2O_4



V. RESULTS

Creep Measurements

Several materials have been tested by measuring the creep characteristics (elongation under constant stress as a function of time).

Polysiloxane (Table 1, Figure 3) exhibits total elongation of 3% after 3000 minutes of stress, the irreversible elongation after release of stress and 3000 minutes of recovery is 2%. When the same polysiloxane material has been exposed to N_2O_4 in a previously evacuated desicator for 7 days, the elongation becomes smaller (1%) and total recovery ($\mathcal{E}_3$=0) of the former dimensions is apparent. This indicates that the polysiloxane forms a less flexible structure upon contact with N_2O_4. It may be due to crosslinking or formation of new chemical structure. This will be substantiated by spectroscopic measurements.

Polyurethane elastomer, originally cured by peroxide, exhibits a definite degradation when exposed to N_2O_4. Whereas the original irreversible elongation ($\mathcal{E}_3$) is 1.5%, the elongation after exposure to N_2O_4 is 10%. This indicates that a process of chain scission has taken place after 7 days in N_2O_4 atmosphere.

It is known that siloxane has a stable Si-O bond which is not readily broken by oxidation mechanism. While polyurethane crosslinks and structure seem to offer a susceptible entity for N_2O_4 addition or radical type of degradation. The exact chemical reactions involved will be determined by spectroscopic measurements.

FEP (fluorinated ethylene propylene) exhibits little if any alteration with 7 day exposure to N_2O_4. It may be, however, that even here some crosslinking is taking place because there is a small contraction ($\mathcal{E}_3$ = -0.2) with exposure.

TABLE 1

CREEP RESULTS AT 25°C

	Not Exposed to N_2O_4		Exposed N_2O_4	
	ε_T^*	ε_3	ε_T	ε_3
Polysiloxane	3.0	2.0	1.	0
Polyurethane (Elastothane 455)	11.5	1.5	20.	10
FEP (fluorinated, ethylene propylene)	0.5	0	0.5	-0.2

*NOTE: Elongations (ε) given in %.

ε_T = total elongation with 500 psi, 3000 minutes

ε_3 = irreversible elongation, 3000 minutes of relaxation

References

1. J. Green, "Resistance of Polymers to Rocket Propellants". Encyclopedia of Polymer Science and Technology, Vol. 3, pp. 687-689, (1966)

2. E. S. Gould, "Mechanism and Structure of Organic Chemistry, H. Hold & Co., N. Y., p. 427 (1959)

3. M. C. Sneed, R. C. Brasted, "Comprehensive Inorganic Chemistry, Van Nostrand, (1956), pp 72, 113

4. W. A. Waters, "Mechanism of Oxidation of Organic Compounds", (1964) p. 26

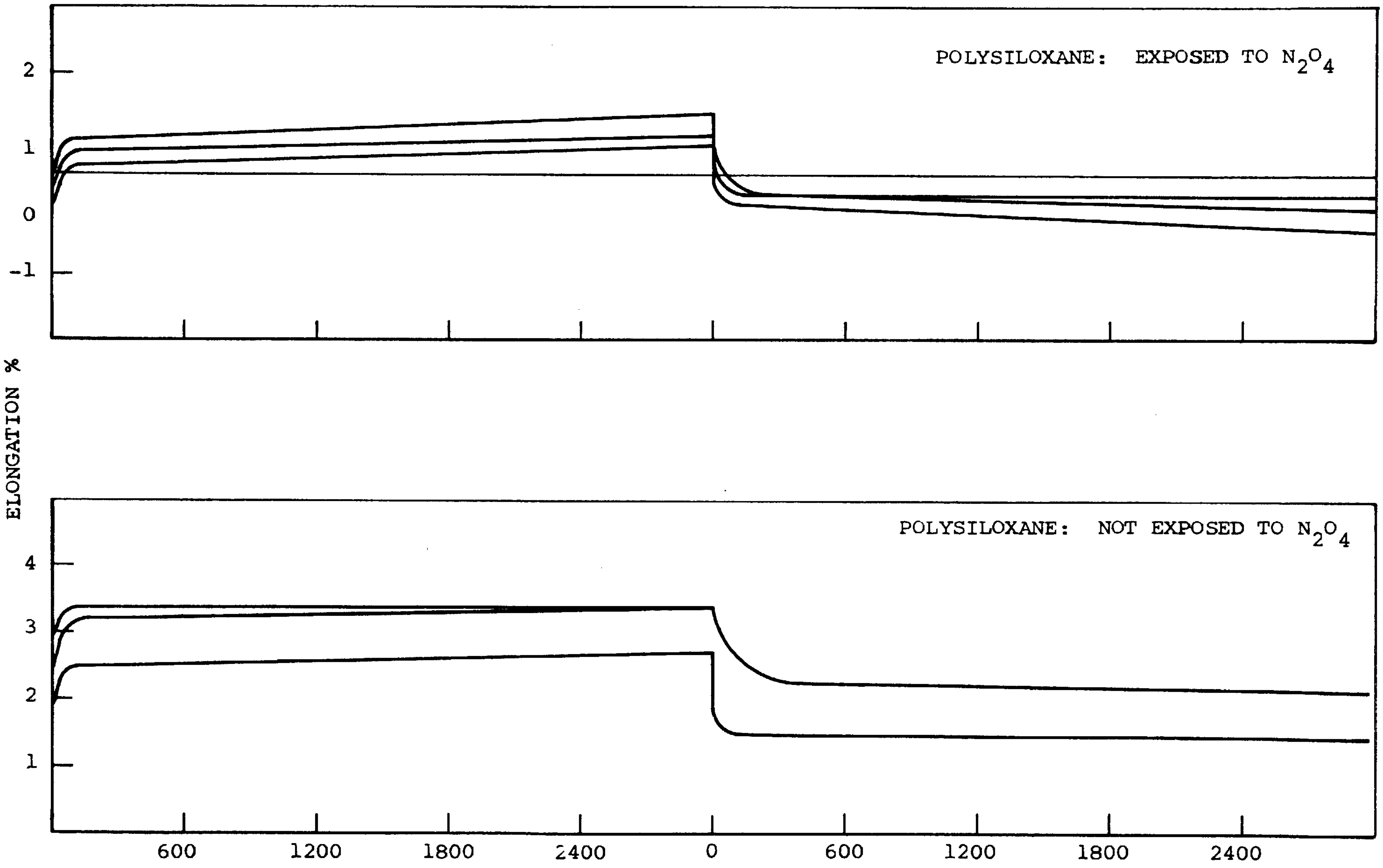


Figure 3
TIME (MINUTES)

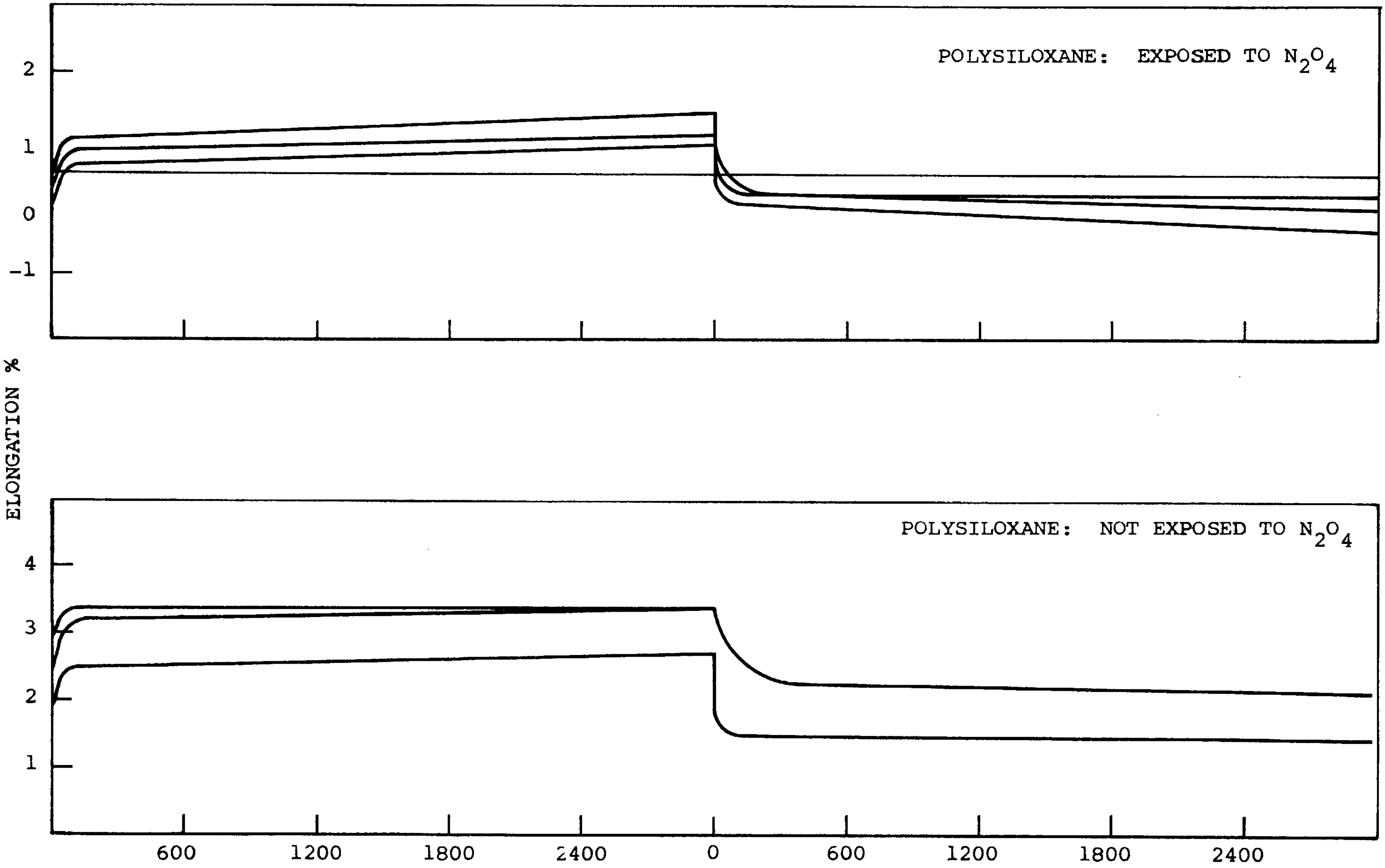

POLYSILOXANE: EXPOSED TO N_2O_4
2
1
0
-1
ELONGATION %
POLYSILOXANE: NOT EXPOSED TO N_2O_4
4
3
2
1
600
1200
1800
2400
0
600
1200
1800
2400
TIME (MINUTES)

Figure 3

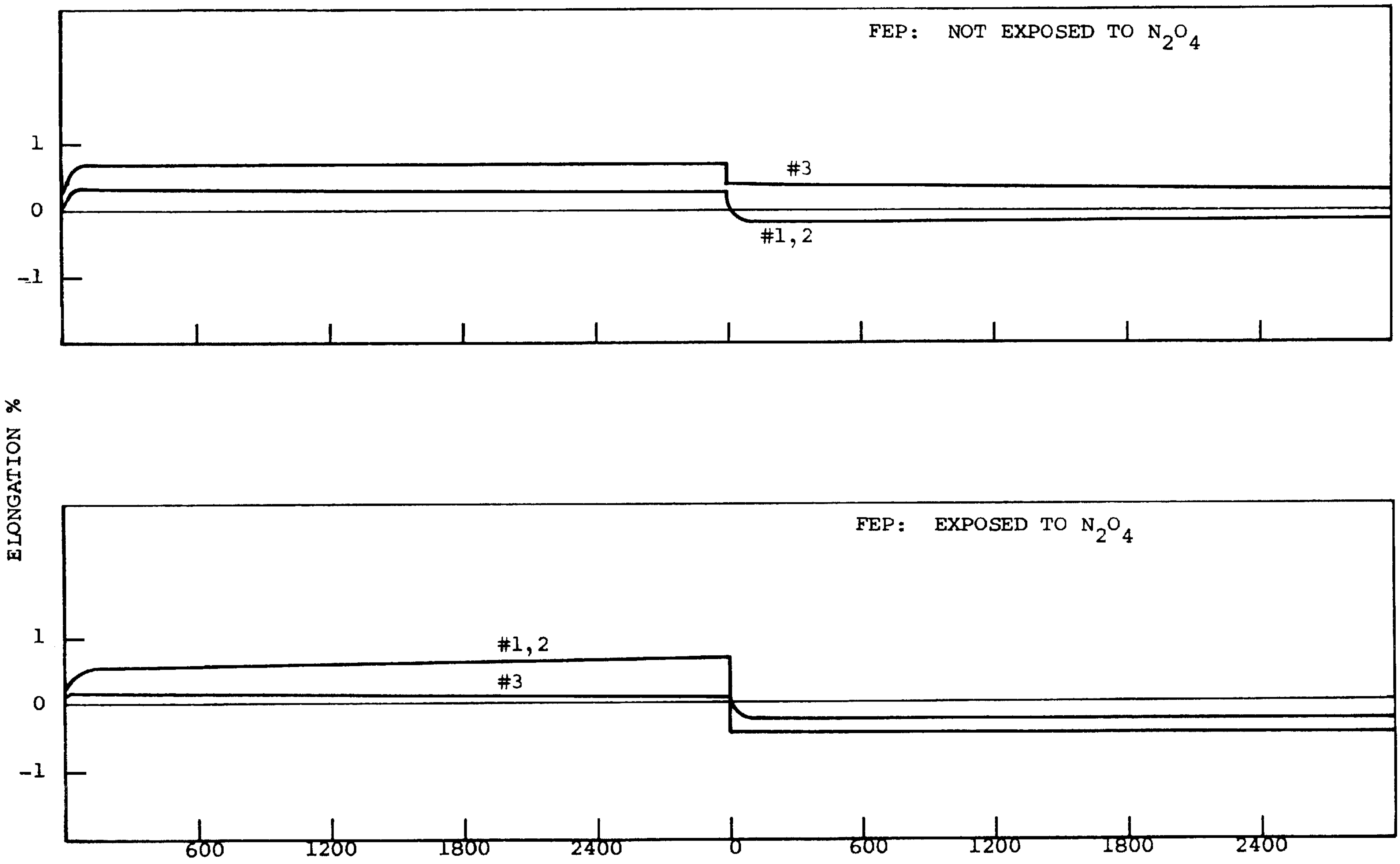

FEP: NOT EXPOSED TO N_2O_4
1
0
-1
#3
#1,2
ELONGATION %
FEP: EXPOSED TO N_2O_4
1
0
-1
#1,2
#3
600
1200
1800
2400
0
600
1200
1800
2400

Figure 4

TIME (MINUTES)

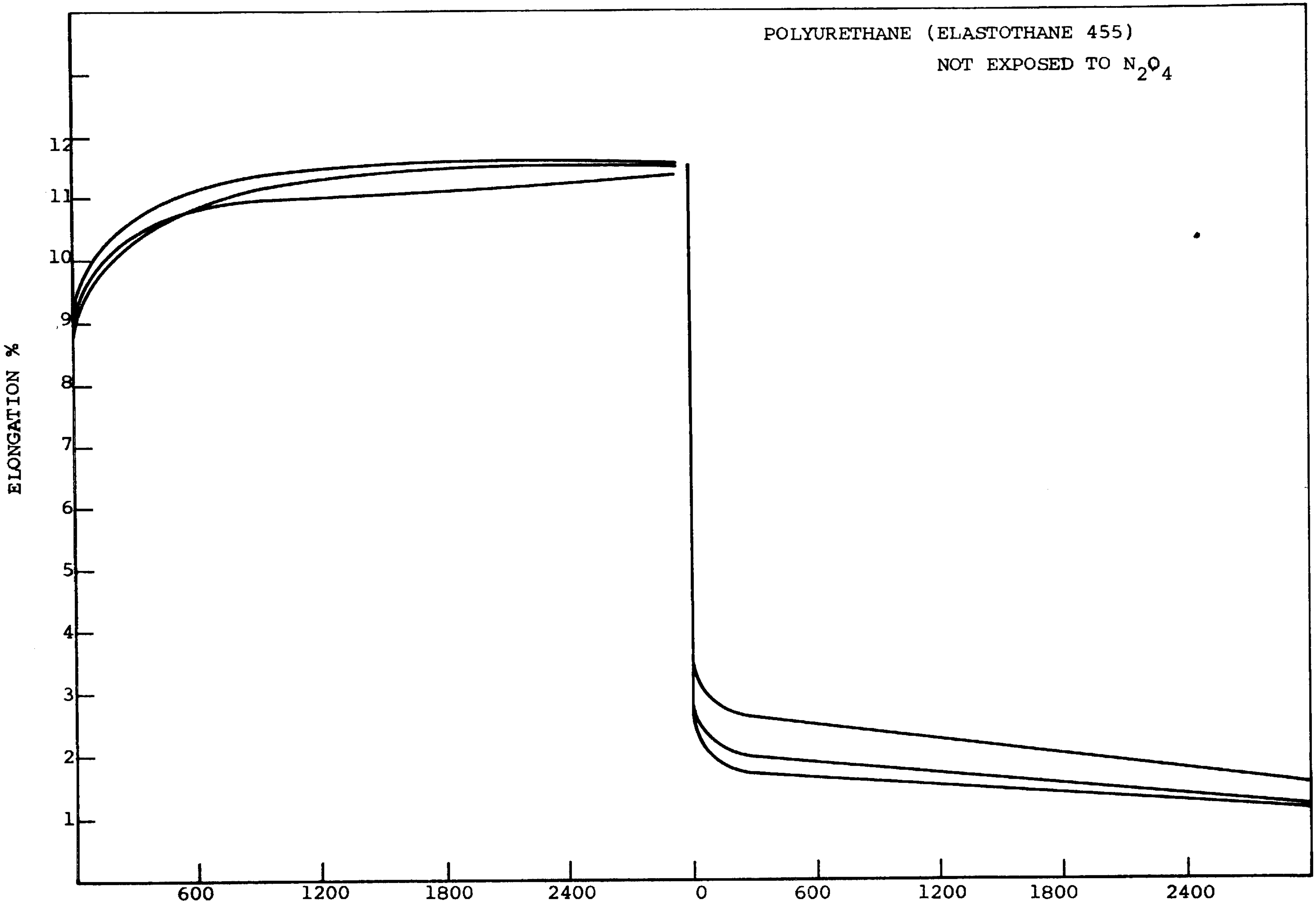


Figure 5
(TIME MINUTES)

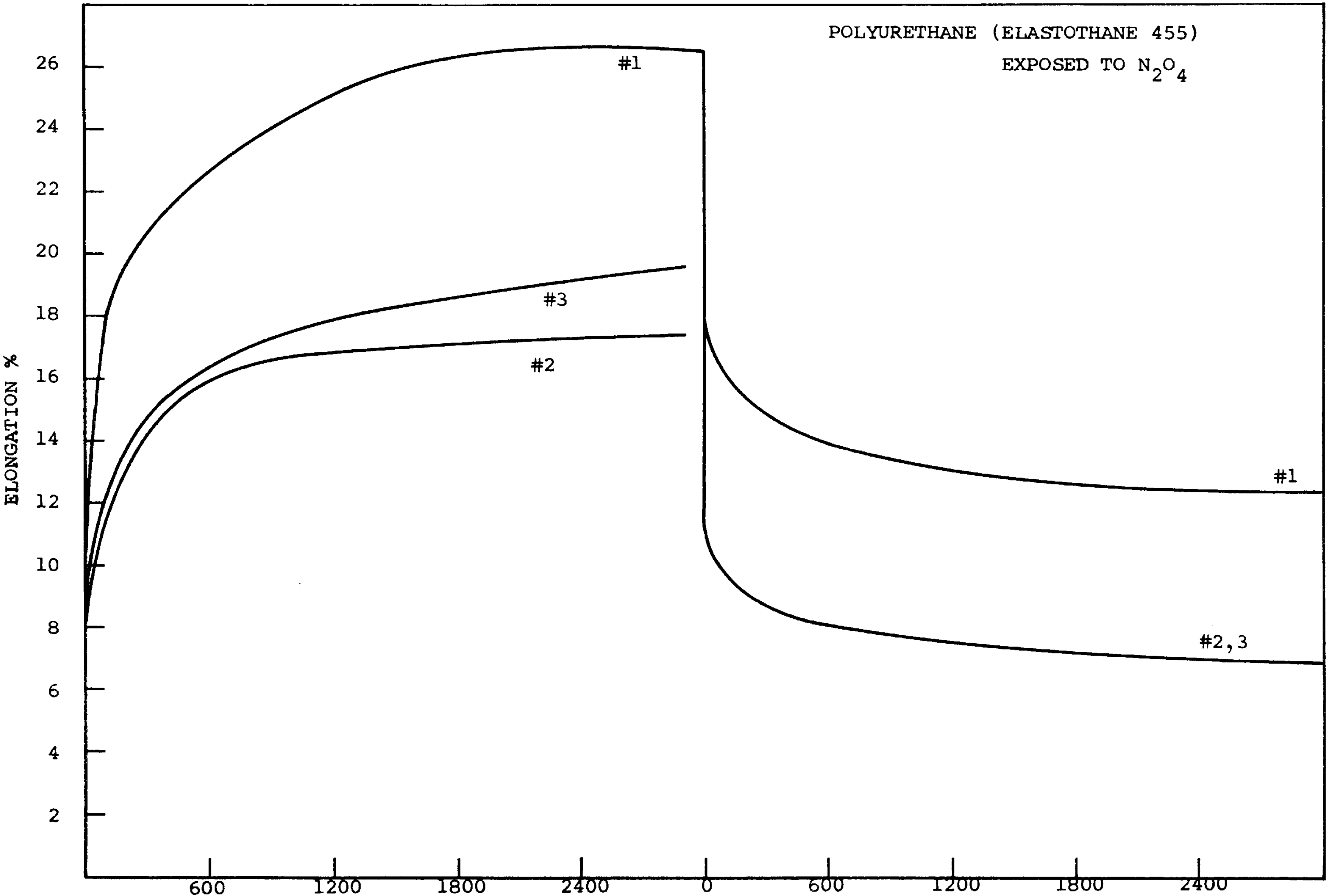


Figure 6
(TIME MINUTES)

Respectfully submitted,
IIT RESEARCH INSTITUTE

a. M. Stake

A. M. Stake
Research Chemist
Polymer Research

Approved:

T. H. Meltzer
Manager
Polymer Research

DISTRIBUTION LIST

Copy No.________

Copy No.	Recipient
1-25 + Reproducible	Jet Propulsion Laboratory California Institute of Technology 4800 Oak Grove Drive Pasadena, California Attention: Mr. R. C. Bartlett Senior Contract Negotiator
26	IIT Research Institute Division U Files
27	IIT Research Institute B. A. Murray
28	IIT Research Institute D. J. McPherson, J. I. Bregman
29	IIT Research Institute Editors, E. H. Schulz, Main Files
30	IIT Research Institute T. H. Meltzer, Manager Division U
31	IIT Research Institute A. M. Stake Division U