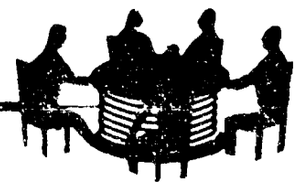
THE EFFECTS OF SPACE ENVIRONMENTS ON INSULATION OF TEFLON® TFE AND FEP RESINS



by

C. E. Jolley
Plastics Department

J. C. Reed
Plastics Department

E. I. du Pont de Nemours & Co. (Inc.), Wilmington, Delaware

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PLASTICS DEPARTMENT, E. I. DU PONT DE NEMOURS & CO. (INC.) WILMINGTON 98, DELAWARE

A copy of the paper "The Effects of Space Environments on Insulation of Teflon" TFE and FEP Resins" is enclosed. The paper has been revised to conform to the presentation on November 30 at the Signal Corps Wire and Cable Symposium. The format and the data on electrical properties of TFE and FEP exposed to radiation have been revised to present the data in more complete and concise form.

It is suggested that you destroy the copy of this paper you received during the symposium.

THE EFFECTS OF SPACE ENVIRONMENTS ON INSULATION OF TEFLON® TFE AND FEP RESINS

By

C. E. Jolley and Joseph C. Reed

Introduction

The selection of materials for use in space vehicles involves considerations not encountered in any other application. Extreme temperatures and vacuum conditions are encountered. Satellites orbiting in the Van Allen Belt are exposed to natural radiation. Future satellites having nuclear power units will add artificial radiation. The severity of the environment prohibits or limits the use of many common materials. Therefore, it is important to weigh all factors and take advantage of all available information for the selection or rejection of materials.

It is the purpose of this paper to make available to the space engineer data for "Teflon" TFE and FEP resins that are the results of unpublished work of the Du Pont Company as well as previously published work of the Du Pont Company and other laboratories. Over one hundred papers were reviewed. Most contained data of more interest to theoreticians than to the practical design engineer. The information presented here is limited to changes in the physical and electrical properties of molded or extruded items during and after exposure to radiation and/or vacuum. The theory of the chemical reactions causing these property changes has been omitted except in the simplest form. Reference 1 is an excellent paper for persons interested in the chemical changes of the polymer during irradiation.

Equipment

Vacuum

The evacuation system used in the Du Pont laboratory consisted of a mechanical roughing pump and a mercury diffusion pump connected to an evacuation chamber through refrigerated baffles and a liquid nitrogen trap to prevent possible contamination from the pump. The high vacuum region was stainless steel with all inside surfaces electropolished to minimize surface area.

The pressure was continuously monitored with a Bayard-Alpert ionization gage having the sensing element located just above the source region. A second sensing element was located at the pump intake.

As the samples were placed in the vacuum chamber, the system was pressurized with helium to reduce contamination with atmospheric air. This usually required 1 to 2 minutes.

Samples were cut from commercially available wire insulated with a "Teflon" resin. The wire was removed and approximately two grams of small cylinders, 2 to 5 millimeters long with an approximate surface area of ten square inches were used.

In starting up, the system was pumped down to a pressure of about 10^{-4} mm Hg. The temperature was then raised to, and maintained at, 100°C. for the duration of the test.

Periodically, samples of the evolved gases were analyzed with a mass spectrometer.

Discussion

Vacuum

One of the most common questions concerning the behavior of materials in high vacuum is that of evaporation or sublimation. With most non-polymeric compounds, this can be calculated by the familiar Langmuir equation. However, such calculations based on vapor or decomposition pressures are not usually useful for the polymeric materials of interest here and it is necessary to turn to more complex calculations involving thermodynamic properties or to direct experimental studies of the weight loss of polymers in vacuum.

Electrical insulation of "Teflon" TFE and FEP was evaluated in a high vacuum. Weight loss was determined by weighing the sample before and after exposure to vacuum. Results are shown in Table 1. At 100°C. and after 100 hours exposure to a pressure of 10^{-7} mm Hg., the weight loss of TFE resin was 0.04% and the FEP resin was 0.08%. Although the rate of weight loss was not measured directly, a reliable indication was obtained by two independent methods. Both methods indicated that the rate of outgassing decreased with time.

A knowledge of the outgassing rate was obtained by comparing the pumping time vs pressure of the vacuum system without a specimen with that of a test run. Figure 1 compares the pump-down of an empty system with the pump-down while evaluating FEP and TFE at 100°C. During the TFE and FEP tests the pressure continued to approach the pressure of the empty chamber, indicating that the outgassing was decreasing. This trend indicated that the entrapped gases were slowly diffusing through the sample and that eventually the pressure for TFE and FEP would stabilize near the value obtained with the chamber empty.

On the mass spectrogram, Figure 2, the horizontal axis identifies mass and the amplitude of the spectrum indicates the concentration of the mass. Mass spectra made periodically throughout the test have decreasing amplitudes, showing that the concentration of that particular mass was decreasing. Continuation of the spectra to approximately 600 mass units indicated only one other substance - mercury - attributed to the mercury diffusion pump used in the vacuum system.

The gases identified in Figure 2 were mostly water vapor with varying amounts of carbon dioxide and other components of air. Except for CO_2, the gases coming off were not composed of elements present in the chemical structure of "Teflon" which indicated that only absorbed gases were being emitted. The decreasing concentration of evolved gases further verified this.

P. H. Bowen[10] previously made a similar study of several plastics used in bearing applications and included "Teflon" TFE. Table 2 gives the volume and identity of the evolved gases at temperatures of 71°C., 180°C. and 200°C. This data was remarkably similar to that obtained in our work.

The absence of fluorocompounds indicates that "Teflon" resins do not dissociate or sublime at a pressure in the order of 10^{-7} mm Hg. at 100°C. This is not surprising. Theoretical calculations using thermodynamic characteristics give a dissociation pressure for "Teflon" resins of 5×10^{-18} and 5×10^{-12} mm Hg. at 27°C. and 100°C. respectively. This dissociation pressure is lower than the vapor pressure of many common metals.

Weight loss may be accompanied by significant changes in properties, as well as in dimensions. In general, however, weight losses of less than 1 or 2% should produce no property changes of engineering significance.

An exception to the above generalization must be made for plastics and elastomers containing additives, such as plasticizers, flame retardants, and other modifiers. In such materials, a slight change in weight can nullify the effects of these modifiers and thus alter the properties that the material was specifically compounded to provide.

A special problem arises with optical and electrical equipment. If materials containing such additives are used in a high vacuum where considerable temperature differences exist, the compounds may redeposit on surfaces intended to transmit light or conduct electricity and heat. This could interfere with the proper operation of the equipment.

Our study, which has been verified by others, indicates that no degradation of "Teflon" resins or their properties occur in high vacuum service. Since the duration of studies made have been measured in hundreds of hours, obviously the next

question is what happens when "Teflon" resins are subjected to vacuum service in the order of years? Tubing of "Teflon" has been used in the vacuum system of the Bendix Mass Spectrometer for more than five years. Since this equipment remains pumped down to prevent contamination, except for the insertion of samples and maintenance, this represents almost continuous vacuum service at pressures of 10^{-6} to 5×10^{-9} mm Hg. (with the sample chamber empty). Periodic mass spectrum analysis to check for leaks and extraneous gases has never detected outgassing or breakdown of the tubing of "Teflon".

Equipment

Radiation

Electron irradiations at the Du Pont laboratories were carried out using 2-Mev electrons from a 3-Mev Van de Graaf accelerator. Radiation dose was varied by changes in the current (5 to 250 microamps) and the number of passes under the beam. The samples, for the most part, were compression molded pieces. Fabrication conditions were controlled to produce uniform samples. Unless otherwise noted, the samples were irradiated at room temperature and normal atmospheric conditions (oxygen present).

Discussion

Radiation

As stated in the introduction, this paper does not discuss the complex chemical changes which take place during irradiation of TFE and FEP resins. There are, however, two basic changes that should be understood. A change in the molecular structure of the polymer during exposure to irradiation produces a change in the physical and electrical properties of the fabricated part. Exposure conditions such as radiation dose, temperature during radiation and the availability of oxygen determine the type and amount of molecular change.

A structure whose parallel molecules have extended sideways and joined sidewise movements of other parallel molecules via radiation or other stimuli is said to have crosslinked. This can sometimes be controlled to give a harder material with increased tensile strength, decreased elongation and increased molecular weight.

If the molecular structure is broken into shorter molecules the structure is said to have exhibited a chain-scission action. This usually results in a softer material with decreased tensile strength and decreased molecular weight. Organic polymers exposed to radiation usually exhibit some action of both types. The final properties are determined by the predominate action.

The common way of determining molecular weight involves getting the material to be analyzed into solution and then measuring certain property changes of the solvent. Since "Teflon" fluorocarbon resins are insoluble, the course of molecular weight change and crosslinking cannot be followed by the usual solution methods. In the absence of direct molecular weight measurements, much work has been done on the determination of physical and electrical properties.

This work consistently shows that the radiation behavior of TFE and FEP resins is very sensitive to the presence of oxygen. As early as July 1959, it was noted that TFE in thin sections was quite stable to irradiation in the absence of oxygen.[3]

Later[4], it was shown that FEP resin crosslinked when exposed to high energy radiation above 80°C. and in the absence of oxygen. With doses greater than 2.6 megarads, ultimate elongation and resistance to deformation under load at elevated temperatures are improved, and the yield stress is increased. The improvements are accompanied by some loss in toughness. When irradiated less than 0.9 megarads, FEP resin retains its flow characteristics at high stresses, while at lower stresses there is an advantageous decrease in flow rate. The crosslinking versus chain scission performance of TFE is not as well defined.

Izod impact strength tests were run on notched bars (1/2" x 2-1/2" x 1/4") of "Teflon" TFE exposed to various irradiation dosages in air. Results of these tests are shown in Table 3. These Izod impact strength values appear to confirm previous reports[5] in which a 590% increase in impact strength at 10^6 rads was noted. Izod impact strength data for samples irradiated in vacuum are unavailable.

As stated in the introduction, over one hundred papers were reviewed as a part of this study. It soon became apparent that a Herculean task in laboratory work and literature review would be required to assemble all data and classify it according to the many variables of the various test procedures. These variables included temperature and pressure during radiation, source of radiation, inclusion of inert gas during radiation and inclusion of oxygen during radiation. For discussion of mechanical properties of TFE, it was decided to show the tensile strength and elongation properties after radiation in the absence of oxygen and in air as a function of dose rate. While the values for these properties shown in Figure 3[2,5,6] may not be absolute, due to the variations in test procedures noted above, it is believed that the changes illustrated are real and of significant value when considering the relative effect of irradiation in the presence of oxygen and in the absence of oxygen.

The curves shown as broken lines in Figure 3 show tensile strength and elongation for TFE irradiated at 25°C. at atmospheric pressure and in the presence of air (oxygen). The solid line shows tensile strength of TFE irradiated at 25°C. in a vacuum of 10^{-5} mm Hg. Data were not available on changes of elongation vs radiation dose in vacuum. The single value shown for elongation in vacuum resulted from studies in which the radiation dose was held constant and other physical conditions were varied.[2]

Data in Figures 4-7 on the electrical properties of TFE and FEP during and after irradiation are compiled from reports of work from other laboratories.

Two distinct types of phenomena occur in organic insulating materials when irradiated: (a) transient effects that disappear when the material is removed from radiation and (b) permanent effects that remain after the radiation has been removed. In most cases, the transient effects are produced by electron excitation; the permanent effects may be caused by electron excitation, by atom displacement, or by both. (7)

The observed behavior(8) of TFE-6 is summarized in the curves of Figures 4 and 5, which show the changes in dissipation factor under two different experimental conditions: (i) irradiation in air; (ii) irradiation in vacuum. Corresponding changes in dielectric constant were observed as shown in Figure 6. (8)

It was noted that the induced losses increase to the same high level when the TFE is irradiated in vacuum or in air (absence or presence of oxygen). The high level maintained during air irradiation is in sharp contrast to the steady decrease in dissipation factor and dielectric constant noted during the latter stages of irradiation in vacuum.

After very long recovery periods the physical and optical changes caused by crosslinking and degradation are still evident. After several months recovery in air, the dissipation factor is below 0.001 and the dielectric constant is within 2% of its original value.

In the case of FEP-100, the dissipation factor and dielectric constant were unaffected by x-ray irradiation in vacuum. Figures 7 and 8. (8) Physical and optical property changes however, were evident. Data for irradiation in air is unavailable.

Conclusions

1. "Teflon" TFE and FEP resins do not evaporate in a vacuum of 10^{-7} mm Hg. Theoretical calculations indicate that these resins will not evaporate in any anticipated space vacuum to an extent which would put a practical limit on their usefulness. Although some outgassing occurs initially, the volatiles are all absorbed atmospheric gases.

2. The presence of oxygen greatly influences the physical and electrical properties of irradiated "Teflon" TFE and FEP resins when irradiated above an approximate value of 4×10^4 rads.

3. With proper design considerations, "Teflon" TFE resins maintain their usefulness after radiation dosages of at least 10^7 rads in the absence of oxygen.

4. "Teflon" FEP resins, when irradiated in the absence of oxygen and above 80°C, show an improvement in certain desirable physical properties with doses greater than 2.6×10^6 rads. An upper dose limit for this material cannot be predicted because of lack of adequate data.

5. Low frequency loss properties of "Teflon" TFE polymers are drastically affected by x-ray irradiation. High frequency loss properties are considerably less affected. The increases in dielectric constant and dissipation factor depend upon the ambient oxygen concentration during exposure and recovery.

6. The dielectric constant and dissipation factor of "Teflon" FEP resins are unaffected by x-ray irradiation in vacuum for measured frequencies of 60 cps to 100 kcps.

The authors wish to express their appreciation for the assistance given by Dr. John O. Punderson and Dr. Ada L. Ryland in obtaining the vacuum data.

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3. Florin, R. E. and Wall, L. A., Journal Applied Polymer Science, Vol. 2, No. 5 (1959) p. 251.

4. Bowers, G. H. and Lovejoy, E. R., "Cross-Linking of 'Teflon' 100 FEP-Fluorocarbon Resin by Radiation", I and EC Product Research and Development, Vol. 1, No. 2, June 1962.

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9. Private conversation with Johns Hopkins University - Dielectrics Lab.

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Table 1

Per cent Weight Loss in Vacuum

Materials	Wt. of Sample Grams	Pressure mm Hg.	Temp. °C.	Time Hrs.	% Wt. Loss
"Teflon" TFE	3.2595	10^{-7}	100°C.	100	0.04
"Teflon" FEP	2.1376	10^{-7}	100°C.	102	0.08

Table 2

Vacuum Data From Other Work[10]

Mol % Gases Evolved

	Wt. of Samples-gm	Temp °C	H_2O	CO_2	N_2	O_2	Vol. of gas cc/gm
"Teflon" TFE*	0.9010	71°C	12.07	-	62.51	25.42	0.0067
	0.9010	180°C	14.10	-	64.64	21.26	0.0164
	0.9010	200°C	6.25	1.78	72.88	19.06	0.0172

*(Pressure at 10^{-6} mm Hg.)

Table 3

Izod Test Results - Irradiated TFE Samples in Air

Dosage rads	4 ft. lb. Pendulum Avg. of 5 Samples
Control	2.3
1×10^6	14.8
8×10^6	14.6
1×10^7	15.2
2×10^7	13.1
5×10^7	6.6

FIGURE I

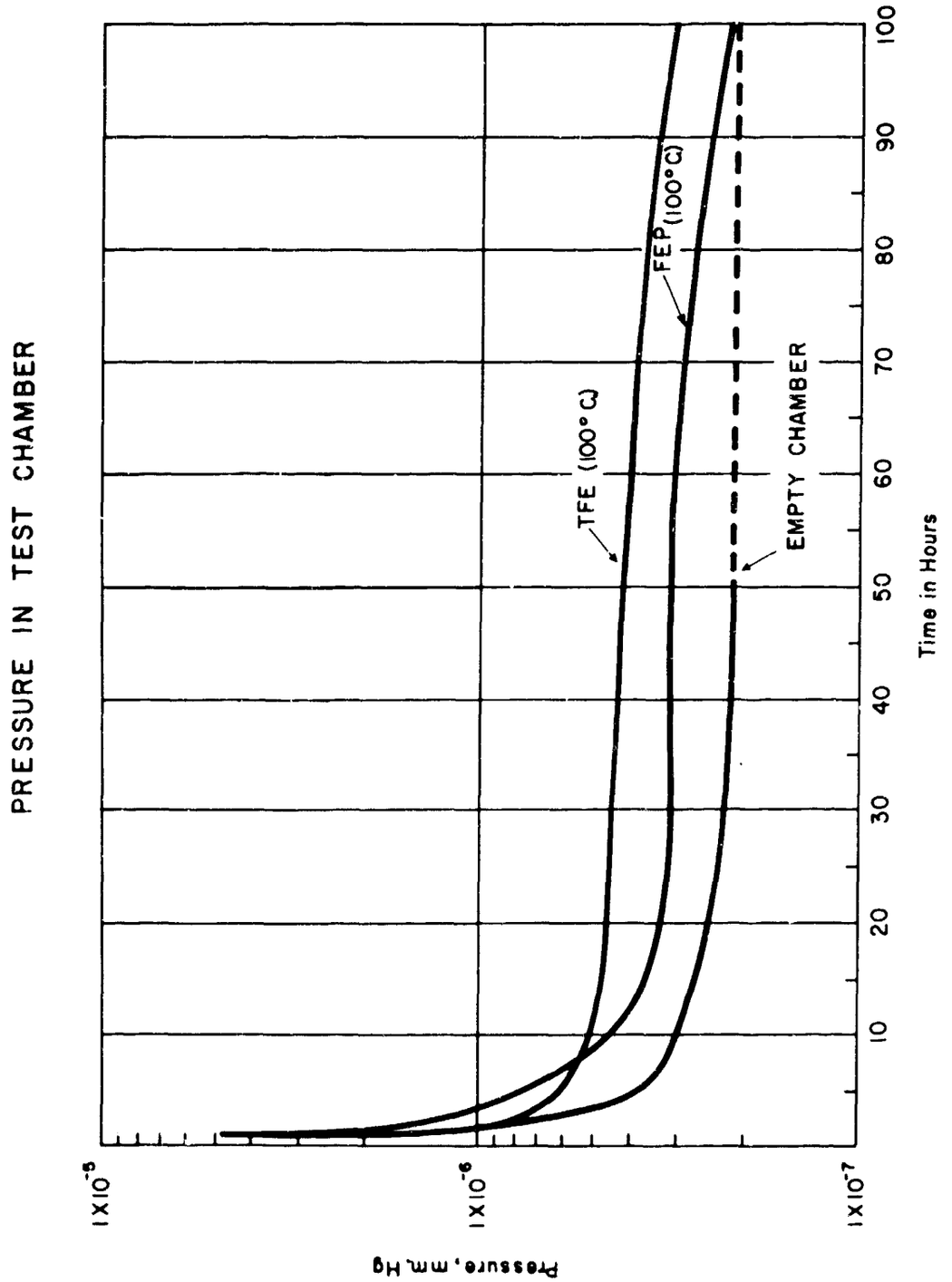
PRESSURE IN TEST CHAMBER
TFE (100° C)
FEP (100° C)
EMPTY CHAMBER
1X10⁻⁵
1X10⁻⁶
1X10⁻⁷
Pressure, mm. Hg
10
20
30
40
50
60
70
80
90
100
Time in Hours

FIGURE 2

PERIODIC SPECTRA OF THE EVOLVED GASES

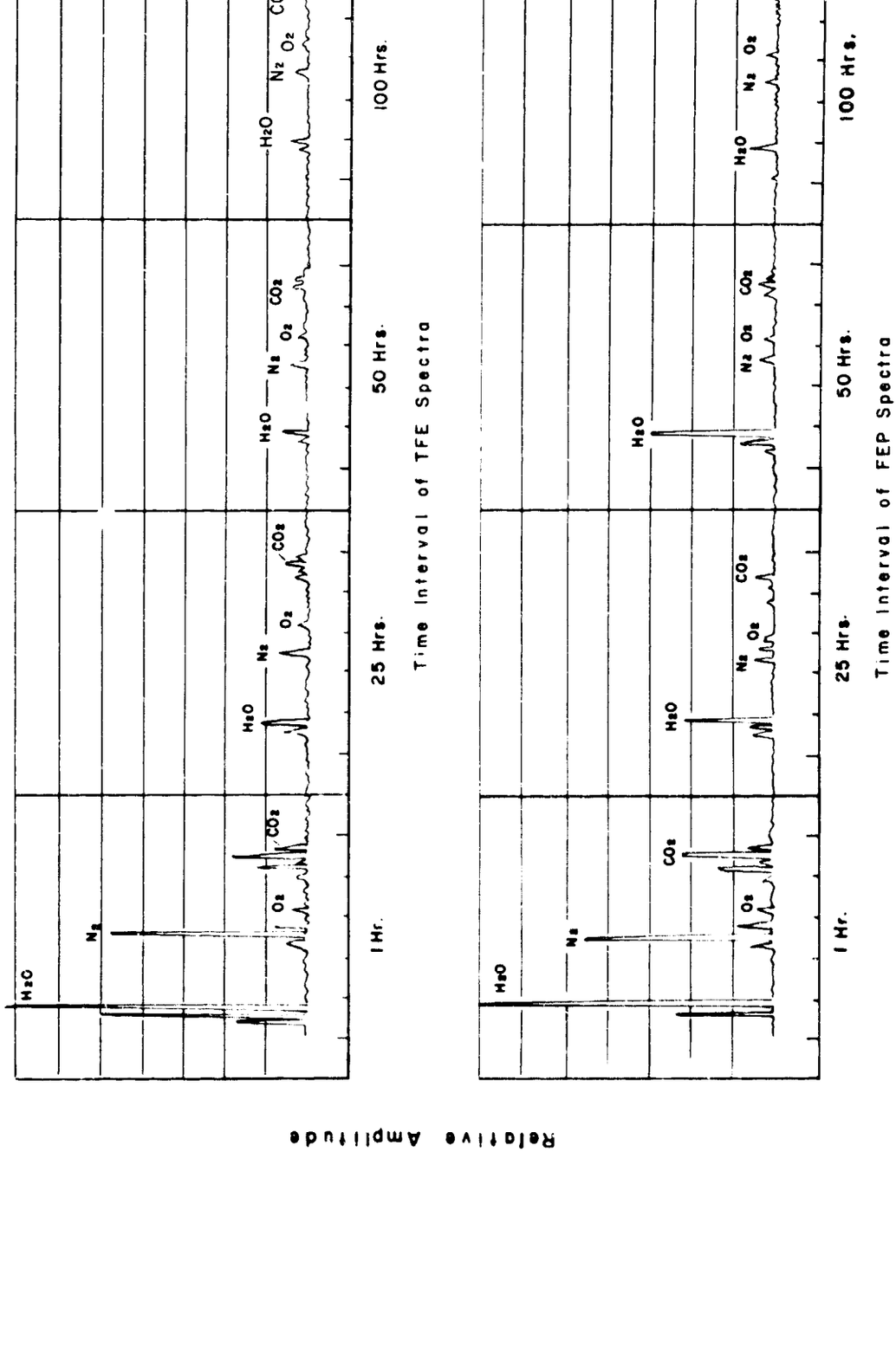

FIGURE 3

TENSILE STRENGTH AND PERCENT ELONGATION – TFE RESINS

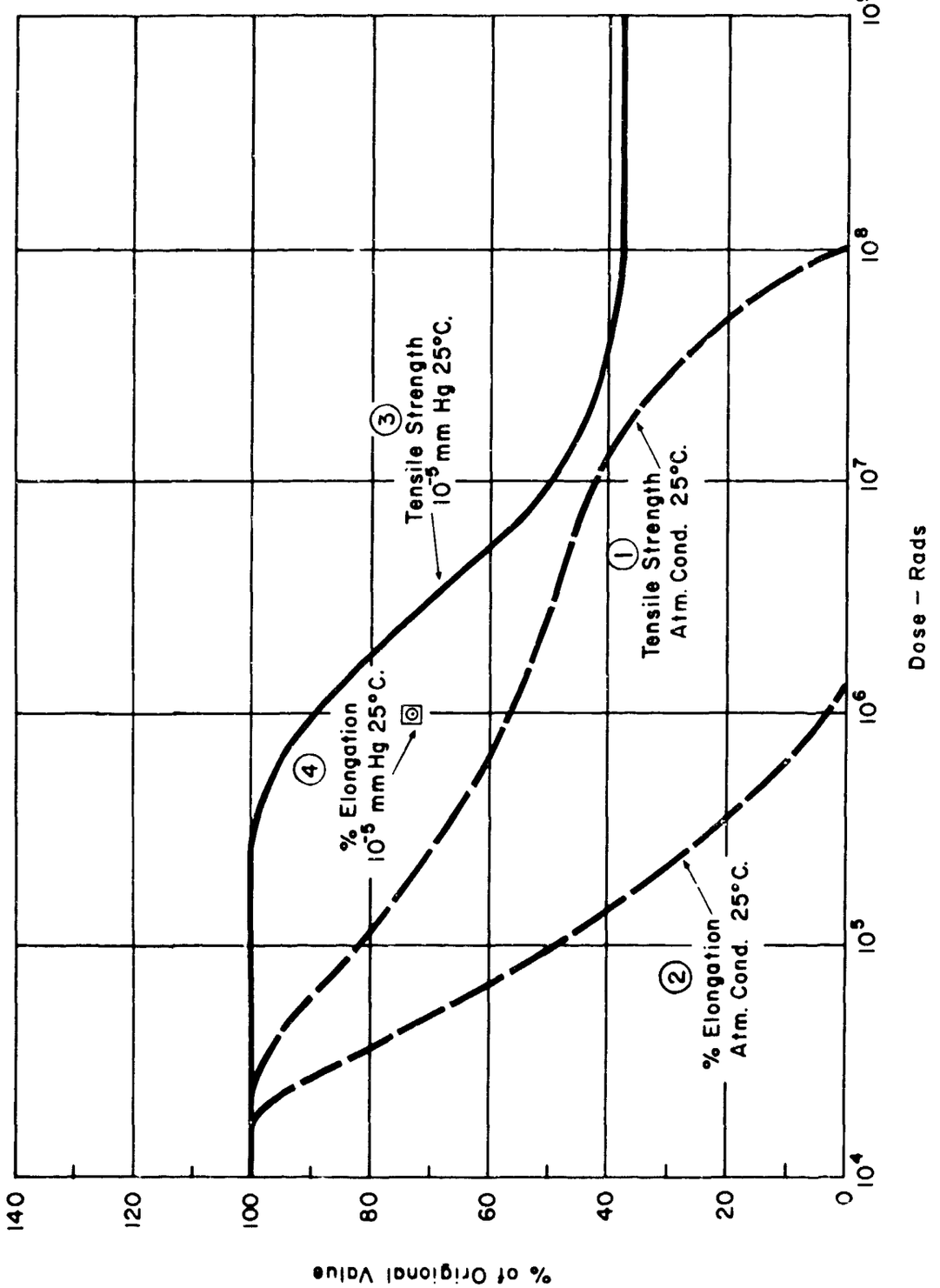

FIGURE 4

EFFECT OF X-RAY IRRADIATION ON TFE-6 (DISSIPATION FACTOR)

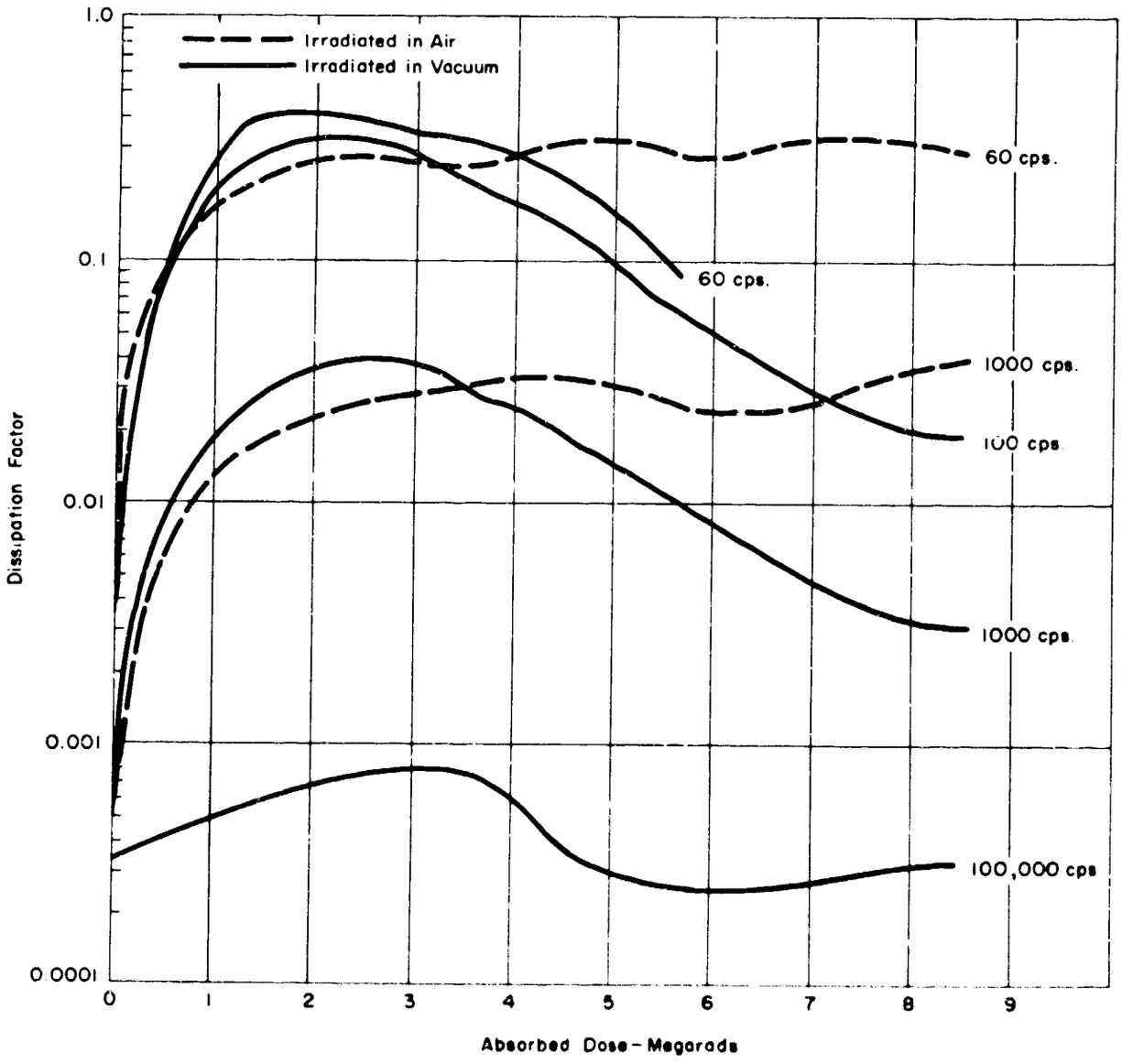

FIGURE 5

RECOVERY CHARACTERISTICS OF TFE-6 SPECIMENS AFTER X-RAY IRRADIATION AS SHOWN IN FIGURE 4

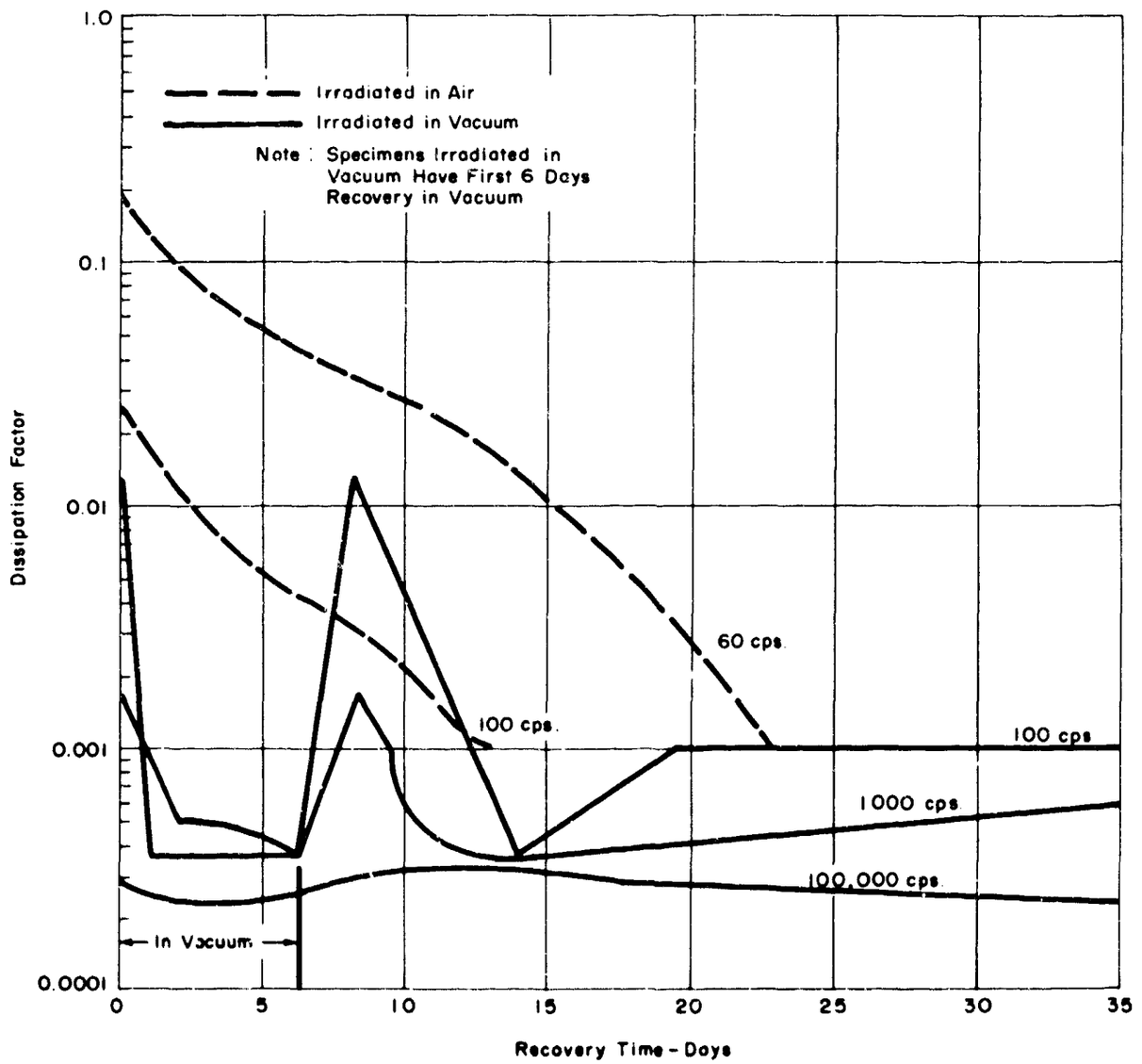

FIGURE 6

EFFECT OF X-RAY IRRADIATION ON TFE-6 (DIELECTRIC CONSTANT)

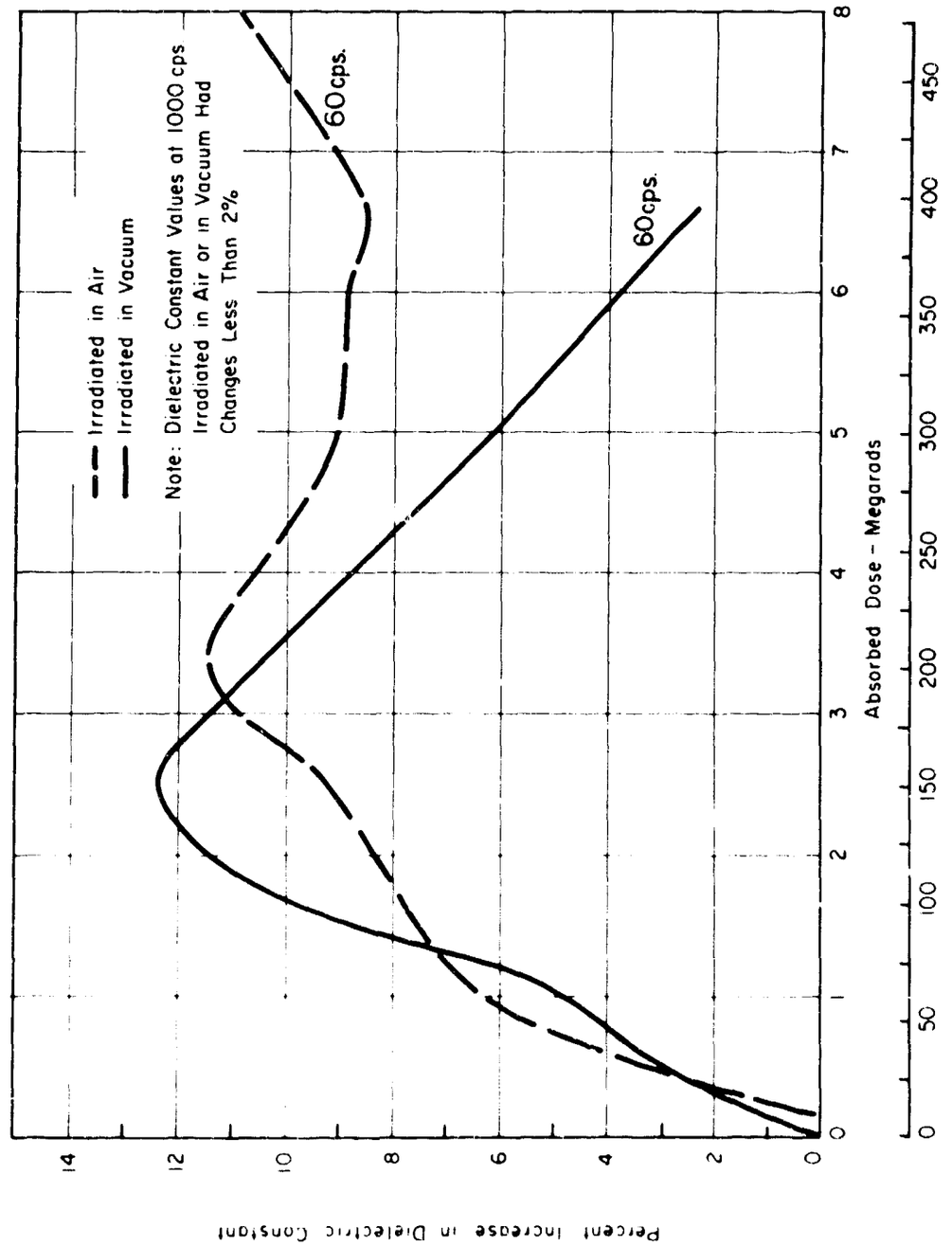

FIGURE 7

EFFECT OF X-RAY IRRADIATION ON FEP-100 (DISSIPATION FACTOR)

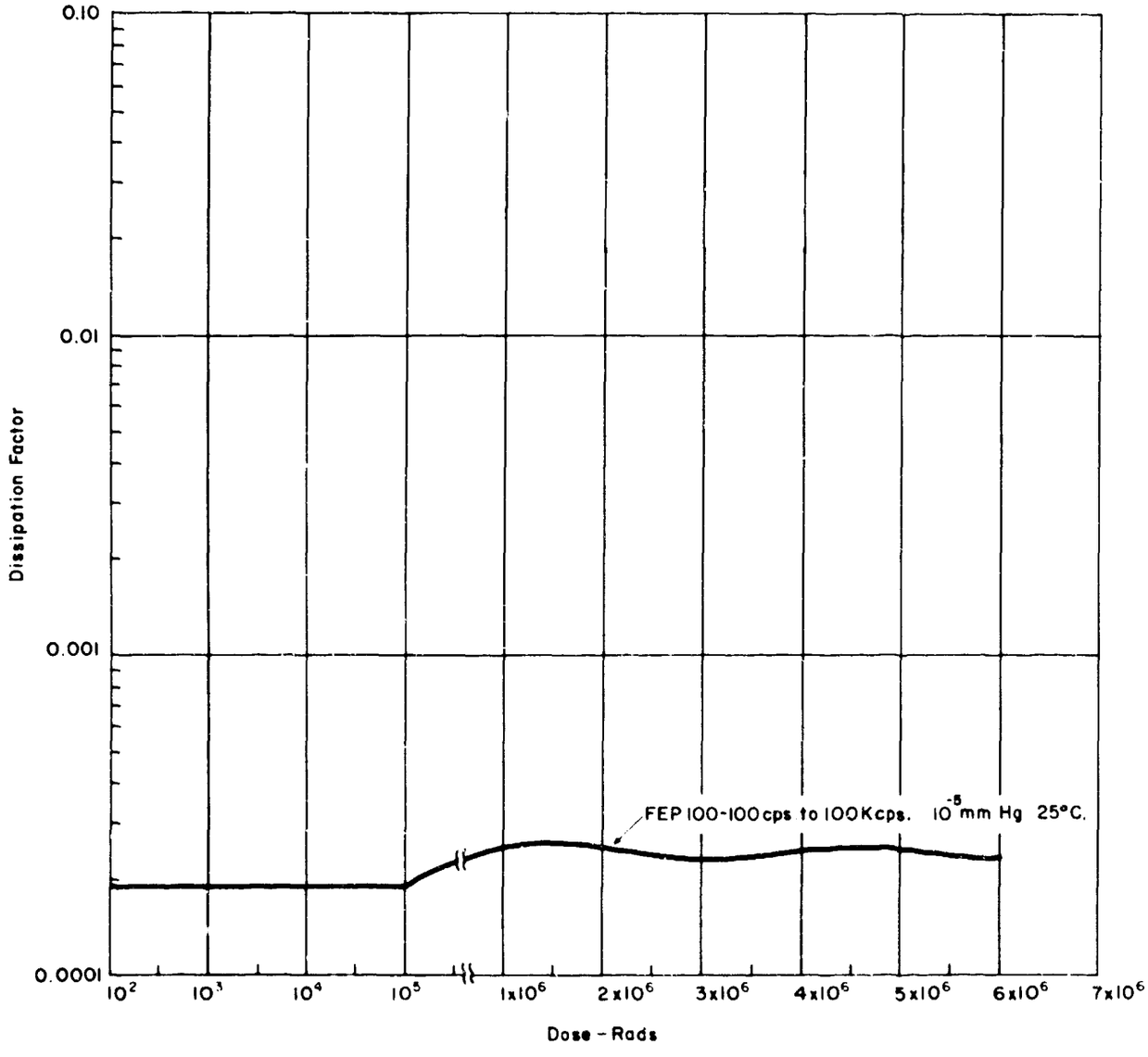

FIGURE 8

EFFECT OF X-RAY IRRADIATION ON FEP-100 (DIELECTRIC CONSTANT)