THIRD SEMI-ANNUAL

radiation effects symposium

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LOCKHEED NUCLEAR PRODUCTS

Lockheed Aircraft Corporation, Georgia Division

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VOLUME 5 OF 6

Lubricants and Plastics Papers

Third Semi-annual

radiation effects symposium

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UNITED STATES AIR FORCE

LOCKHEED NUCLEAR PRODUCTS
LOCKHEED AIRCRAFT CORPORATION
GEORGIA DIVISION – MARIETTA, GEORGIA

FOREWORD

The proceedings of the Third Semi-Annual ANP Radiation Effects Symposium, held at the Dinkler-Plaza Hotel in Atlanta, Georgia, October 28 through 30, 1958, are in six volumes. Each of the first five volumes presents the unclassified papers from one of the five sessions; the sixth volume presents classified papers from all five sessions.

Each volume contains a complete table of contents and an index of authors. Volume One contains a list of the names of all who attended the Symposium.

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2. RADIATION EFFECTS TESTING OF AIRCRAFT SUBSYSTEMS AND COMPONENTS AT AIR FORCE PLANT No. 67 FOR THE ANP PROGRAM by W. L. Bridges, Lockheed Nuclear Products, Lockheed Aircraft Corporation, Georgia Division, Marietta, Georgia

3. *MISSION AND TRAFFIC CONTROL REQUIREMENTS FOR THE WS/125A by James R. Burnett, Bendix Systems Division, Bendix Aviation Corporation, Ann Arbor, Michigan

4. NEW RADIATION TEST FACILITIES IN THE GENERAL ELECTRIC COMPANY by S. S. Jones, Vallecitos Atomic Laboratory, General Electric Company, San Jose, California,and W. R. Langdon and T. T. Naydan, General Electric Company, Schenectady, New York.

5. THE CONVAIR RADIATION EFFECTS TESTING SYSTEM by J. W. Allen, Convair, A Division of General Dynamics Corporation, Fort Worth, Texas

6. RADIATION EFFECTS REACTOR by W. T. Scarborough, Lockheed Nuclear Products, Lockheed Aircraft Corporation, Georgia Division, Marietta, Georgia

7. A DESCRIPTION OF A MULTI-KILOCURIE IRRADIATION FACILITY AND THE ASSOCIATED RADIATION DOSIMETRY by R. E. Simpson, Lockheed Nuclear Products, Lockheed Aircraft Corporation, Georgia Division, Marietta, Georgia,and M. Z. Fainman, M. E. Krasnow, E. R. Rathbun, C. R. Memhardt, Inland Testing Laboratories and Cook Research, Morton Grove, Illinois

8. START-UP OF THE CRITICAL EXPERIMENT REACTOR by M. A. Dewar, Lockheed Nuclear Products, Lockheed Aircraft Corporation, Georgia Division, Marietta, Georgia

9. REMOTE AREA MONITORING SYSTEM AT AIR FORCE PLANT No. 67 by E. N. Lide, Lockheed Nuclear Products, Lockheed Aircraft Corporation, Georgia Division, Marietta, Georgia

* This paper is classified and is bound in Volume Six.

10. AREA MONITORING FOR RADIOACTIVITY by Roy Shipp, Lockheed Nuclear Products, Lockheed Aircraft Corporation, Georgia Division, Marietta, Georgia

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31. EFFECT OF RADIATION ON THE CRITICAL SHEAR STRESS OF A METAL SINGLE CRYSTAL by C. E. Morgan, Convair, A Division of General Dynamics Corporation, Fort Worth, Texas

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33. THE EFFECTS OF NUCLEAR ENVIRONMENT ON METALLIC AND NONMETALLIC MAGNETIC MATERIALS by E. I. Salkovitz and A. I. Schindler, U. S. Naval Research Laboratory, Washington, District of Columbia

34. *THE EFFECT OF NUCLEAR RADIATION ON COMMUNICATIONS SET AN/ARC-34 by D. L. Jacobs, Convair, A Division of General Dynamics, Fort Worth, Texas

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* This paper is classified and is bound in Volume Six.

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THE BEHAVIOR OF FUELS AND LUBRICANTS IN DYNAMIC TEST EQUIPMENT OPERATING IN THE PRESENCE OF GAMMA RADIATION

by

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Morton Grove, Illinois

Seventy-nine fuels and forty-one lubricants were studied to determine their suitability for use in a nuclear-powered aircraft. The materials were evaluated in dynamic test equipment operating in a gamma-radiation environment provided by 50,000 curies of Cobalt 60. The mechanical test machines used were those that have been useful in predicting the performance of fuels and lubricants in the aircraft gas turbine. These mechanical tests conducted at elevated temperatures in a radiation environment often affect materials more drastically and at lower doses of radiation than anticipated, indicating that it is necessary to assess the effects of mechanical, thermal, and radiation stresses as a combined environment. Ten fuels and six lubricants were chosen which showed the best performance. Sufficient data were accumulated to show that a number of these products will operate satisfactorily at radiation doses of at least 10^{10} ergs/gram carbon. These materials are suggested as the most satisfactory of those evaluated for use in a nuclear-propelled aircraft.

INTRODUCTION

The increasing use of nuclear reactors as mobile power sources emphasizes the problem of radiation-induced damage to organic materials. This damage may be minimized with adequate shielding. However, the high cost of this shielding, together with attendant weight penalties, requires the development of materials that perform well in a radiation environment.

Reactors, both stationary and mobile, require hydraulic fluids and lubricants that are not adversely affected by radiation. In addition, nuclear-powered aircraft will require support fuels. Programs to develop these materials supplement each other by supplying information needed for the design of nuclear-powered equipment from the submarine below the sea to the satellite in space.

In particular, the Air Force has requirements for fuels and lubricants that must operate in the combined environments of radiation and high temperature. As a consequence, these substances must be considered as engineering materials since they influence the design of the components and machinery in which they are to function. This, in turn, means that engineering data for these materials in a radiation environment must be obtained for presently available specimens and also for new samples as they are developed.

The purpose of this study is to evaluate the performance of fuels and lubricants in dynamic test machinery operating in a radiation environment. This permits the choice of materials showing the best behavior and should lead to the requirements necessary for good performance and subsequent specification criteria.

Fuels and lubricants submitted by Wright Air Development Center were evaluated according to the appropriate specification tests listed in Table I. If the fuels or lubricants were found satisfactory after specification tests, they were tested in the applicable mechanical equipment, Table II. Where performance was adequate in the laboratory, they were run in the duplicate rig in the radiation cell. Bench tests were used to evaluate radiation-induced damage in the materials, both with static irradiation alone, and also after dynamic tests performed with and without radiation.

This paper summarizes the results obtained from the evaluation of 79 fuels and 41 lubricants.[1]

EXPERIMENTAL

A. Laboratory Evaluation

The laboratory evaluation of fuels and lubricants was conducted in accordance with appropriate specifications, Table I. Samples were obtained from Wright Air Development Center, from statically irradiated materials, and from the test rigs operating both in and out of the radiation environment.

B. Mechanical Evaluation

The mechanical test systems used in the evaluation of fuels and lubricants were: (1) The CFR Fuel Coker; (2) The WADC Deposition Tester; and (3) The Model C Panel Coker. Two each of these machines were used, one in the radiation environment. Wherever possible, the modifications of test systems were kept to a minimum as governed by the desired radiation levels and the need to maintain correlation with other investigators. The test machinery and operation are discussed in detail by Fainman, et al.[1]

C. Dosimetry

Radiant energy was provided by a 50, 145 curie Cobalt 60 source positioned in the test cell on an elevating mechanism. When not in use it was lowered into a well under 22 feet of water. The radiation emitted by the decay of Cobalt 60 consists of a 0.3 Mev beta particle followed by two gamma photons of energy 1.33 Mev and 1.17 Mev in cascade.

The basic dosimetry instrument is an Oak Ridge type graphite CO_2 ionization chamber modified for the energy range of Cobalt 60.[1] Ferrous-ferric chemical dosimetry was used to supplement the ionization chamber. All dosimetry measurements were based on absorbed energy in terms of ergs per gram carbon (1 roentgen $\cong$ 87.1 ergs per gram carbon).

Isodose maps of the cell were made for reference purposes. A plot taken through the vertical midplane, front view, is shown in Figure 1. The placement of heavy test machinery in the cell altered the isodose lines. As a consequence, the dose rates on the dynamic test equipment were determined individually, using both the graphite CO_2 ionization chamber and the ferric-ferrous method.[1] The maximum dose rate observed for the test machines was approximately 5×10^7 ergs per gram carbon.

RESULTS

This study covers the investigation of 79 fuels and 41 lubricants. The results of specification tests and mechanical evaluation, both with and without the presence of radiation, are reported in detail by Fainman, et al.[1]

Results obtained clearly indicate that it is necessary to assess the effects of mechanical, thermal, and radiation stresses simultaneously. It has been observed that mechanical tests in a radiation environment often affect materials more drastically and at lower doses of radiation than the same tests conducted with statically irradiated samples without attendant radiation. Relative ratings of 10 of the most promising fuels and 6 lubricants with the best performance characteristics are listed below.

A. Fuels

Fuel properties show little change with static radiation up to doses of 10^8 ergs/gram carbon. However, with doses beyond 10^9 ergs/gram carbon changes in some parameters such as flash point, initial boiling point, gum, and viscosity at -30°F become evident. Individual fuels behave differently, but at higher doses the flash point, initial boiling point, and viscosity at -30°F will usually decrease, while the gum content will increase.

Relative performance of fuels under normal conditions and in a radiation environment were determined with the CFR Fuel Coker. Many fuels were preirradiated and tested in a conventional environment. This preirradiation and subsequent mechanical evaluation often indicated an improvement or no change in the relative fuels rating. The same evaluation conducted in a radiation environment indicated a decrease in goodness rating or a rapid failure. For some fuels these failures have been associated with observed precipitate formation during or after static irradiation. Comparison of the results of mechanical evaluation with specification tests at various dose levels indicate that determining the effect of radiation alone on fuel properties is not sufficient to predict future performance.

Ten fuels were chosen from those studied as showing the least change in performance and, thus, the most promise for application for use with an airborne reactor. The following criteria for the CFR Fuel Coker were applied in this selection:

(1) In the screening test, the increase in differential pressure shall not exceed 11.5 inches of mercury.

(2) In mechanical evaluation in a radiation environment, the preheater rating shall not exceed Code 2.

Table III lists the fuels meeting these requirements. They are tabulated in order of the increasing differential pressure observed with mechanical evaluation in a radiation environment.

The maximum dose rate to which the fuels were exposed in the test rig was 5 x 10^7 ergs/gram carbon. Relative behavior was assessed at approximately 10^8 ergs/gram carbon, since this represents the average accumulated dose obtained without extensive preirradiation of the fuel samples. Additional tests with preirradiation indicate that these fuels should perform satisfactorily up to doses of 10^{10} ergs/gram carbon.

B. Lubricants

Lubricants show no significant changes in physical properties upon static radiation until a dose of about 10^9 ergs/gram carbon is reached. When this dose is exceeded, the flash point and viscosity will generally decrease, while the neutralization number, the tendency toward metal corrosion, and the deposit forming tendency will usually increase.

Lubricants were mechanically evaluated with the Model C Panel Coker and the WADC Deposition Tester, both with and without the presence of gamma radiation. Results of preirradiation and subsequent mechanical evaluation generally indicated less coke and sludge formation than observed with comparable runs in a radiation environment. Specification tests at various gamma doses indicate a possible correlation with mechanical evaluation results; however, considerable work will be necessary to establish this. The mechanical evaluation in a radiation environment revealed no general behavior trend; however, individual lubricants yield definite repeatable behavior patterns. With additional work it may be possible to predict engine performance from specification and mechanical test data.

Six lubricants were selected which performed well in a radiation environment. Oils were first chosen which gave less than 80 mg of deposits at both 600°F and 700°F in the Model C Panel Coker. A second group was chosen with deposition numbers of less than 5.0 in the WADC Deposition Tester. Oils common to both groups were then arranged in order of increasing Deposition Number at the lowest level of total radiation, which was approximately 10^8 ergs/gm carbon. The relative rating of these lubricants is given in Table IV.

The maximum dose rate to which the lubricants were exposed was 3×10^7 ergs/gm carbon. Relative performance is at an approximate radiation dose of 10^8 ergs/gm carbon, since that is the dose on the WADC Deposition Tester without preirradiation. Additional tests on preirradiated lubricant samples indicate these materials should be satisfactory at doses approaching 10^{10} ergs/gm carbon.

CONCLUSIONS

The results of this study clearly demonstrate that it is necessary to evaluate the fuels and lubricants for use with an airborne reactor in a combined environment. Ten fuels and six lubricants performed well in dynamic test machinery operating in a radiation environment. Dose rates approached 5×10^7 ergs/gram carbon, while the total dose on many of these materials was as high as 10^{10} ergs/gm carbon (including preirradiation). These fuels and lubricants should be satisfactory for use in a nuclear-propelled aircraft.

No general trends of the effect of radiation on fuels or lubricants is evident. However, as pertinent data is obtained, it should be possible to establish criteria for specifications covering the materials to be used in a radiation environment.

REFERENCE

1. Fainman, M. Z., et al, The Behavior of Fuels and Lubricants in Dynamic Test Equipment Operating in the Presence of Gamma Radiation, WADC Technical Report 58-264, ASTIA Document No. 155-596, 31 March 1958.

TABLE I

SPECIFICATIONS FOR FUELS HYDRAULIC FLUIDS AND LUBRICANTS

Specification	Title
MIL-F-5624C	Fuels, Aircraft Turbine and Jet Engine Grades JP-3, JP-4, JP-5
MIL-F-25656	Grade JP-6 Turbojet Fuel
MIL-F-25558	Ramjet Fuel
MIL-F-25576	Rocket Fuel RP-1
MIL-G-3278	Greases: Aircraft and Instruments (For low and high temperature)
MIL-G-25013A	Grease, Ball and Roller Bearing, Extreme High Temperature
MIL-H-8446A	Hydraulic Fluid, Nonpetroleum Base, Aircraft
MIL-O-6081B	Oil, Lubricating, Jet Engine
MIL-L-6082	Lubricating Oil, Aircraft Reciprocating Engine
MIL-L-7808C	Lubricating Oil, Aircraft Turbine Engine Synthetic Base
MIL-L-9236A	Lubricating Oil, Aircraft Turbine Engine, High Temperature
MIL-L-25336	Lubricating Oil, Aircraft Turbine Engine, High Film Strength, Synthetic Base
MIL-H-5606A	Hydraulic Fluid, Petroleum Base, Aircraft and Ordnance

TABLE II

DYNAMIC TEST EQUIPMENT

Machine	Purpose of Test	Design Modification
CFR Fuel Coker	To evaluate deposit forming tendency of fuels.	The preheater filter section and manometer mounted on a portable rack. Remainder outside the cell for remote control.
WADC Deposition Tester	To evaluate stability, corrosivity, and sludging tendency of oil.	The complete oil test loop is mounted on a portable rack in the test cell. The teflon seals are replaced with silicone seals. Instrumentation is outside the cell for remote control.
Model C Panel Coker	To evaluate coking tendency of fluid lubricants.	The motor is shielded with lead against radiation damage. The operation is controlled remotely outside the cell.

TABLE III

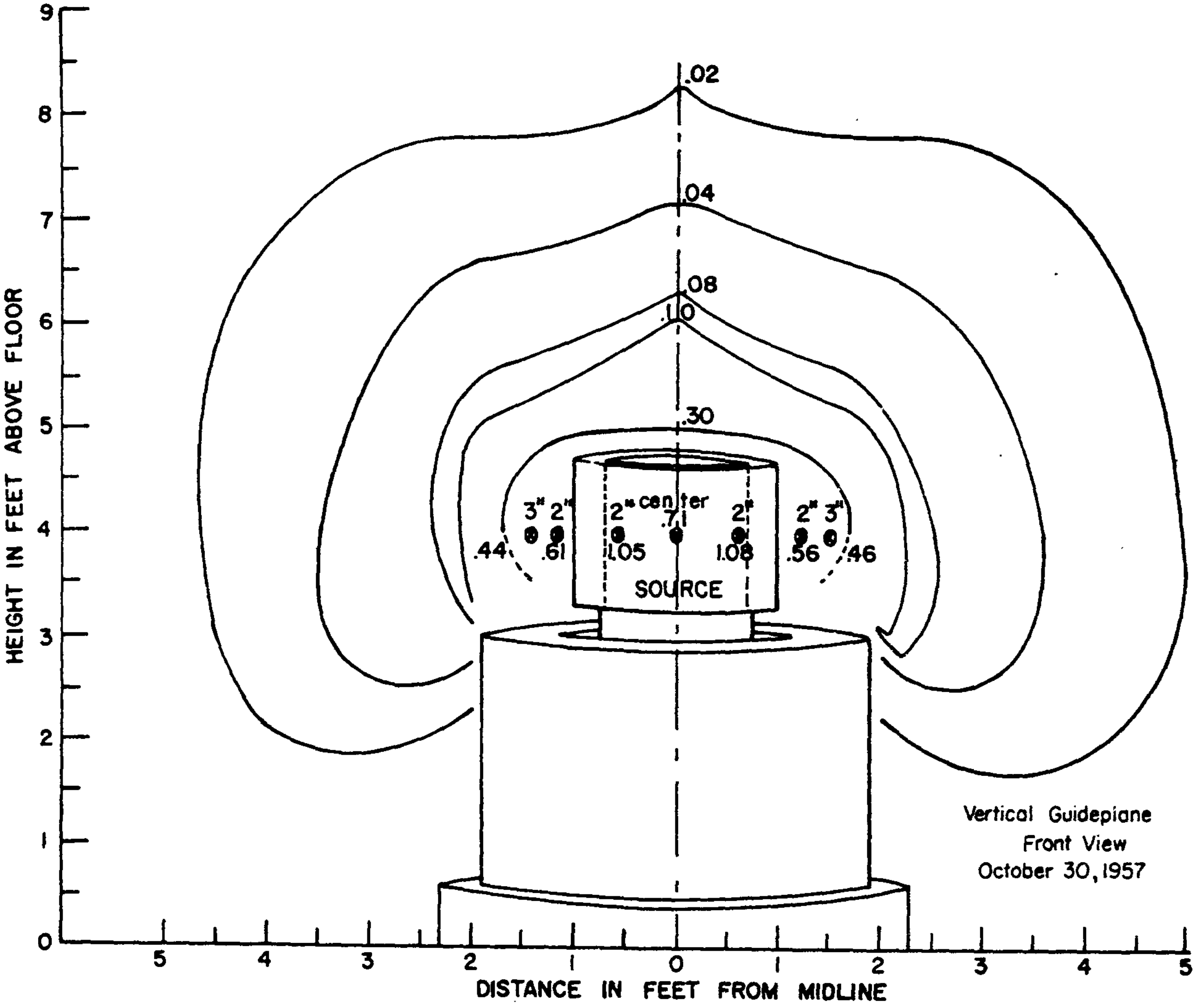
RELATIVE RATING OF FUELS BASED ON RADIATION STABILITY IN THE CFR FUEL COKER

Relative Rating in Fuel Type	Fuel Designation ANPF No.	Fuel Type	Test Temp. °F	ΔP, inches Hg at 300 min.		Maximum Preheater Deposits CRC Code	
				No Radiation	10^8 ergs/gmC (approximate)	No Radiation	10^8 ergs/gmC (approximate)
1	57-95	JP-4	300/400	0.08	0.15	0	1
2	57-112	JP-4	300/400	0.0	4.60	0	1
1	57-120	JP-5	400/500	0.0	0.0	1	2
2	57-107	JP-5	400/500	0.0	0.0	1	2
3	57-51	JP-5	400/500	0.9	0.0	1	2
4	57-105	JP-5	400/500	0.2	0.0	0	2
5	57-56	JP-5	400/500	0.1	0.0	2	2
6	57-102	JP-5	400/500	0.6	0.15	1	0
7	57-57	JP-5	400/400	11.15	0.6	2	0
1	57-96	Thermally Stable	400/500	0.15	9.4	0	2

TABLE IV

RELATIVE RATING OF LUBRICATING OILS

			Unirradiated Results			Radiated Results (approx. 10^8 ergs/gmC		
Relative Rating	Designation ANP No.	Oil Type	Panel Coker		Deposition Test	Panel Coker		Deposition Test
			600°F	700°F		600°F	700°F	
1	80	Ester	10.7	22.6	3.61	4.3	28.3	1.31
2	79	Ester	15.7	55.6	1.69	15.1	221.2	1.86
3	78	Ester	16.7	22.6	0.80	22.6	28.3	2.54
4	70	Polyglycol	-	37.5	2.20	-	126.2	2.63
5	76	Ester	46.7	39.8	4.74	30.0	67.2	3.24
6	61	Olefin Polymer (Poly Butene)	2.7	-	2.55	87.7	-	4.47



Vertical Guideplane
Front View
October 30, 1957

Isodose Plot of Cobalt 60 Source, Megaroentgens/Hour

Figure 1.

THE DEVELOPMENT OF NUCLEAR RADIATION RESISTANT SOLID FILM LUBRICANTS

by

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Materials Laboratory
Wright Air Development Center

The effect of radiation on solid film lubricants is discussed. Data on wear life, corrosion resistance, fluid resistance, and thermal stability are reported for twelve films. Exposures were conducted in the presence of both gamma and neutron irradiations. In general, little change was noted in the film performance indicating stability of the films.

Introduction

Nuclear radiation resistant lubricants are of major importance to the development of nuclear powered weapon systems. The divided shield concept for manned aircraft, for example, has resulted in greatly increased radiation levels in the zone between the reactor shield and the crew shield. This radiation intensity is unique to flight vehicles, since it is only in systems operating off the surface of the earth or out of the oceans that weight is so critical, with the resultant reduction in shield weights to minimum values.

A great deal of research has been conducted and is currently in progress with the intent of developing radiation resistant lubricating oils, greases, hydraulic fluids, and related materials. This research has resulted in the development of outstanding materials, chief among them being the unsubstituted polyphenyl ethers. However, it appears at present that there is little possibility of developing organic fluids capable of extended operation for temperatures much above the range of 800°F to 900°F, unless one is willing to use materials of exceptionally high melting point and resultant limited low temperature useability.

Among the more interesting possibilities for lubrication at extended temperatures are the solid film lubricants. These lubricants consist in general of a finely divided solid material, such as graphite or molybdenum disulfide, affixed to the bearing surface by a resin bonding agent. Details of past work on solid film lubricants in non-nuclear environments are presented in many excellent references (1, 2, 3, 5, 6, and 11).

The advantages of solid film lubricants are manyfold. They are independent of temperature, up to the decomposition point, since there need be no consideration of melting point or limiting viscosities. They require no maintenance, since they are expected to remain functional during the normal operational lifetime of the bearing surface. And, quite important for applications in the presence of nuclear radiation, the binder and the dispersed material would be expected to show resistance to radiation effects to higher dosage levels than organic fluids.

The development efforts discussed herein represent the first phase in the Air Force program to assess the potentialities of solid film lubricants for use in nuclear powered systems.

Manuscript released by authors 9 September 1958 for publication as a WADC Technical Report.

Evaluation Criteria

In the past efforts on the development of solid film lubricants, many and varied criteria were established, depending on the expected end item use. Air Force requirements for solid film lubricants are reflected in the provisions of Specification MIL-L-25504. This specification establishes the minimum performance and testing requirements for a bonded, solid film lubricant applied to the surface of parts used in aircraft and missiles to reduce wear and prevent galling and seizure. The test provisions of this specification are given in Appendix I. The solvent resistance, corrosion resistance, and thermal stability studies reported in Tables I, II, and III were performed in accordance with these specification methods.

The most interesting consideration in the use of a solid film lubricant is its wear life. Many devices have been used to measure the frictional characteristics of solid film coated surfaces. One such machine, the Falex Wear Tester, had its inception in studies of lubricating oils. This machine has been extensively used in evaluation of solid film lubricants. Details of operation are given in references (6) and (10). Tables IV and V give data obtained through use of this machine. Table VI gives wear-life data using a Midwest Research Institute friction tester, details of which are outlined in reference (8). Wear life data for Table VII are based on the Hartmann-Modified MacMillan machine.

Requirements for film performance under Specification MIL-L-25504 (USAF) are outlined in Appendix I. Unless special environmental tests are conducted, most laboratory evaluation at the Wright Air Development Center is now conducted in accordance with said requirements.

Irradiation of Samples

Details of the irradiation history of the Falex sets and coated panels are given in Appendix II. Dosimetry values for gamma exposures in the MTR gamma canal are reported in roentgens. The roentgen values have been converted to the basis of ergs per gram carbon, as recommended by reference (4). It was assumed that one roentgen is equivalent to 87.1 ergs per gram carbon.

The gamma irradiation facility at the MTR is under some twenty feet of water for shielding purposes. Occasionally, an irradiation canister leaks due to a defective lead seal. Samples of coated panels for several coatings were contaminated due to such water leakage. There are many places in Tables I, II, and III where data could not be obtained due to panels ruined in this manner.

Lubricant Composition

The materials used in this preliminary study were from commercial sources. Composition of the binder or dispersed solids is unknown for all lubricants. It was thus deemed advisable to code all lubricants used, since compositions were unknown anyway. No solid film lubricant compounded to date has been specifically designed for use in a nuclear radiation environment. Thus, the coding serves to avoid comparison of materials subjected to conditions for which they were not designed.

Other concepts have arisen in lubrication by solid surfaces that do not depend on bonding materials to the surface. One idea is that of incorporating a lubricating material (graphite or molybdenum disulfide) in a sintered metal matrix and using this composition as a self-lubricating medium. Another type of material is one of a relatively high carbon content metal alloy of self-lubricating characteristics. While not directly related to the purposes of this report, data on such materials might be of certain related interest. Therefore, Appendix III presents data on a sintered metal product and Appendix IV discusses a brief study made of a series of self-lubricating metal alloys.

Performance of Irradiated Solid Film Lubricants

The reaction of the irradiated films under a number of external environments and their ability to lubricate under load were considered as indices of the performance of the films. The film reaction to immersion in potential solvents, to the corrosive effects of salt spray, and to wide variation in temperature are shown in detail in the tables of data. The picture, based on this series of evaluations, is as follows:

The fluid resistance tests performed on the irradiated solid film coated panels, while of a somewhat qualitative nature, were nevertheless conclusive. It was observed, in general, that if a coated panel showed good resistance to solvent action prior to irradiation, it could be expected to show the same relative resistance subsequent to irradiation. Also, panels of exceedingly poor solvent resistance could not be expected to improve with exposure to radiation.

In only one instance was an irradiated panel corroded to a greater extent than the uncoated anodized panel. Other than that, the radiation appeared to have little detrimental effect on those panels that had good initial resistance to the salt spray. Salt spray corrosion would not appear to be increased, therefore, as a result of irradiation.

The same conclusions could be reached for the coated panels subjected to -65°F or 600°F as were reached for the fluid resistance data. If a composition had good initial properties, radiation did not change them seriously. If a composition did not show resistance to thermal extremes prior to irradiation, then little improvement, if any, could be expected as a result of exposure.

The major function of these films is to reduce or prevent wear of rubbing surfaces. The geometry of the specimens used in the Falex tester offers a simple and qualitative approach to comparison of pre-irradiation and post-irradiation effects.

Interpretation of the Falex wear life of the irradiated compositions was complicated by an error on the part of the operators. The runs were to have been at 250 pounds applied load, but many were conducted at 355 pounds, which explains the lack of control in many instances.

Figure 1 shows the results of testing of film A. The neutron and gamma irradiation data are shown on the same figure for convenience only. The data points are not to be considered as being at equivalent dosages on an absorbed energy basis. Falex life was apparently better for the samples tested at 250 pounds after neutron exposure and showed a slight decrease for the 355 pound jaw load. The same general trend was observed for the gamma irradiated pins, but the scatter is so great that further testing would be necessary to verify this point.

In Figure 2, it is seen that film C showed apparent improvement as a result of reactor irradiation, while the gamma exposures were detrimental. Film B showed greater wear life after neutron exposure and apparently some improvement with gamma irradiation. However, the low wear life for the irradiation at 8.71 x 10^{10} ergs/gm C casts some doubt on the effects of the gamma radiation.

Film D unfortunately had no control data run, but appears to improve with gamma exposure. Wear life after neutron irradiation is questionable.

Film G, as shown in Figure 3, displayed improvement with gamma irradiation. There is no control point for the wear life at 355 pounds, but it would appear that reactor irradiation also improves the wear life for this lubricant.

Film H had considerable scatter in wear life data points, as shown in Figure 3. It is apparent, however, that exposure to radiation was undoubtedly harmful to the wear life characteristics of this film.

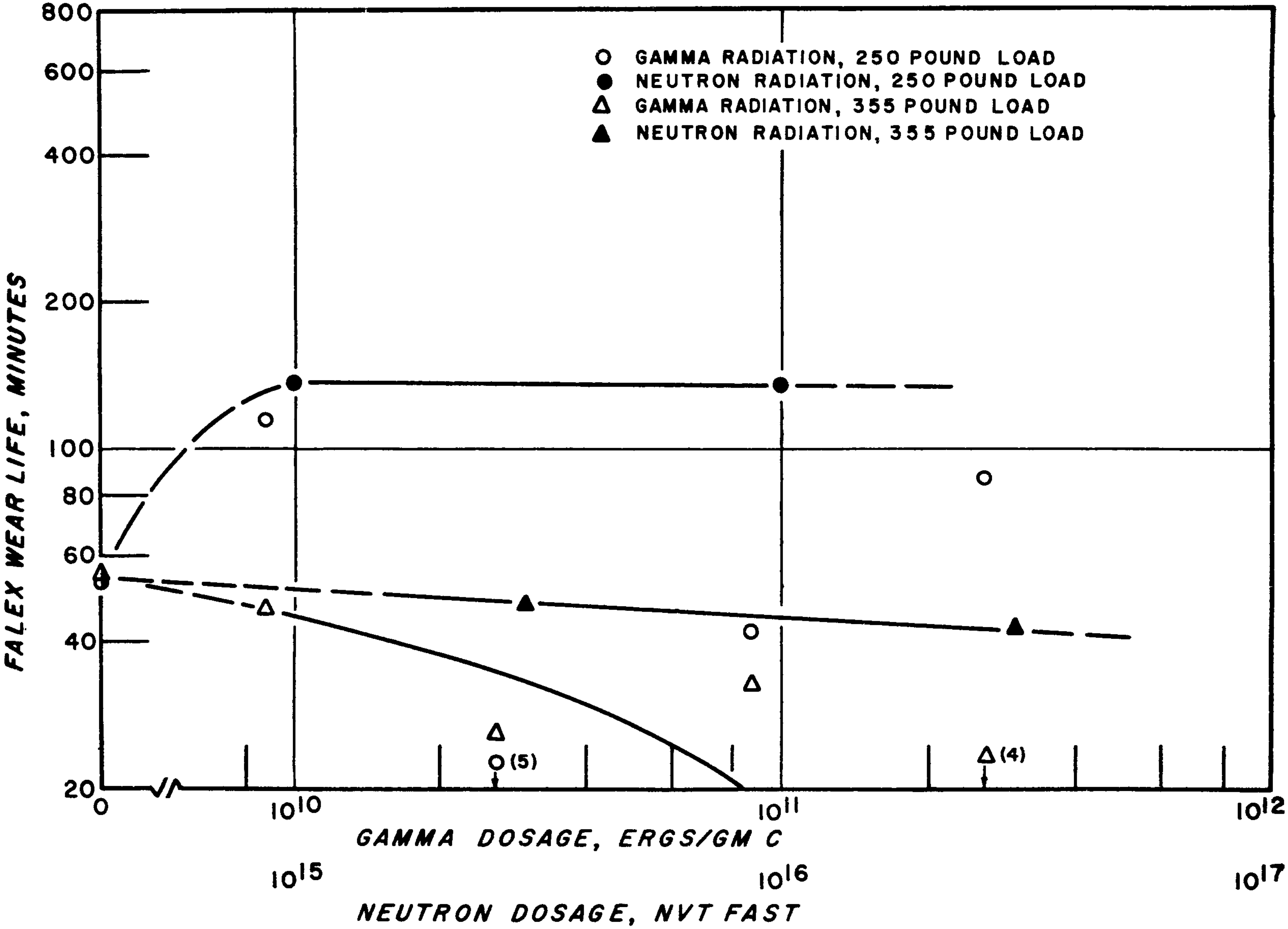


FIGURE I. FALEX WEAR LIFE OF SOLID FILM A

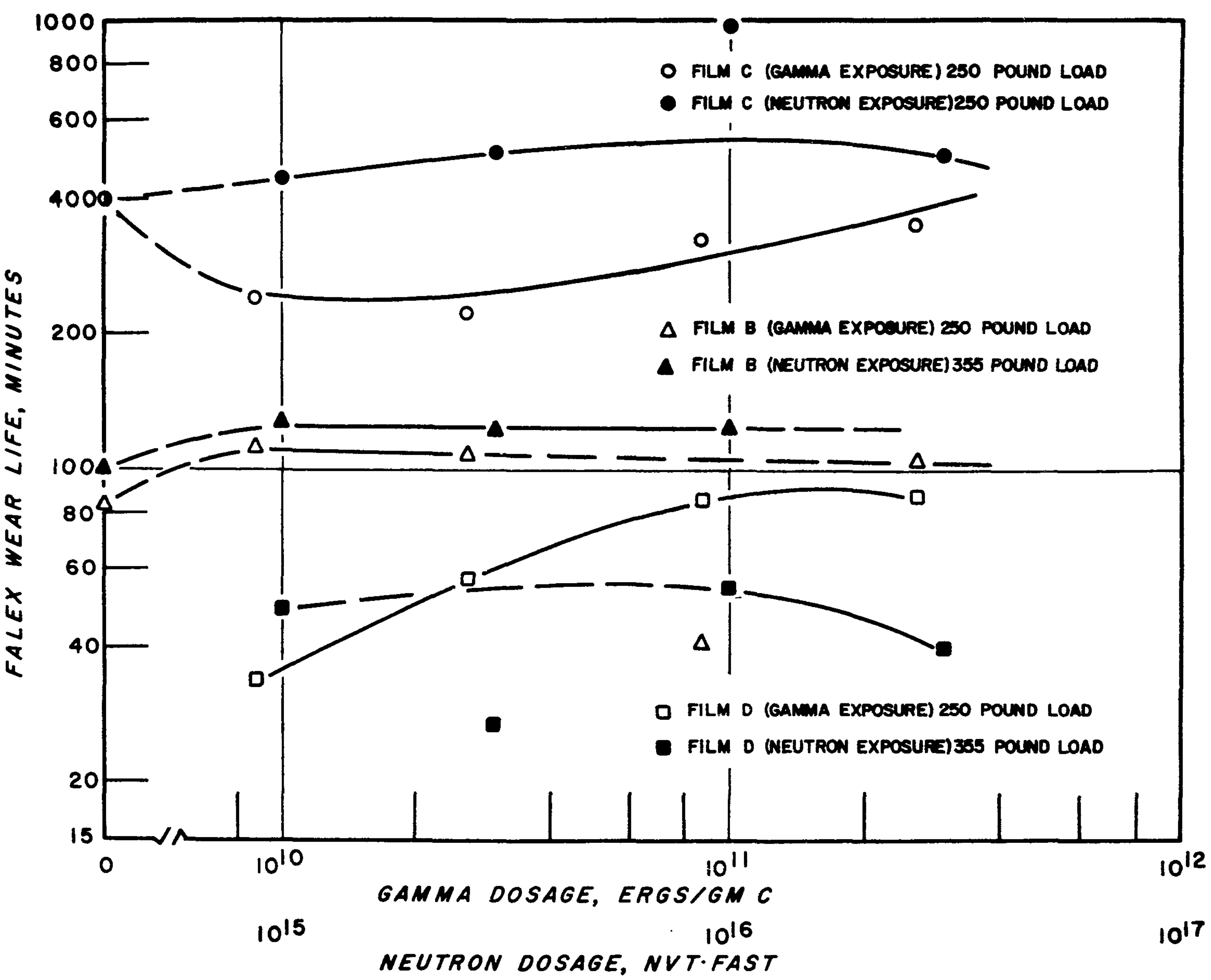


FIGURE 2. FALEX WEAR LIFE OF SOLID FILMS B, C, AND D

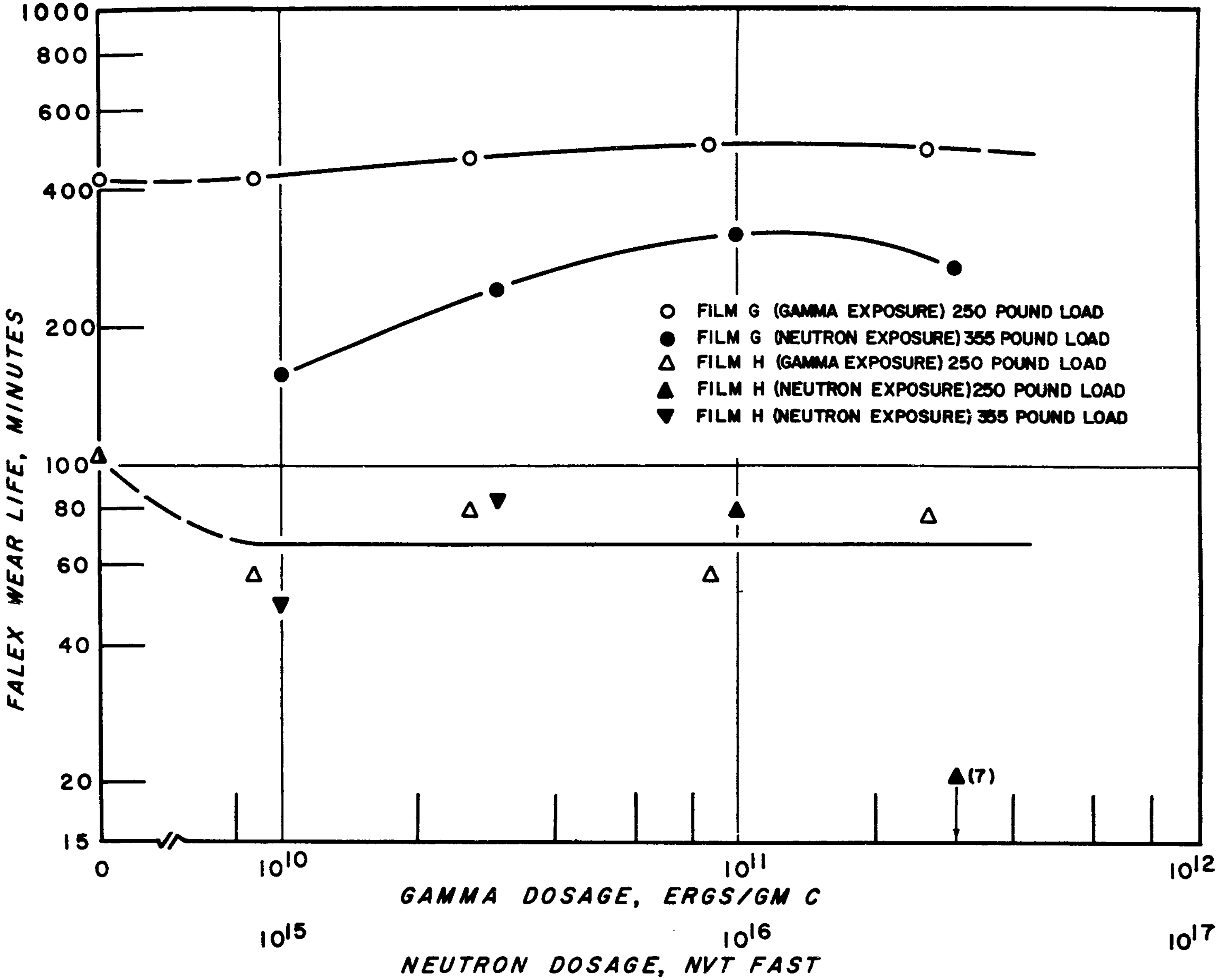


FIGURE 3. FALEX WEAR LIFE OF SOLID FILMS G AND H

It is interesting to note that film E, which was exposed only to gamma radiation (Table V), had very poor wear life both for the control and for the dosages up to 2.61 x 10^{10} ergs/gm C. At this level, the film displayed a very remarkable improvement in wear life, comparatively speaking.

Film F was poor in wear life both for the control and for all dosages of gamma radiation, as shown in Table V.

Based on the data obtained, two facts became apparent. First, it is entirely possible that exposure to nuclear radiation could improve the lubricating characteristics of solid film lubricants, at least as indicated by the Falex Tester at ambient temperature. Secondly, compositions of superior wear life under non-nuclear environments would probably be preferable for use in a radiation field, since one would have no reason to believe that relatively poorer films would have superior radiation resistance.

Figure 4 shows data for solid film wear life at 400°F and 550°F following exposure to gamma radiation (8). As could be expected, the wear life at the higher temperature is considerably reduced. The general trend is to an improvement in wear life or at least relatively little change. The only exception is film D, which showed a remarkable drop in 400°F stability but little change in wear life at 550°F. The reason for this difference is not apparent. It was postulated by the experimenter, reference (8), that this difference might be due to different stress concentration relief at the higher temperature. If so, this is a strong function of the film composition, since film I showed a marked improvement with irradiation in the 400°F evaluation.

Further data will be published by the Midwest Research Institute on similar tests conducted on neutron irradiated samples.

Conclusions and Future Plans

Based on the preliminary data thus far, it becomes evident that there is great promise for using solid film lubricants at extended temperatures and in the presence of nuclear radiation.

Studies to date have been mainly devoted to evaluation of the properties of commercial products of unknown composition. Research in the future will be limited mainly to use of known resin binders and specified lubricants and lubricant to binder ratios.

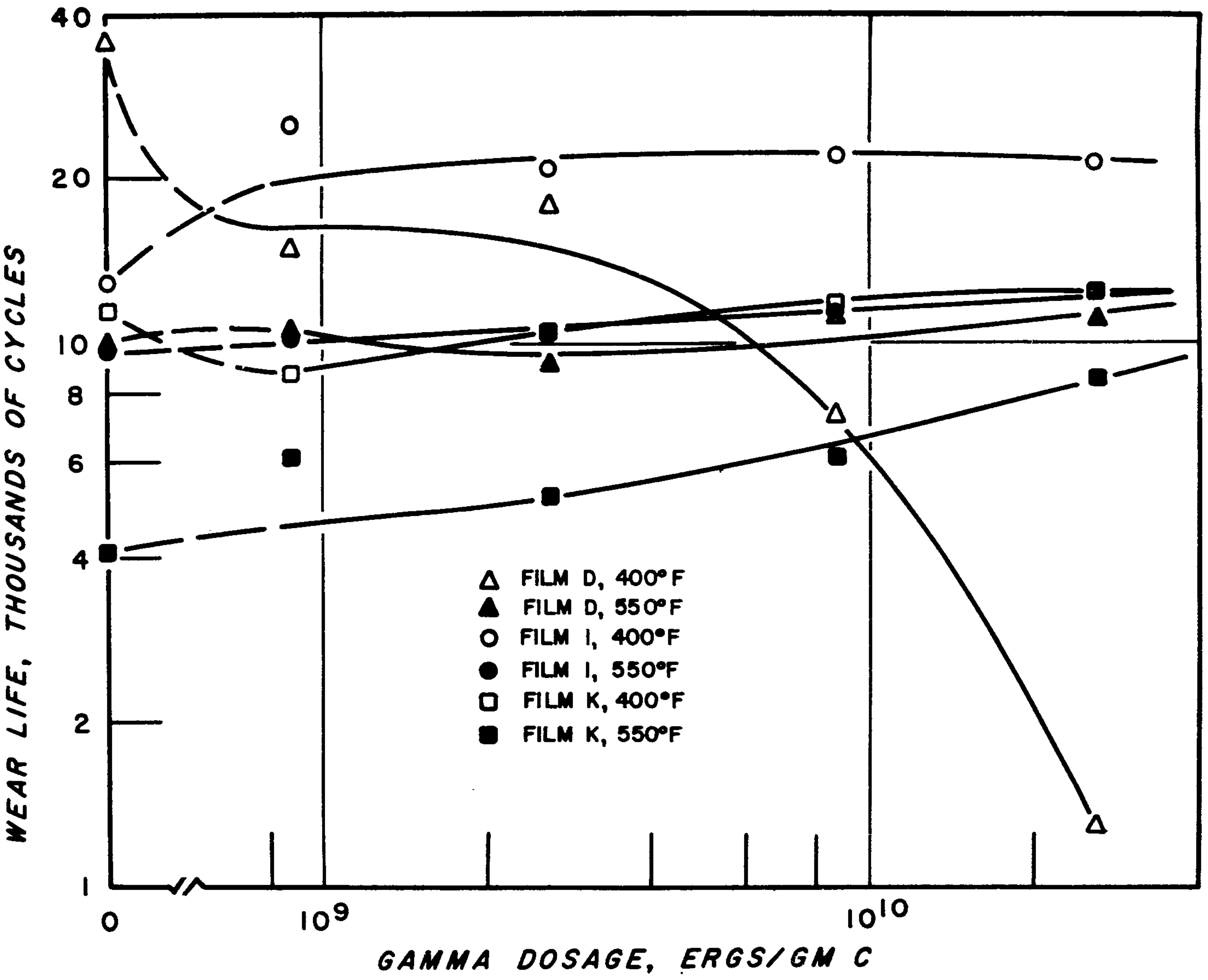


FIGURE 4. SOLID FILM WEAR LIFE AT 400°F. AND 550°F.

Work on stability of glass laminates to nuclear radiation has indicated a very interesting trend. Certain phenolic resins have actually shown improvement when irradiated at 500°F in the presence of gamma radiation as compared to the control held at the same temperature for the same time. They have also shown the highest stability to gamma radiation of the various resin types. Thus, the phenolics will receive major attention as binder materials for low temperature films.

Unlike other lubricant compositions, the solid film lubricants have a different reaction to reactor radiation. Since the binder and lubricant are in the solid form rather than liquid, solid state radiation effects become of importance. It is therefore planned to devote considerable effort to the study of reactor irradiation on the graphite used in solid film lubricants in order to determine the effect on the lubricity characteristics. Also to be studied will be the effect of reactor irradiation at temperature, to find the rate of defect annealment, if any, and its influence on lubricity characteristics.

From planned work on binder materials and lubricating additives, solid film lubricant formulations will be studied for resistance to nuclear radiation. Based on knowledge obtained to date, it is felt that a substantial increase will be made in the stability of solid film lubricants to nuclear radiation.

TABLE I. FLUID RESISTANCE OF IRRADIATED SOLID FILM LUBRICANT COATED ALUMINUM PANELS (ADHESION TEST)

Gamma Dosage*		0	2.61×10^{10}	8.71×10^{10}	2.61×10^{11}
Coating	Solvent				
A	MIL-H-3136	No discoloration, trace of powder, tendency to flake	No discoloration, trace of powder	No discoloration, powder	No panels
	MIL-H-5606	No discoloration, trace of powder, tendency to flake	No discoloration, powder, 90% flaking not to metal	No discoloration, powder	
	MIL-L-7808	No discoloration, trace of powder, tendency to flake	No discoloration, trace of powder	No discoloration, powder	
	MIL-H-8446	No discoloration, trace of powder, tendency to flake	No discoloration, trace of powder	No discoloration, powder	
	DC-550	No discoloration, trace of powder, tendency to flake	No discoloration, trace of powder	No discoloration, trace of powder	
B	MIL-H-3136	No discoloration, 50% flaking not to metal	No discoloration, no powder, tendency to flake	Nothing	No discoloration, 50% flaking not to metal
	MIL-H-5606	No discoloration, 30% flaking not to metal	No discoloration, flaking not to metal	No discoloration, no powder, flaking not to metal	No discoloration, 60% flaking not to metal
	MIL-L-7808	No discoloration, no flaking	No discoloration, no powder, tendency to flake	Nothing	No discoloration, 60% flaking not to metal
	MIL-H-8446	No discoloration, flaking not to metal	No discoloration, no powder, tendency to flake	Nothing	No discoloration, 5% flaking not to metal
	DC-550	No discoloration, trace of powder	No discoloration, no powder, tendency to flake	Nothing	No discoloration, 50% flaking not to metal
C	MIL-H-3136	Nothing	Nothing	Nothing	No panels
	MIL-H-5606	Nothing	No discoloration, 2% flaking to metal	Nothing	
	MIL-L-7808	Nothing	No discoloration, 2% flaking to metal	Nothing	
	MIL-H-8446	Nothing	No discoloration, 2% flaking to metal	Nothing	
	DC-550	Nothing	No discoloration, 2% flaking to metal	Nothing	
D	MIL-H-3136	No discoloration, powder	No panels	No discoloration, powder	No panels
	MIL-H-5606	No discoloration, powder		No discoloration, powder	
	MIL-L-7808	No discoloration, powder		No discoloration, powder	
	MIL-H-8446	No discoloration, powder		No discoloration, powder	
	DC-550	No discoloration, powder		No discoloration, powder	

TABLE I. FLUID RESISTANCE OF IRRADIATED SOLID FILM COATED ALUMINUM PANELS (ADHESION TEST) (Continued)

Gamma Dosage*		0	2.61×10^{10}	8.71×10^{10}	2.61×10^{11}
Coating	Solvent				
E	MIL-H-3136	No discoloration, trace of powder	No discoloration, trace of powder	Nothing	Nothing
	MIL-H-5606	No discoloration, trace of powder	No discoloration, trace of powder	Nothing	Nothing
	MIL-L-7808	No discoloration, trace of powder	No discoloration, trace of powder	Nothing	No discoloration, 1% flaking to metal
	MIL-H-8446	No discoloration, trace of powder	No discoloration, trace of powder	Nothing	Nothing
	DC-550	No discoloration, trace of powder	No discoloration, trace of powder	Nothing	Nothing
F	MIL-H-3136	No discoloration, trace of powder	No discoloration, trace of powder	No discoloration, trace of powder	No discoloration, trace of powder
	MIL-H-5606	No discoloration, trace of powder	No discoloration, trace of powder	No discoloration, trace of powder	No discoloration, trace of powder
	MIL-L-7808	No discoloration, trace of powder	No discoloration, trace of powder	No discoloration, trace of powder	No discoloration, trace of powder
	MIL-H-8446	No discoloration, trace of powder	No discoloration, trace of powder	No discoloration, trace of powder	No discoloration, trace of powder
	DC-550	No discoloration, trace of powder	No discoloration, trace of powder	No discoloration, trace of powder	No discoloration, trace of powder
G	MIL-H-3136	No discoloration, trace of powder	No discoloration, 2% flaking to metal	No discoloration, 30% flaking to metal	No panels
	MIL-H-5606	No discoloration, trace of powder	No discoloration, 2% flaking to metal	No discoloration, 2% flaking to metal	
	MIL-L-7808	No discoloration, trace of powder	Powder	Trace of powder	
	MIL-H-8446	No discoloration, trace of powder	Trace of powder	Trace of powder	
	DC-550	No discoloration, trace of powder	No discoloration, 2% flaking to metal	Trace of powder	
H	MIL-H-3136	No discoloration, 100% flaking to metal	No discoloration, 2% flaking to metal	Nothing	No panel
	MIL-H-5606	Nothing	No panel	No discoloration, 2% flaking to metal	No panel
	MIL-L-7808	Nothing	Nothing	Nothing	No discoloration, 2% flaking to metal
	MIL-H-8446	No discoloration, 5% flaking to metal	Nothing	No discoloration, 10% flaking to metal	Nothing
	DC-550	No discoloration, 50% flaking to metal	No discoloration, 2% flaking to metal	Flaking to metal (slight)	No panel

* Gamma dosages are in ergs per gram carbon.

TABLE II. SALT SPRAY CORROSION OF IRRADIATED SOLID FILM COATED ALUMINUM PANELS (ADHESION TEST)

Gamma Dosage*	Control		2.61×10^{10}		5.71×10^{10}		2.61×10^{11}	
Coating	Corrosion	Adhesion	Corrosion	Adhesion	Corrosion	Adhesion	Corrosion	Adhesion
A	High	Not run	High	Not run	High	Not run	High	Not run
B	None	Tendency to flake (2%)	None	Tendency to flake with some powder (2%)	None	Flaking (not to metal) (10-15%)	None	Traces of powder, flaking (not to metal)
C	None (1)	No powder	None (1)	Flaking to metal along edges (1%)	None (1)	Flaking to metal along edges (1%)	No panels	
D	High (1)	Not run	No panels		High (1)	Not run	No panels	
E	None (1)	Powder	None (1)	Traces of powder	None (1)	No powder, water marked	None (1)	No powder
F	None (1)	Powder	None (1)	Powder	(3)	Powder and flaking to metal	None (1)	Powder, water marked
G	None (1)	Traces of powder	None (2)	Slight powder, flaking to metal (10%)	Slight (1)	Powder and flaking to metal (20%)	No panels	
H	High (1)	Not run	High	Not run	High	Not run	High	Not run

* Gamma dosages are expressed in ergs per gram carbon.
(1) Anodized uncoated panel corroded.
(2) Anodized uncoated panel uncorroded.
(3) Corrosion high and worse than anodized panel.

TABLE III. THERMAL STABILITY OF IRRADIATED SOLID FILM COATED STEEL PANELS (ADHESION TEST)

Gamma Dosage*	Control		2.61 x 10^{10}		8.71 x 10^{10}		2.61 x 10^{11}	
Coating	-65°F	600°F	-65°F	600°F	-65°F	600°F	-65°F	600°F
A	Slight powder, flaking not to metal (1%)	Flaking not to metal (50%)	Slight powder	Flaking not to metal (50%)	Slight powder, flaking not to metal (1%)	Flaking not to metal (50%)	No panels	No panels
B	Flaking not to metal (30%)	Flaking not to metal (95%)	Slight powder, flaking not to metal (1%)	Flaking not to metal (95%)	No panels	No panels	Flaking not to metal (1%)	Flaking not to metal (95%)
C	Nothing	No flaking	Nothing	No flaking	Nothing	No flaking	No panels	No panels
D	Powder	Powder (95%)	No panels	No panels	Powder	Powder (95%)	No panels	No panels
E	Nothing	Nothing	Nothing	Nothing	Nothing	Nothing	Nothing	Nothing
F	Powder	Traces of powder	Powder	Traces of powder	Nothing	Nothing	Nothing	Nothing
G	Nothing	Powder (95%)	No panels	No panels	Nothing	Powder (95%)	No panels	No panels
H	Nothing	Traces of powder	No panels	Traces of powder	No panels	Traces of powder	No panels	Traces of powder

* Gamma dosages are expressed in ergs per gram carbon.

TABLE IV. FALEX WEAR LIFE FOR NEUTRON IRRADIATED SOLID FILM COATED PINS AND V-BLOCKS

Neutron Dosage (nvt fast)	Control		1×10^{15}		3×10^{15}		1×10^{16}		3×10^{16}	
Coating	Wear Life (Min.)	Total Wt. Loss (mg)	Wear Life (Min.)	Total Wt. Loss (mg)	Wear Life (Min.)	Total Wt. Loss (mg)	Wear Life (Min.)	Total Wt. Loss (mg)	Wear Life (Min.)	Total Wt. Loss (mg)
A	55* 81 24 (53)	2.7 4.1 —	120 154 (137)	4.4 6.0	58* 38* (48)	3.2 5.0	89 179 (134)	4.6 2.8	52* 33* (43)	3.7 4.6
B	101* 84	17.4 11.7	136* 119* (128)	9.8 6.8	118* 127* (123)	11.8 10.2	99* 149* (124)	10.5 9.3	194 153 (174)	16.9 46.0
C	371 285 538 (399)	6.2 8.9 7.7	394 495 (445)	28.7 39.0	655 370 (513)	19.9 14.3	1045 894 (970)	16.0 23.1	656 346 (501)	26.7 15.5
D	Pins lost		41* 57* (49)	24.5 68.3	17* 36* (27)	— —	41* 68* (55)	7.8 11.8	20* 59* (40)	— 10.2
G	409 443 (426)	19.9 17.7	165* 152* (159)	17.0 8.0	216* 271* (244)	7.4 7.4	304* 339* (322)	7.7 6.0	245* 300* (273)	7.1 7.0
H	111 100 (106)	10.8 10.7	69* 28* (49)	3.6 —	51* 116* (84)	2.7 3.7	86 72 (79)	2.6 3.7	9 5 (7)	— —

* 355 lb. load (all other data for 250 lb. load).
Note: Values in parenthesis ( ) represent average wear life.

TABLE V. FALEX WEAR LIFE FOR GAMMA IRRADIATED SOLID FILM COATED PINS AND V-BLOCKS

Gamma Dosage (ergs/gm C)	Control		8.71×10^{9}		2.61×10^{10}		8.71×10^{10}		2.61×10^{11}	
Coating	Wear Life (Min.)	Total Wt. Loss (mg)	Wear Life (Min.)	Total Wt. Loss (mg)	Wear Life (Min.)	Total Wt. Loss (mg)	Wear Life (Min.)	Total Wt. Loss (mg)	Wear Life (Min.)	Total Wt. Loss (mg)
A	55* 81 24 (53)	2.7 4.1 —	47* 97 130 (114)	5.0 6.6 5.0	26* 5	— —	33* 42	4.8 6.5	4* 71 102 (87)	— 3.3 4.7
B	101* 84	17.4 11.7	124* 113	10.4 10.9	90* 123 93 (108)	4.9 14.0 12.1	43 39 (41)	10.8 17.6	17 113 185 (105)	— 10.3 15.2
C	371 285 538 (399)	6.2 8.9 7.7	190 153 383 (242)	5.9 2.9 8.2	189 255 (222)	8.2 7.2	172 479 (326)	5.3 9.7	513 189 (351)	9.6 7.4
D	Pins lost		58 9 (34)	3.4 —	106 7 (57)	2.9 —	74 116 69 (86)	2.6 3.1 3.0	65 111 (88)	3.8 3.2
E	25 43 (34)	— 9.8	16 9 (13)	— —	20 11 14 (15)	— —	52 11 7 (23)	6.9 — —	101 138 (120)	10.5 3.6
F	3 4	— —	3 3	— —	2 1	— —	2 2	— —	3 3	— —
G	409 443 (426)	19.9 17.7	504 349 (427)	27.6 18.1	423 528 (476)	37.4 32.7	319 693 (506)	17.9 33.6	475 521 (498)	19.8 18.3
H	111 100 (106)	10.8 10.7	39 84 (57)	11.2 9.4	63 92 (79)	17.0 5.0	32 89 (57)	24.7 8.4	88 74 (77)	8.1 7.4

* 355 lb. load (all other data for 250 lb. load).
Note: Values in parenthesis ( ) represent average wear life.

TABLE VI. WEAR-LIFE TEST RESULTS FOR LUBRICANTS EXPOSED TO GAMMA IRRADIATION

Gamma Dosage (ergs/gm C)		Control	8.71×10^8	2.61×10^9	8.71×10^9	2.61×10^{10}
Coating	Rub Shoe Temperature (°F)					
D	400	35.7*	14.8	18.0	7.3	1.3
	550	9.9	10.4	9.1	11.2	11.0
I	400	12.8	25.1	20.8	22.0	21.6
	550	9.7	10.1	10.3	11.4	12.3
J	400	0.71	----	0.22	0.60	0.38
	550	Not run				
K	400	11.4	8.8	10.3	11.7	12.2
	550	4.1	6.1	5.2	6.1	8.6

* Wear life, thousands of cycles.

Test conditions:
Load - 400 pounds
Speed - 130 ft/min (375 cycles/min)
Thickness - Approximately 0.0004 in.
Motion - Unidirectional
Substrate hardness - 40-45 R_c
Machine - Hohman Friction Machine, Model A-3
Timken cups (Part No. T-54148)
Irradiated in MTR gamma canal.

Data from reference (8).

TABLE VII. EVALUATION OF SOLID FILM LUBRICANTS IN THE PRESENCE OF GAMMA RADIATION

Coating	Relative Humidity (%)		Ambient Temperature (°F)		Steady State Temperature (°F)	Wear Scar Area (sq. in.)	Radiation to Failure (ergs/gm C)	Wear Life (Hours)
	Start	End	Start	End				
C	69	60	72	76	158	0.0267	None	85.5
	59	60	76	75	146	0.0230	None	20.7
	66	66	75	76	160	0.0273	None	14.7
	69	68	75	71	155	0.0204	None	60.6
			67	67	144	0.0209	8.85 x 10^8	34.7
G	66	61	77	73	139	0.0164	None	151.9
	54	55	75	75	138	0.0229	None	87.7
	65	78	74	76	150	0.0167	None	77.2
			67	67	124	0.0158	1.58 x 10^9	60.6(1)
K	70	74	76	74	157	0.0231	None	17.8
	61	61	75	79	140	0.0192	None	33.9
	69	67	75	76	150	0.0233	None	7.5
	63	53	75	79	156	0.0188	None	48.2(1)
			67	67	147	0.0200	5.87 x 10^8	20.2(1)
L	51	74	76	76	145	0.0172	None	129.7
	74	58	74	78	140	0.0202	None	114.7
	62	66	76	75	144	0.0263	None	79.8

(1) Tests interrupted for approximately 5 hours due to power failure. Load was removed before re-starting and replaced gradually.

Test conditions:
Load - 630 pounds
Speed - 72 ± 2 rpm
Machine - Hartmann-Modified MacMillan
Timken cups (Part No. T-54148)
Irradiated in Inland Testing Laboratory's 52,000 Curie Co-60 source (all test results in this table were obtained under Contract AF 33(616)-3865.
Tested according to CRC method dated 2 February 1958, Appendix B.

APPENDIX I

SPECIFICATION MIL-L-25504 (USAF)

MIL-L-25504(USAF)

15 January 1957

MILITARY SPECIFICATION

LUBRICANT, SOLID FILM

1. SCOPE

1.1 This specification establishes the minimum performance and testing requirements for a bonded, solid-film lubricant applied to the surface of parts used in aircraft and missiles to reduce wear and prevent galling and seizure.

2. APPLICABLE DOCUMENTS

2.1 The following documents, of the issue in effect on date of invitation for bids, form a part of this specification:

SPECIFICATIONS

Federal

QQ-A-355	Aluminum Alloy (2024), Plate and Sheet
QQ-M-151	Metals; General Specification for Inspection of

Military

JAN-P-127	Packaging and Packing for Overseas Shipment - Tape, Adhesive, Pressure-Sensitive, Water-Resistant
MIL-H-3136	Hydrocarbon-Fluid, Standard Test
MIL-O-5606	Oil; Hydraulic, Aircraft, Petroleum Base
MIL-L-7808	Lubricating Oil, Aircraft Turbine Engine, Synthetic Base
MIL-L-7870	Lubricating Oil, General Purpose, Low Temperature
MIL-H-8446	Hydraulic Fluid, Nonpetroleum Base, Aircraft
MIL-A-8625	Anodic Coatings, For Aluminum and Aluminum Alloys
MIL-S-18729	Steel Plate, Sheet, and Strip, Alloy, 4130 Aircraft Quality

(Copies of documents required by contractors in connection with specific procurement functions should be obtained from the procuring activity or as directed by the contracting officer.)

3. REQUIREMENTS

3.1 Qualification.- The solid film lubricant furnished under this specification shall be a product which has been tested and has passed the qualification tests specified herein.

3.2 Materials.- The materials shall be such that the resulting film shall meet all the requirements of this specification.

3.3 Process.- A detailed description of the process for application and methods of control of variables shall be submitted by the contractor in the form of a titled, numbered, and dated process specification, together with the required number of processed metal panels and specimens, to the qualifying activity for approval. After approval, the process specification shall form a part of this specification and copies shall be made available by the contractor for use by authorized Government inspectors at the contractor's plant. It shall be the responsibility of the contractor to keep up-to-date with the changing requirements of this specification. When a change is made in processing, a revised process specification with amended code number and new date shall be submitted to the qualifying activity for approval. The process specification shall contain all necessary procedures, controls, precautions, and inspection methods to insure the satisfactory application of an approved material. The process specification shall also assure that variations within the specified thickness of 0.0002 inch to 0.0005 inch shall be no more than 0.0002 inch, except as indicated in 3.5.1.1.

3.4 Appearance.- The solid film lubricant, when tested in accordance with 4.3.1, shall be uniform in color and free from blisters or irregularities with no trace of grit, rough particles, nor separation of the ingredients. Scratches which have penetrated through to the pretreated surface of base material shall be cause for rejection.

3.5 Film Properties

3.5.1 Application.- Application methods shall not be limited. The lubricant shall be suitable for application in a coating thickness of at least 0.0002 inch, but no more than 0.0005 inch, except as indicated in 3.5.1.1.

3.5.1.1 Close Tolerance Applications.- On parts such as nuts, bolts, lock nuts, blind bolts, turbine blade roots, etc, where extreme coating thinness is mandatory and where extended wear life is not important, coating thinness may range as low as 0.0001 inch, as specified by the contractor. But for this type of application, the solid film lubricant material used shall still perform acceptably as described in 4.3.6 when applied at a thickness as prescribed in 3.5.1 on the test specimens.

3.5.2 Maximum Curing Cycle.- If the lubricant after application is to be cured, the film shall be fully curable at a maximum of 325°F for a maximum period of 60 minutes. The total time at a temperature above 275°F shall not exceed 75 minutes. Determination of adequate curing shall be in accordance with the wear and friction test specified herein. In production application of approved materials, curing temperature will be limited by the effects of heat on the properties of the base material.

3.5.3 Adhesion.- The coating shall demonstrate satisfactory adhesion when tested in accordance with 4.3.3.

3.5.4 Resistance Properties

3.5.4.1 Fluid Resistance.- A coating of solid film lubricant shall be chemically stable when in contact with fluids commonly found in aircraft and missiles. When tested as specified in 4.3.4.1, panels coated with the solid film lubricant shall be unaffected after a minimum of 120 hours immersion in each of the following fluids:

a. Distilled water
b. Hydrocarbon test fluid, Specification MIL-H-3136, Type III
c. Hydraulic fluid, Specification MIL-O-5606
d. Dioxane solvent
e. Engine oil, Specification MIL-L-7808
f. Dow-Corning silicone fluid DC-550, or equal
g. Skydrol 500
h. Lubricating oil, general purpose, Specification MIL-L-7870
i. Hydraulic fluid, Specification MIL-H-8446

3.5.4.2 Corrosion Resistance.- When tested in accordance with 4.3.4.2, coatings of solid film lubricants shall not accelerate the corrosion of 2024 aluminum, Specification QQ-A-355, which has been anodized in accordance with Specification MIL-A-8625.

3.5.5 Thermal Stability.- When tested in accordance with 4.3.5, the solid film lubricant coatings shall not be adversely affected by exposure to temperatures in the range of -65°F to 600°F.

3.5.6 Wear and Friction Properties.- Coatings of solid film lubricants shall exhibit satisfactory lubrication for 70 hours when tested in accordance with 4.3.6. The coefficient of friction shall not exceed 0.065 after initial burnishing. An increase to 0.1 or more during the test shall be cause for rejection.

3.6 Workmanship.- The workmanship shall be in accordance with high-grade commercial practice for high quality solid film lubricants.

4. QUALITY ASSURANCE PROVISIONS

4.1 Classification of Tests.- The inspection and testing of solid film lubricants shall be classified as follows:

a. Acceptance tests
b. Qualification tests

4.2 Acceptance Tests.- Acceptance tests shall consist of sampling tests only.

4.2.1 Sampling Plan and Tests

4.2.1.1 Lot.- For the purpose of sampling, a lot shall be defined as all solid film lubricant manufactured as one batch and offered for delivery at one time.

4.2.1.2 Sampling Plan.- Unless otherwise specified, a sample of lubricant sufficient to coat four test panels (see 4.2.1.3) shall be selected from each lot. The sample coated panels shall be subjected to the tests described in 4.3.1 through 4.3.3, as specified.

4.2.1.3 Preparation of Test Panels

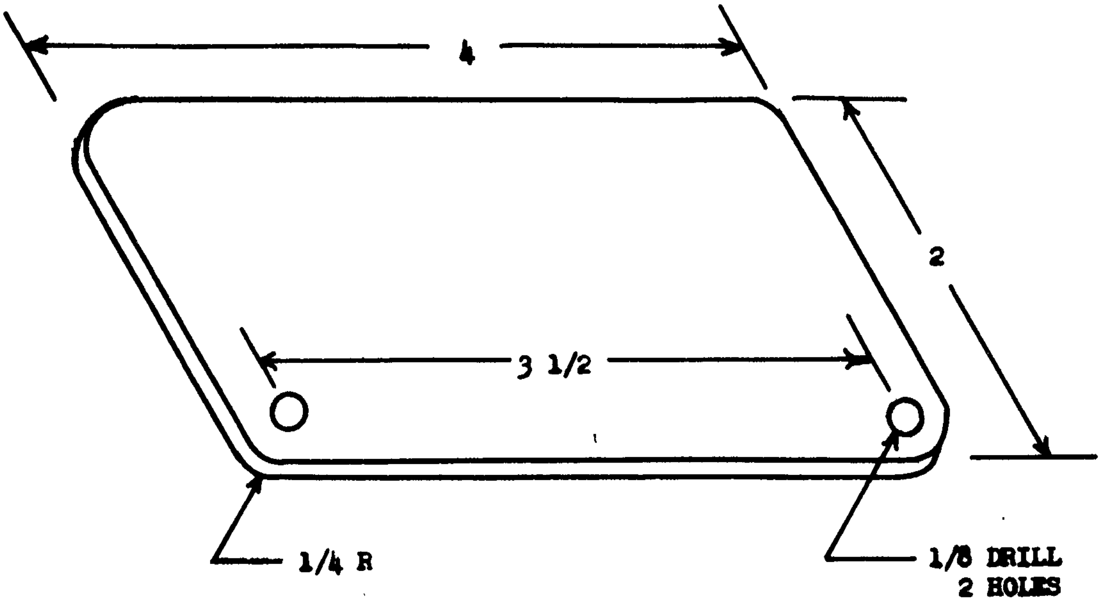
4.2.1.3.1 Test Panels for Appearance and Adhesion.- Three test panels of steel, SAE 4130, conforming to Specification MIL-S-18729, shall be prepared in accordance with Figure 1. The panels shall be fully coated in accordance with the contractor's approved process specification. The panels shall be subjected first to the appearance test and then to the adhesion test.

4.2.1.3.2 Test Panel for Film Thickness.- One test panel shall be prepared in accordance with 4.2.1.3.1 with the exception that the lubricant shall be applied in a 1-inch wide strip on the surface of the panel, centered along the 4-inch dimension. The coated test panel shall be subjected to the test described in 4.3.2.

4.2.1.4 Rejection and Retest.- When any panel coated with a sample of lubricant selected for acceptance testing as being representative of a certain lot fails to meet the requirements specified herein, one additional set of panels shall be prepared and coated with lubricant from the same lot. Failure of any of the second set of panels shall be cause for rejection of the lot represented.

4.3 Test Methods

4.3.1 Appearance (Visual).- The test panels prepared in accordance with 4.2.1.3.1 shall be inspected and examined visually for compliance with 3.3.



Thickness of panels shall
be between 0.125 in. and 0.040 in.

DIMENSIONS IN INCHES
UNLESS OTHERWISE SPECIFIED
TOLERANCES: FRACTIONS ± 1/8

Figure 1. Test Panels

4.3.2 Film Thickness (Application).- The test panel prepared in accordance with 4.3.1.3.1 shall be inspected for conformance to 3.5.1, using suitable precision micrometers to measure the difference between the uncoated portion of the panel and the coated portion.

4.3.3 Adhesion.- The panels shall be tested for adhesion of the film to the base material. A piece of tape conforming to Specification JAN-P-127, grade A, type I, shall be firmly pressed by hand onto the coated samples. The tape shall be 2 inches square. The tape shall be removed in one abrupt stripping motion and examined visually. The presence of traces of fine powdery material is acceptable; however, the presence of large flakes shall be cause for rejection.

4.3.4 Resistance Tests

4.3.4.1 Fluid Resistance.- Aluminum panels, as specified in Figure 1, coated in accordance with the contractor's process specification shall be immersed halfway into each of the fluids specified in 3.5.4.1 for a period of 120 hours. The panels shall be removed, rinsed quickly at room temperature in carbon tetrachloride or trichloroethylene, dried with a blast of clean dry air, and examined visually. Any indication of discoloration due to corrosion, lifting, softening, or other deterioriation shall be cause for rejection. Each panel shall then be subjected to the test specified in 4.3.3.

4.3.4.2 Corrosion Resistance.- Four aluminum panels, as specified in 4.4.1.1, shall be anodized in accordance with Specification MIL-A-8625. Two of these panels shall be coated with the solid film lubricant in accordance with the process specification. The four panels shall be subjected to the salt spray (fog) test outlined in Specification QQ-M-151 except that the surface of the test panels shall be inclined approximately 6° from the vertical. The test period shall be for a minimum of 240 hours. The four panels shall then be inspected visually for signs of corrosion. The presence of corrosion on the two uncoated panels to an extent greater than a few minute, isolated pits shall necessitate preparation of new panels and retesting. Any evidence of more extensive attack on the two coated panels than that on the two uncoated panels shall be cause for rejection. The two coated panels shall then be cleaned, dried, and subjected to the adhesion test, 4.3.3.

4.3.5 Thermal Stability.- Steel test panels, as shown in Figure 1, shall be pretreated and coated on both sides with the solid film lubricant in accordance with the contractor's process specification and subjected to the following tests.

4.3.5.1 High Temperature.- Two panels shall be placed in a circulating air oven at 600° ± 10°F. The panels shall remain in the oven for at least 5 hours and shall then be removed and allowed to cool slowly to room temperature. Any visual evidence of blistering, flaking, softening, or other deterioriation of the coating shall be cause for rejection. The panels shall then be subjected to the adhesion test specified in 4.3.3.

4.3.5.2 Low Temperature.- Two coated steel test panels shall be placed in a cold chamber at -65° ± 10°F for a minimum of 50 hours. The panels shall then be removed and allowed to return to room temperature, then dried and examined visually. Any lifting, flaking, or other deterioriation of the coating shall be cause for rejection. The test panels shall then be subjected to the adhesion test, 4.3.3.

4.3.6 Wear and Friction Properties.- The evaluation of the wear and friction properties of solid film lubricants shall be made in a bench-type tester capable of subjecting the test specimens to the test conditions listed below. Six Timken cups, Part No. T-54148, shall be coated with solid film lubricant according to 3.3, 3.4, and 3.5.2, and tested as follows:

a. Speed - 72 ± 2 revolutions per minute (rpm)
b. Load - 620 pounds
c. Temperature - Room temperature shall be maintained between 75° - 85°F
d. Humidity - 50 ± 5 percent
e. Loading Procedure - The weights shall be applied while the cup specimen is rotating by the following schedule:

Time-min	Actual Wts Applied-Lbs	Normal Load-Lbs
0-1	Bale Rod Only	30
1-2	do 3	120
2-3	do 6	210
3-4	do 9	300
4-5	do 12	390
5-6	do 15	480
6-7	do 16	510
7-8	do 17	540
8-9	do 18	570
9-10	do 19	600
10 to failure	do 20	630

f. Block Specimen - 4130 steel having a Rockwell C hardness of 30 ± 3. Surface roughness shall be 4-8 microinches, rms. Dimensions of the block shall be 0.250 ± 0.0002 by 0.620 ± 0.0002 by 0.400 ± 0.0002 inch. The 0.250-inch dimension shall be parallel to the axis of the cup.

g. Direction of Rotation - the test cup shall rotate in a counterclockwise direction when viewed from the specimen end of the test shaft.

h. Deviation of Lever System - the deviation of the bale rod end from the horizontal when fully loaded shall not exceed 1/8 inch.

The coated test cups shall run continuously on the bare 4130 steel blocks for a minimum of 70 hours without an increase in friction to 0.1. Failure of any one sample to meet these requirements shall be cause for rejection. The initial friction measurement shall be made 10 minutes after full load is applied.

4.4 Qualification Testing

4.4.1 Qualification Test Samples.- The size of the panel specimens, except for panel specimens for the corrosion resistance tests, shall be in accordance with Figure 1. The material to be used for a specific test and the number of panels required shall be as specified in Table II. Samples shall be identified with the manufacturer's own part number and any additional information required by the letter of authorization (see 6.3).

TABLE II

Qualification Test Panels

Quantity	Material 1/	Test Paragraph
---	Use panels below	4.3.1
2	Steel panels coated as specified in 4.2.1.3.2	4.3.2
1	Steel panels pretreated & coated	4.3.3
9	Aluminum panels pretreated & coated	4.3.4.1
4	Aluminum panels anodized & coated	4.3.4.2
4	Aluminum panels anodized only	4.3.4.2
4	Steel panels pretreated & coated	4.3.5

1/ Steel shall conform to Specification MIL-S-18729, SAE 4130, and aluminum shall conform to Specification QQ-A-355, 2024-T3 or T4.

4.4.1.1 Sample for Corrosion Resistance Test.- Four panels shall be cut from the same sheet of 2024-T3 or T4 aluminum conforming to Specification QQ-A-355. Each panel shall be 3-inches wide by 10-inches long by 0.040-inch thick. The 10-inch side shall be transverse to the rolling direction.

4.4.2 Coating of Test Panels.- All test panels which require a coating of the solid film lubricant shall be coated by the contractor in accordance with the contractor's process.

4.4.3 Qualification Tests.- The qualification tests shall consist of all the tests described under 4.3 "Test Methods."

5. PREPARATION FOR DELIVERY

5.1 Not applicable.

6. NOTES

6.1 Intended Use.- The solid film lubricants covered by this specification have been found to be generally suitable for sliding motion types of applications such as plain spherical bearings, flap tracks, hinges, cam surfaces, gears, etc. In addition, solid film lubricants may be adaptable for other applications where temperature, inaccessibility, contamination, etc, render conventional lubricants unsatisfactory or impractical. Solid film lubricants may also be used to minimize fretting corrosion.

6.1.1 Solid film lubricants have not generally been successful when used in ball bearing screw-jacks or internal parts of anti-friction bearings. It is recommended that when these coatings are contamplated for use in aircraft or missiles in these types of applications approval be obtained from the cognizant project office or laboratory.

6.1.2 Solid film lubricants may have their endurance properties shortened by exposure to high temperatures in service. It is therefore recommended that each application where service temperatures exceed 450°F be investigated for actual performance.

6.1.3 Reapplication.- The use of solid film lubricants should be limited to those parts which will not require reapplication of the film during the normal use life of the part except where the material will be used for break-in purposes in conjunction with other approved oils and greases.

6.2 Ordering Data.- Procurement documents should specify the following:

a. Title, number, and date of this specification.

6.3 Qualification.- With respect to products requiring qualification, awards will be made only for such products as have, prior to the bid opening date, been tested and approved for inclusion in the applicable Qualified Products List whether or not such products have actually been so listed by that date.

6.3.1 The attention of suppliers is called to this requirement, and manufacturers are urged to arrange to have the products that they propose to offer to the Federal Government tested for qualification in order that they may be eligible to be awarded contracts or orders for the products covered by this specification. Information pertaining to qualification of products covered by this specification may be obtained from the Commander, Wright Air Development Center, Attn: WCLTR-1, Wright-Patterson Air Force Base, Ohio.

6.4 Base Material Finish.- The surface roughness of parts to be coated for use in sliding motion should be not greater than 63 micro-inches for best endurance life and maximum adhesion. Parts such as threaded fasteners, which are not in frictional motion frequently, may be as rough as 125 micro-inches or more, with respect to the direction of motion, without reducing the effectiveness of the coating.

6.5 Vapor and Grit Blasts.- It is recommended that all grit blasts performed on parts to be coated with solid film lubricants be done with No. 120, Al_2O_3 or SiO_2 which is clean and sharp. The maximum coarseness of material should be No. 120 Alundum, or equivalent. The choice of material used will depend on the surface hardness and the finish roughness desired.

6.6 Detail Drawing Call-Outs.- Engineering detail drawings of parts to be coated should give specific pretreatments to be used and allowable limits on pretreatment and solid film lubricant thicknesses.

6.7 Threaded Fasteners.- Where solid film lubricants are used on threaded fasteners, a considerably lower torquing value should be used than that normally recommended for unlubricated threaded fasteners. In general, the torquing values for (a) thread coated and (b) thread and head coated fasteners should be about 70 percent and 40 percent, respectively, of the recommended values for unlubricated steel fasteners.

NOTICE When Government drawings, specifications, or other data are used for any purpose other than in connection with a definitely related Government procurement operation, the United States Government thereby incurs no responsibility nor any obligation whatsoever; and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any right or permission to manufacture, use, or sell any patented invention that may in any way relate thereto.

APPENDIX II

IRRADIATION HISTORY OF TEST SPECIMENS

Gamma Irradiations

The metal test panels and Falex sets exposed to gamma radiation and tested as shown in Tables I through V were irradiated in the gamma canal of the Materials Testing Reactor, Arco, Idaho. For details of exposure techniques and dosimetry, a summary is given in reference (9). Such information will not be presented herein.

For each gamma dosage, five coated steel and eight coated aluminum panels were irradiated for each solid film lubricant studied. Also, two anodized, uncoated aluminum comparison panels were irradiated to each given dosage. The panels were irradiated in packs, each pack consisting of two or three steel panels in the center with two aluminum panels on each side. These packs were mounted vertically in the standard irradiation canisters at the midplane and exposed in the gamma canal.

All gamma dosages are given in terms of the unperturbed fuel element array, that is, before the canisters with contents were inserted. Therefore, no corrections have been made for attenuation in the canister wall or in the outer panels shielding the interior panels. This should be carefully noted, since the gamma exposures are to be considered as nominal rather than absolute and serve to give comparative effects of increasing gamma irradiation only.

For each gamma dosage, three sets of Falex pins and V-blocks were irradiated for each solid film lubricant studied. Each set, consisting of one Falex pin and two V-blocks, was irradiated with the notch of each V-block facing outward from the vertically positioned pack. As in the case of the test panels, no attenuation corrections were made either for the canister or its contents. The wear data given in Tables IV and V should be considered therefore as based on comparative exposures and not on well defined exposures to the coatings.

Neutron Irradiations

Only Falex sets were exposed to neutron irradiation. For each solid film lubricant studied, three Falex sets were irradiated to each of the given dosages. Exposures were in the X-10 reactor at Oak Ridge, Tennessee. Information pertinent to the irradiations is as follows:

Relative thermal neutron flux: $6.50 \pm 0.05 \times 10^{11}$ n/cm^2/sec

Epithermal (cadmium ratio): 10.8

Fast neutron dosages:

neutrons above 2.9 mev	2.0×10^9 n/cm^2/sec
neutrons above 6.3 mev	$1.40 \pm 0.06 \times 10^9$ n/cm^2/sec
neutrons above 8.1 mev	$0.93 \pm 0.01 \times 10^9$ n/cm^2/sec

The above data were obtained by the use of Co-Al, S, Al, and Mg monitors.

APPENDIX III

EFFECT OF GAMMA RADIATION ON A SINTERED METAL LUBRICATING MATERIAL

TABLE VIII. EFFECT OF GAMMA RADIATION ON THE FALEX WEAR OF A SINTERED METAL LUBRICATING MATERIAL

Gamma Dosage (ergs/gm C)	Run 1	Run 2	Run 3	Average
None	22.1(1)	29.2	53.9(2)	25.7
2.61×10^9	(3)	(4)	(5)	----
8.71×10^9	32.7	30.1	28.9	30.6
2.61×10^{10}	18.4	32.6	24.7	25.2
8.71×10^{10}	26.3	22.5	26.7	25.2

(1) Weight loss in mg (after run).
(2) At 200 pound load.
(3) Pin sheared after 9 minutes, gummy substance deposited during run.
(4) Pin sheared after 14 minutes, gummy substance deposited during run.
(5) Pin sheared after 18 minutes, gummy substance deposited during run.

Test conditions:
Load - 100 pounds for 30 minutes
Speed - 290 rpm
Machine - Falex Lubricant Testing Machine
Samples irradiated in the WADC 1500 Curie Cobalt-60 pipe
Pins were cleaned with fine sand paper, washed with naphtha, and oven dried for 30 minutes at 120°F prior to testing. The pins were then run on standard steel V-blocks.

APPENDIX IV

FALEX MACHINE EVALUATION OF DEVA METALS

Falex Machine Evaluation of Deva Metals

The purpose of this evaluation was to investigate four Deva Metal types to determine if any show superiority to commercial dry film lubricants. A chemical analysis was conducted concurrently to allow nuclear activation calculations should any of the metals prove attractive enough to merit reactor irradiation for purposes of studying their nuclear radiation resistance.

Deva Metal, a "self-lubricating" bearing material, has potential interest in areas where environmental conditions preclude the use of conventional lubricants. Examples would be areas of extreme high or low temperature. It would also be of interest for use in the presence of nuclear radiation where organic lubricants are readily degraded and lose their lubricating characteristics.

Four Deva Metal types were machined to standard Falex Pin size and evaluated on the Falex Test Machine using conventional steel V-blocks. The results of the testing are shown in Table IX. Chemical analyses of the metals are given in Table X.

The Deva Metal specimens were first run at a 500 pound jaw load on the Falex machine. At this load, the pins machined to such an extent that results could not be obtained. It was evident that test conditions were too severe so the pins were then tested at 50 and 100 pound jaw loads. Under these lighter loads, the metals gave similar results, either machining to such an éxtent that jaw load could not be maintained or breaking at the shear pin.

Uncoated steel Falex Pins were run under the same loads against bare V-blocks. Machining again took place at an even greater rate than for the Deva Metal pins. By comparison, certain commercial solid film lubricants, when coated on similar steel pins, give the following results: When run at a 500 pound jaw load for the standard one-half hour, weight losses were obtained varying from 0.6 mg up to 250 mg, depending on the coating used. Average values for the better coatings are about 10 to 12 mg weight loss for the pin following this test.

On the basis of the tests conducted, it can be concluded that when compared with commercial solid film lubricants, the four Deva Metal types evaluated perform quite poorly when tested on the Falex machine. However, when compared to bare steel on steel, they show a superiority, limited though it might be. It should be noted that the conclusions reached herein are valid only with respect to the conditions described. Under lighter loads, it is quite possible that Deva Metals would show superior qualities to other methods of lubrication, especially at elevated temperatures where organic solids would tend to decompose.

As a result of the testing described above, it was decided to discontinue further evaluation of the Deva Metal specimens and to abandon plans to subject them to nuclear radiation. With the test apparatus used, the Falex Test Machine, the test conditions were so severe that it would not be possible to determine what effect, if any, nuclear radiation would have on the metal properties. Any decrease in the already poor qualities measured would not show up as a significant change in the metal capabilities.

It is felt that in applications where use of solid film lubricants is required, Deva Metals of the type described herein be used only if solid film lubricants can be shown to be inferior.

TABLE IX. FALEX MACHINE EVALUATION OF DEVA METALS

Pin Composition	Run #	Time to Failure (minutes) 50 lb. load	100 lb. load
Steel (1)	1	2	1
1F-15-S4	1 2	2 (Broke) 3 (Broke)	1 (Broke) 2 (Broke)
1F-10-S5	1 2	12 16	0.2668 gm wt loss(2) 0.2601 gm wt loss(3)
2N-15-S4	1 2	17 18	24 20
2N-8-S2	1 2 3	17 16 --	12 14 9

(1) SAE 3140 or 3145 steel
(2) Original weight was 6.9458 gm
(3) Original weight was 6.9640 gm

Note: All tests were run at 295 rpm (or 19.3 ft./min.) and room temperature (about 75°F). Steel V-blocks were used for all tests, the composition being SAE 1141 or 1144 steel. Failure time is the time at which the pins machined to such an extent that the jaw load could not be maintained. No pins were weighed, since the tests did not run full half hour (except for the 1F-10-S5).

TABLE X. CHEMICAL ANALYSIS OF DEVA METALS

Metal Type	1F-15-S4	1F-10-S5	2N-15-S4	2N-8-S2
% Carbon (total)	13.75	9.31	13.59	6.90
% Iron	79.38	83.85	-----	-----
% Nickel	-----	-----	79.32	87.13
% Copper	3.47	3.54	3.93	3.94
% Aluminum	1-3.4(1)	1-3.3(2)	1-3.2(3)	1-2.0(4)

(1) The aluminum, which is approximately 10 times as great as any other element, plus silicon, magnesium, calcium, manganese, tin, and chromium constitute the remainder.

(2) The aluminum, which is approximately 10 times as great as any other element, plus silicon, magnesium, calcium, manganese, tin, chromium, and titanium constitute the remainder.

(3) The aluminum, which is approximately 10 times as great as any other element, plus silicon, magnesium, calcium, manganese and tin constitute the remainder.

(4) The aluminum, which is approximately 10 times as great as any other element, plus silicon, magnesium, lead, calcium, manganese, and tin constitute the remainder.

APPENDIX V

LIST OF VENDORS

The following list gives the addresses of the vendors supplying the coatings to the panels and Falex sets summarized in Tables I through V:

Company	Product
Acheson Colloids Company Attn: Mr. F. M. Hunter Sales Engineering Lab. Port Huron, Michigan	'Dag' Dispersion #213 'Dag' Dispersion #223
Electrofilm, Incorporated Attn: Mr. Ralph E. Crump Chief Engineer Post Office Box 106 7116 Laurel Canyon Boulevard North Hollywood, California	Solid Film Lubricant #4396 Solid Film Lubricant #4856
Everlube Corporation of America Attn: Mr. A. R. Booker Exec. Vice President 6940 Farmdale Avenue North Hollywood, California	Everlube #620 Everlube #810
McGee Chemical Company, Inc. Attn: Mr. Zell G. McGee President 8000 West Chester Pike Upper Darby, Pennsylvania	McLube MoS_2-830 McLube MoS_2-835
Deva-Metal Corporation Attn: Mr. Charles G. Welchman President Post Office Box 146 Ridgewood, New Jersey	Deva-Metals

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THE INTEREFFECTS OF REACTOR RADIATION AND OIL

by

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In an experiment to investigate the intereffects of oil and reactor radiation, six specimens of MIL-L-7808C aircraft turbine oil were irradiated in the form of slabs of one-half inch thickness. The specimens were stacked so that each acted to shield those behind it and the neutron and gamma radiation was measured between specimens.

Comparison of measured values with theoretical curves for the change in the radiation field as it progressed through the oil shows that the attenuation of neutrons and gammas through oil can be predicted with reasonable accuracy.

Although the doses received by the specimens were not sufficient to cause extensive degradation of properties, some increases in viscosity and neutralization number were noted, the extent of change in the oil nearer the reactor being greater than in the more remote specimens.

INTRODUCTION

When a sample of material is placed in a radiation field, certain incremental volumes - the molecules near the surface - act to shield other, more interior portions. Relatively solid materials or very viscous liquids, as a result, experience greatest damage near the surface upon which the radiation is incident. However, for free-flowing liquids or for liquids deliberately agitated, all molecules are subjected to essentially the same dose. This dose is necessarily somewhat less than that incident upon the source side of the sample, and can be assumed to be an average of the dose received in all volumes of the sample. For this reason, any expression of sample dose which disregards the change in the radiation through the sample is unrealistic. The true sample dose can be expressed only after the following factors contributing to the magnitude of the change are considered:

1. The nature of the radiation field - the type, flux, and the energies of the particles;
2. The particular composition and density of the sample material; and,
3. The thickness of the specimen as seen by the radiation field.

The evaluation of fluids for nuclear environment applications requires extensive properties testing, for which relatively large volumes of fluid are needed. It is to advantage that we have a knowledge of fluid self-shielding so that a sample thickness can be selected which will minimize this shielding and at the same time provide a sample volume sufficient for property testing.

In the interest of investigating these problems, a recent experiment was conducted at the Convair Nuclear Laboratories involving the irradiation of MIL-L-7808C aircraft turbine oil. The experiment had the following objectives:

1. To investigate the magnitude of neutron and gamma attenuation by oil;
2. To collect data to aid in selecting an optimum sample thickness for oil irradiation experiments; and,
3. To augment the radiation effects data already available on MIL-L-7808C aircraft turbine oil.

DESCRIPTION OF SPECIMENTS AND SPECIAL EQUIPMENT

Experimental Fluid

MIL-L-7808C aircraft turbine lubricant ranks very high among commercially available jet engine lubricants and can probably satisfy many of the nonnuclear requirements for a nuclear powered engine oil. It has been previously established[1] that this oil is fairly stable when irradiated under static conditions to doses below 10^9 ergs/gm(C).

The particular sample used was a synthetic diester with a sebacate base - approximate structure $(C_{26}H_{50}O_4)x$. The sample was obtained commercially and probably contained small amounts of additives to impart oxidation stability, corrosion-preventive and anti-wear properties. Six specimens, approximately one liter each, were irradiated under a dry helium atmosphere.

Irradiation Container

A seven-unit container, consisting of one large rectangular tank, 15-½" x 14" x 10" (outside) and constructed of 3/4-inch thick **aluminum,** and six smaller cans, each 14¼" x 10" x ½" (inside), and constructed of 1/8-inch thick aluminum, was fabricated. Figure 1 is a sketch of this container.

The large tank served as a drip pan, atmosphere retainer, and supporting frame for the smaller cans. Between each of the smaller cans holding the six oil specimens, a 3/8-inch air space was provided to accommodate the radiation detectors.

Radiation Detectors

Five sets of dose monitors were located in the spaces between adjacent cans and five behind the sixth. Thus, a total of 35 sets of monitors were used, each set consisting of the following:

1. A magnesium disc to monitor fast neutrons above the 6.3 Mev threshold.

2. A pair of gold foils - one bare and one cadmium-covered - to monitor thermal neutrons of energies below the 0.48 ev cutoff.

3. A pair of chemical dosimeters to monitor the gamma dose. Two dosimeters were used at each point to increase accuracy; at the 95 percent confidence level two of these dosimeters agree within ±6 percent. These dosimeters are calibrated in roentgens. In reporting the gamma dose in this paper, one roentgen is considered equivalent to one rem and to 87.7 ergs/gm(C).

The dose monitors were arranged as shown in Figure 1. Monitors were deliberately not positioned at the outer extremities so that reaction with scattered particles could be minimized.

IRRADIATION CONTAINER

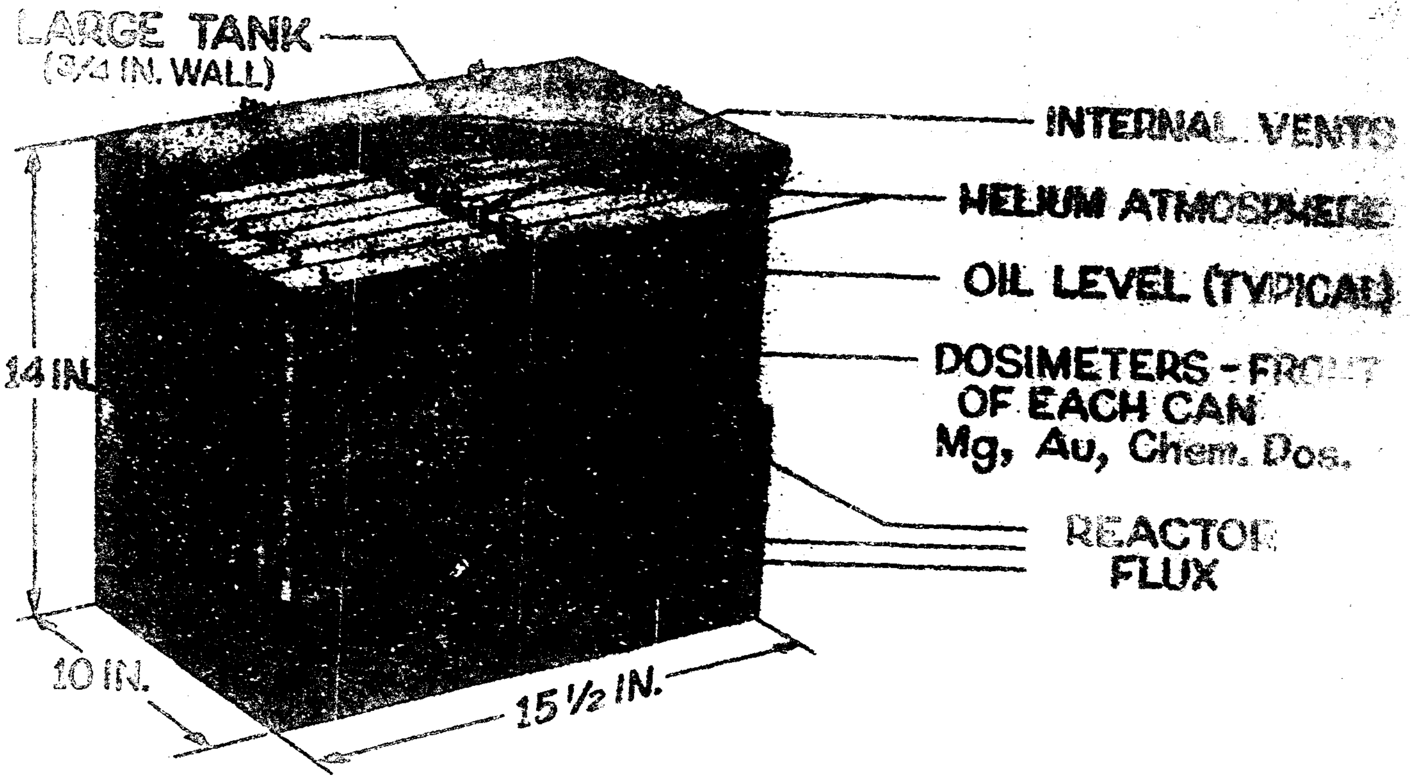

FIGURE 1

THE IRRADIATION

The oil container was loaded into one of the boral-clad aluminum chambers usually used to hold materials during ambient-temperature irradiations. Orientation between the container and the Ground Test Reactor was such that all the small cans were parallel with the reactor face. The first specimen was nearest the reactor, so that each specimen shielded, to some extent, those behind it.

A configuration was thus established in which each group of dose monitors were shielded by oil and aluminum of a particular thickness. This shielding thickness increased by one-half inch increments of oil and one-quarter inch increments of aluminum between successive groups.

A 20-hour irradiation was made at a nominal reactor power level of 500 kw.

TEST METHODS AND RESULTS

Oil Testing

Physical property testing was performed on the six irradiated oil specimens and on a control specimen from the original sample. The tests, methods, and results are listed in Table I. Figure 2 gives a plot of some of these properties as a function of the dose received on the specimen face. Neutron-to-gamma ratios are shown because they varied between specimens.

Dosimetry

The data from the dose monitors, reduced by standard methods and analyzed with respect to the effect of the oil and aluminum on the radiation field, are listed in Table II. Each value represents an average of the data from the five sets of monitors on a particular can.

The percent of fast neutron transmission through oil and aluminum is shown in Figure 3. Figure 4 shows the percent transmission of gamma radiation of the GTR spectrum. Theoretical curves are included in these figures to show comparison with experimental curves. The neutron cross sections and gamma absorption coefficients used in the calculations are indicated on the figures.

TABLE I

MIL-L-7808C - TESTS, METHODS AND RESULTS

Test	Irradiation Can No. and Data (See Table II for Radiation Dose)						
	Control	1	2	3	4	5	6
Viscosity (ASTM D445-53T)							
Centistokes @ 100°F	13.65	14.86	14.64	14.50	14.45	14.37	14.23
Centistokes @ 210°F	3.49	4.27	3.66	3.74	3.61	3.57	3.58
Neutralization No. (ASTM D664-54)	0.32	6.71	5.71	5.29	4.79	4.05	3.67
Precipitation No. (ASTM D91-52T)	Trace	0.13	0.13	0.13	Trace	Trace	Nil
Bromine No. (ASTM D1158-55T)	0.37	1.94	1.15	0.76	0.99	0.64	0.99
Specific Gravity @ 60/60°F (ASTM D1298-55)	0.932	0.929	0.931	0.929	0.929	0.929	0.931
AFTER OXIDATION/CORROSION TEST (FTMS-791 Method 5308.3)							
Viscosity							
Centistokes @ 100°F	14.57	15.27	15.19	15.06	15.02	14.69	14.78
Centistokes @ 210°F	3.62	3.85	3.82	3.81	3.71	3.65	3.72
Viscosity Change % @ 100°F	+6.74	+2.76	+3.76	+3.86	+3.94	+2.23	+3.72
% @ 210°F	+3.73	+9.84	+4.37	+1.87	+2.77	+2.24	+3.91
Neutralization No.	0.72	7.88	7.33	6.31	4.49	4.01	2.96
Neut. No. Change	+0.40	+1.17	+1.62	+1.02	-0.30	-0.44	-0.71
Weight Change, metal Specimens (mg/cm^2)							
Copper	+0.28	-0.66	-0.22	-0.09	-9.26	-0.33	-0.18
Silver	+0.52	+0.36	+0.37	+0.52	+1.10	+0.20	+0.25
Steel	+0.29	+0.35	+0.02	+0.05	-0.80	-1.20	-1.00
Magnesium	+0.37	-0.06	-0.51	-1.16	-2.55	-4.29	-6.39
Aluminum	+0.35	+0.44	+0.29	+0.23	+1.84	+0.12	+0.19
Appearance Metal Specimens	Fail	Fail	Fail	Fail	Fail	Fail	Fail
Precipitation No.	0.13	0.49	0.35	0.33	1.25	0.30	0.22

TABLE II

RADIATION DOSE ON OIL SAMPLES

Container Number	Shielding (inches)		Gamma Dose (rem)	Gamma Dose (ergs/gm(C)	Fast Neutrons $E>6.3$ Mev (n/cm^2)	*Fast Neutrons $E>0.33$ Mev (rem)	Thermal Neutrons $E<0.48$ ev (n/cm^2)	Neutron to Gamma Ratio (rem/rem)	Total Dose (Total rem)
	Oil	Al.							
1	0.00	0.00	**1.16(8)	1.02(10)	6.21(13)	4.45(7)	2.06(14)	0.384	1.61(8)
2	0.50	0.25	1.05(8)	9.21(9)	4.95(13)	3.54(7)	5.64(14)	0.338	1.40(8)
3	1.00	0.50	8.50(7)	7.45(9)	3.91(13)	2.78(7)	5.32(14)	0.328	1.13(8)
4	1.50	0.75	7.01(7)	6.15(9)	2.70(13)	1.92(7)	4.32(14)	0.272	8.93(7)
5	2.00	1.00	5.70(7)	5.00(9)	2.02(13)	1.43(7)	4.07(14)	0.251	7.13(7)
6 (Front)	2.50	1.25	4.53(7)	3.96(9)	1.68(13)	1.20(7)	2.56(14)	0.265	5.73(7)
6 (Back)	3.00	1.50	3.34(7)	2.92(9)	1.41(13)	1.01(7)	1.04(14)	0.300	4.35(7)

* This column was calculated to account for the large number of fast neutrons below 6.3 Mev and assumes the presence of 18 neutrons above 0.33 Mev for each neutron above 6.3 Mev. This number is valid only for the particular chamber used.

** 1.16 (8) $= 1.16 \times 10^8$

EFFECT OF TOTAL DOSE ON MIL-L-7808C

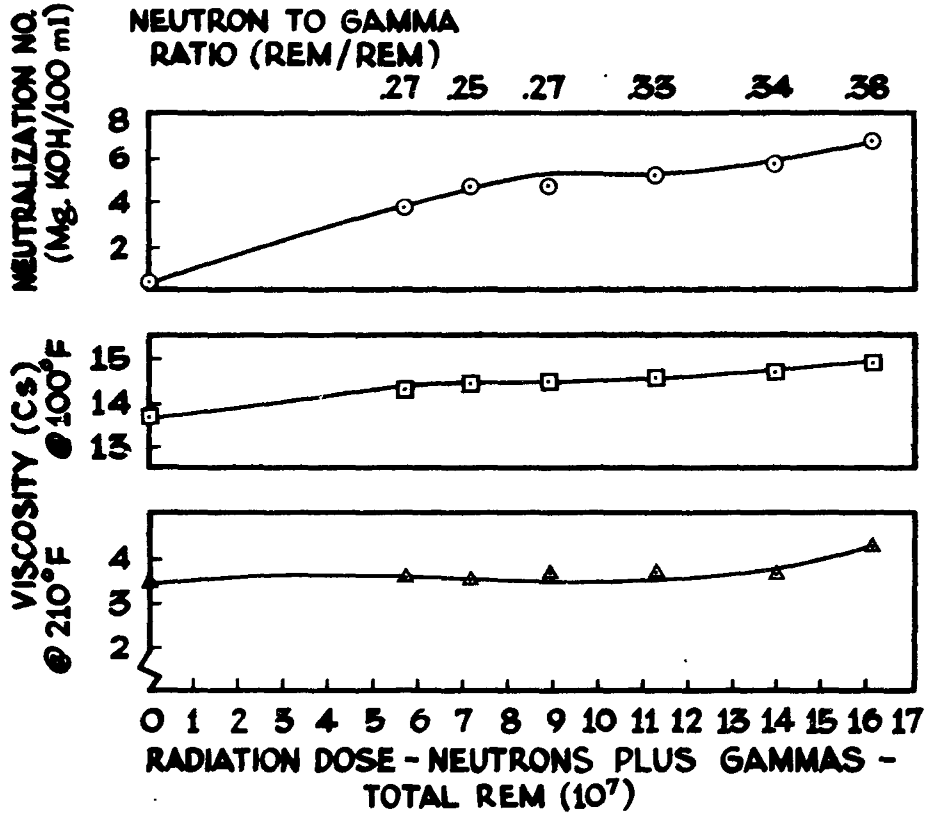

FIGURE 2

FAST NEUTRON TRANSMISSION THROUGH OIL AND Al

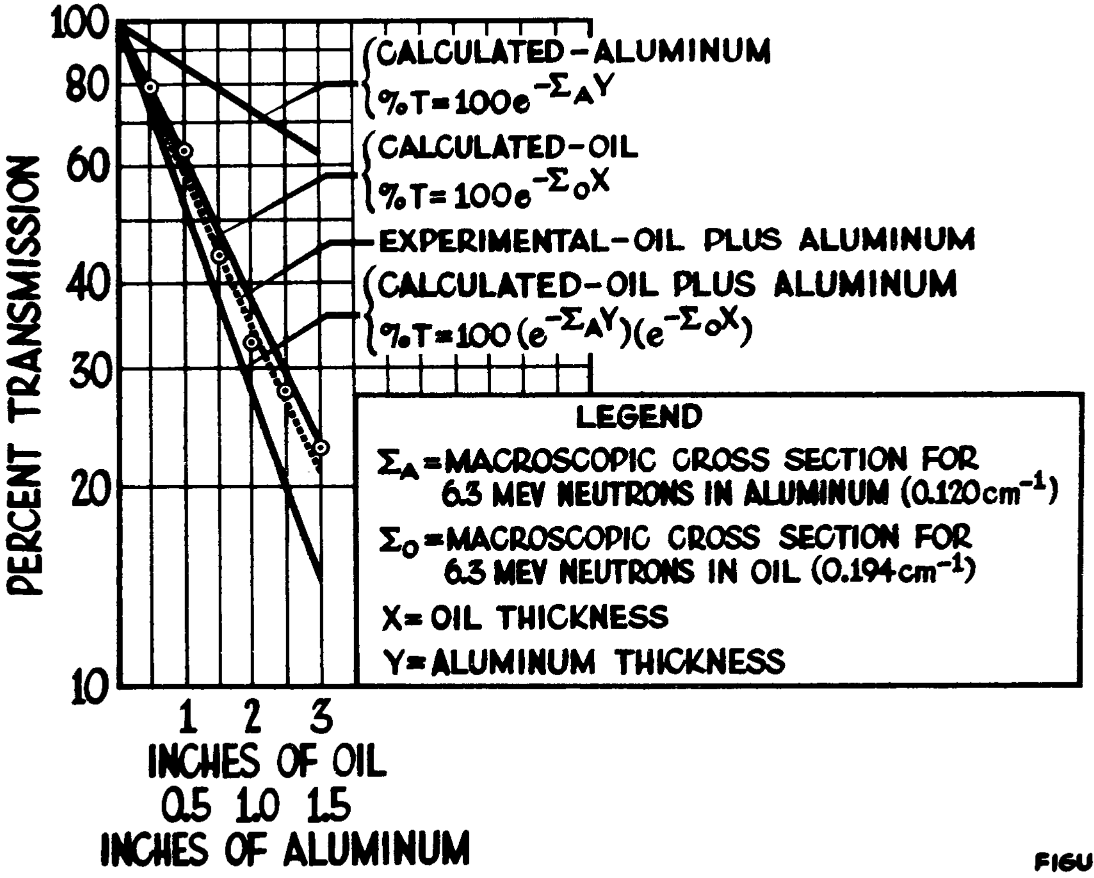

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FIGURE 5

GAMMA TRANSMISSION THROUGH OIL AND Al

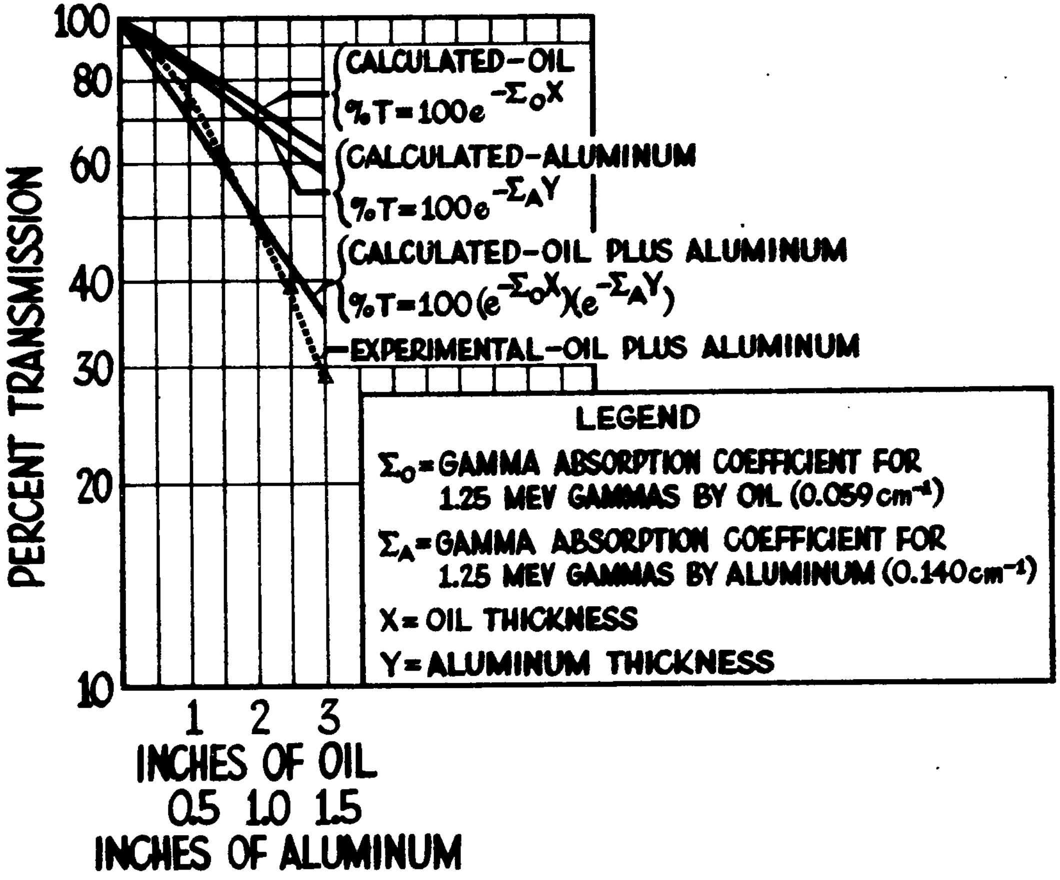

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FIGURE 4

The integrated thermal neutron fluxes received by the specimens are plotted in Figure 5. The obvious thermal flux increase through the interior specimens is attributed to the thermal neutrons which resulted from the slowing down of fast neutrons in the highly hydrogeneous oil. Figure 5 also shows the change in the ratio of neutrons to gamma rays through the assembly.

CONCLUSIONS

The radiation doses received by the six oil samples in this experiment were not of a magnitude sufficient to cause extensive degradation of properties. However, the oil was definitely affected in all specimens, and a threshold for extensive damage was probably being approached in the first specimen.

An oil sample one-half inch thick transmits roughly 75 percent of the incident fast neutron flux and 93 percent of the total incident gamma radiation of the GTR spectrum. A half-inch seems to be a reasonable sample thickness for future oil irradiations for two reasons. First, the flux field is not disturbed to an extent that highly inaccurate dose expressions are likely and, second, this thickness, when used with other reasonable specimen dimensions, yields a volume sufficient for the post-irradiation testing of the oil.

Neutron and gamma attenuation through oil can be calculated with reasonable accuracy if the percentage composition and density of the oil are known.

REFERENCES

ASTIA AD-154432 "The Effect of Nuclear Radiation on Lubricants and Hydraulic Fluids" REIC Report No. 4 April 30, 1958.

INTEGRATED THERMAL FLUX THROUGH OIL AND Al

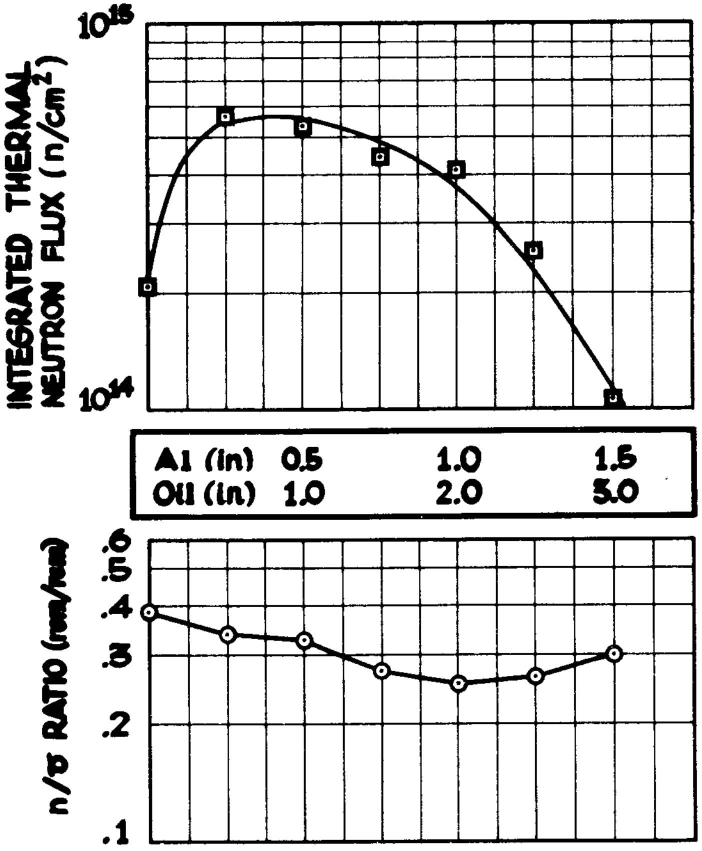

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FIGURE 5

DEVELOPMENT OF RADIATION-RESISTANT HIGH-TEMPERATURE LUBRICANTS

by

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ABSTRACT

Polyphenyl ethers are very promising materials for further development as radiation-resistant high-temperature lubricants. The unsubstituted polyphenyl ethers are far more stable than presently-used lubricants and can be classed with the most resistant types of aromatic compounds (polyphenyls, aromatic silanes, etc.) with respect to radiation, oxidation and thermal stability. Furthermore, these ethers have much lower melting points, better physical properties and much better lubrication characteristics than the other aromatic materials. Liquid unsubstituted ethers having pour points of 5°F and 40°F have been prepared. Initial thermal decomposition temperatures of these ethers are 830°F or higher.

Selected alkyl-substituted polyphenyl ethers, α-cumyl and tert-butyl derivatives, although less stable than the unsubstituted compounds are much more resistant to radiation, oxidation and thermal decomposition than typical antioxidant-containing oils.

Practical methods of preparing liquid polyphenyl ethers are being actively investigated with real promise of success.

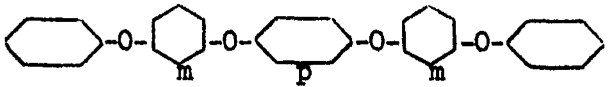
Introduction

A major portion of the work during the past year has been devoted to exploring the physical property and stability relationships of aromatic materials. Polyphenyl ethers have shown a number of important advantages over the other aromatic types and, therefore, have received most attention. Most preliminary evaluation studies have been performed on easily-prepared para-linked ethers having relatively high melting points. The real promise shown by the ethers for use at high temperatures in the presence of oxygen and radiation now justifies additional effort to produce low-melting, stable ethers.

Physical Properties of Polyphenyl Ethers

Melting Points

Syntheses of compounds having the highest possible number of meta linkages afford the best means of procuring liquid or low-melting unsubstituted ethers. The pour points or melting points of unsubstituted ethers linked in various positions are compared in Table I. Since the names of these compounds can be confusing, an abbreviated nomenclature has been adopted. For example, the compound p-bis(m-phenoxyphenoxy)benzene having the structure,



, would have the abbreviated nomenclature, mpm-5P4E, indicating the orientation of the linkages, the number of phenyl groups and ether oxygens present.

Table I. MELTING POINTS AND POUR POINTS OF UNSUBSTITUTED POLYPHENYL ETHERS

Compound	Abbreviated Nomenclature	Melting Point, °F	Pour Point, °F
Bis(p-phenoxyphenyl) Ether	pp-4P3E	229-231	-
Bis(o-phenoxyphenyl) Ether	oo-4P3E	249-251	-
Bis(m-phenoxyphenyl) Ether	mm-4P3E	Liquid	5
m-Phenoxyphenyl p-Phenoxyphenyl Ether	mp-4P3E	109-111	10a)
p-Bis(p-phenoxyphenoxy)benzene	ppp-5P4E	298-300	-
m-Bis(m-phenoxyphenoxy)benzene	mmm-5P4E	Liquid	40
p-Bis(m-phenoxyphenoxy)benzene	mpm-5P4E	171-174	40a)
Reference Compound			
m-Quaterphenyl	-	187	-

a) Viscous pour points determined on the super-cooled liquid.

It is evident that the para- and ortho-linked ethers are high melting solids while the meta compounds are liquids whose low temperature limits are set by the viscous pour point. Compounds containing mixed meta and para linkages have melting points intermediate between the all-para and all-meta ethers.

Viscosity

The viscosity-temperature characteristics of polyphenyl ethers are very good considering their highly aromatic structure. As shown in Figure 1, the ethers have viscosity-temperature slopes only slightly greater than di-2-ethylhexyl sebacate. The slope of bis(o-phenoxyphenyl) ether (oo-4P3E) is markedly better than that of the related o,o-quaterphenyl, showing that the ether linkages impart a high degree of flexibility to the molecule.

For compounds of equal molecular size, the para-linked unsubstituted ethers have the highest viscosities and the lowest viscosity-temperature slopes. Meta-linked derivatives have lower viscosity-temperature slopes than the ortho-linked ethers but are inferior to the para derivatives in this respect. Compounds having both para- and meta-links are intermediate in viscosity-temperature slope between the related all-meta and all-para linked isomers.

Effect of Radiation on Viscosity

Polyphenyl ethers are appreciably less sensitive to radiation-induced viscosity changes than are aliphatic esters such as di-2-ethylhexyl sebacate.

The average viscosity changes of polyphenyl ethers at various radiation levels are plotted in Figure 2. Moderate differences in sensitivity to radiation do exist within the polyphenyl ethers. Unsubstituted ethers are slightly less sensitive than alkyl-substituted ethers (tert-butyl or α-cumyl-derivatives) and compounds of high molecular weight show the greatest change. Meta-linked ethers are as resistant to viscosity changes as the para-derivatives. It is also evident from Figure 2, that increases in viscosity due to radiation are proportionally greater when measured at low temperatures than at high temperatures.

Aromatic compounds such as m-terphenyl, phenanthrene and triphenyl-p-biphenylylsilane are only slightly more resistant to radiation induced viscosity changes than the unsubstituted ethers, Table II. At least part of the difference would be due to the lower molecular weight of the two aromatic hydrocarbon compounds.

Table II. EFFECT OF RADIATION ON THE VISCOSITY OF VARIOUS AROMATIC COMPOUNDS

Compound	Temperature of Viscosity Measurements, °F	Viscosity Increase, %, At Various Radiation Dosages,[a] ergs/g			
		1.1×10^{10}	5×10^{10}	1×10^{11}	5×10^{11}
1-(p-α-Cumylphenoxy)-4-phenoxybenzene	210	7	20	40	320
"	400	1	10	18	95
Bis(p-phenoxyphenyl) Ether	400	3	12	19	80
Bis(m-phenoxyphenyl) Ether	210	2	16	-	-
"	400	1	8	-	-
Di-2-ethylhexyl Sebacate	210	8	190	1700	Gelled
m-Terphenyl	210	2	5	9	52
"	400	1	3	5	25
Triphenyl-p-biphenylyl-silane	400	-	8	12	64
Phenanthrene	400	-	-	7	17

a) Samples irradiated in a nitrogen atmosphere with electrons from a 3 Mev Van de Graaff generator.

Volatility and Flash Points

The volatility of polyphenyl ethers is highly dependent on their molecular weight. With unsubstituted ethers of equal molecular size, the volatility is also influenced by the molecular configuration. As shown in Table III, the ortho-linked unsubstituted ethers are appreciably more volatile than the meta compounds which in turn are more volatile than the para-linked derivatives. Mixed para-meta ethers have volatilities intermediate between the related all-meta and all-para ethers.

The flash points and fire points of these ethers are greatly affected by their volatilities. The effect of molecular configuration and molecular weight on volatility and flash point is illustrated in Table III.

The relatively high volatilities and low flash and fire points of the liquid meta-linked ethers compared to the para-linked compounds indicate that derivatives at least as high in molecular weight as the five-phenyl-four-ethers will be needed for high-temperature applications.

Table III. VOLATILITIES AND FLASH POINTS OF UNSUBSTITUTED POLYPHENYL ETHERS

		Evaporation Loss, %w at		Flash Point, °F
Compound	Abbreviated Nomenclature	400°F	500°F	
Bis(p-phenoxyphenyl) Ether	pp-4P3E	2	22	500
Bis(o-phenoxyphenyl) Ether	oo-4P3E	-	55	445
Bis(m-phenoxyphenyl) Ether	mm-4P3E	2.9	33	465
m-Phenoxyphenyl p-Phenoxyphenyl Ether	mp-4P3E	1.8	28	465
m-Bis(m-phenoxyphenoxy)benzene	mmm-5P4E	-	3.6	540
p-Bis(m-phenoxyphenoxy)benzene	mpm-5P4E	-	3.4	545
Bis[p-(p-phenoxyphenyl)phenyl] Ether	pppp-6P5E	-	0.1	635
m-Bis[m-(p-phenoxyphenoxy)phenoxy]benzene	pmmmp-7P6E	-	<0.1	660
Di-2-ethylhexyl Sebacate	-	8	96	458

Stability of Polyphenyl Ethers

Thermal Stability

The initial decomposition temperature as measured in an isoteniscope can serve as a useful guide to the upper temperature performance limit of potential lubricants. Other factors, such as rate of decomposition, type of decomposition products formed, time at various temperatures and intimacy of contact with oxygen, etc., have to be considered for any specific application but the highest possible initial decomposition temperature is always desirable. The initial decomposition temperature, the temperature at which thermal fragmentation of the base molecule causes a measurable change in the vapor pressure, is approximately 560°-625°F for most ester and hydrocarbon oils currently used as lubricants. The vapor pressure-temperature curve for di-2-ethylhexyl sebacate is shown in Figure 3. It can also be noted that unsubstituted polyphenyl ethers have initial decomposition temperatures above 800°F. For example, both bis(m-phenoxyphenyl) ether (mm-4P3E) and bis(p-phenoxyphenyl) ether (pp-4P3E) did not show decomposition until a temperature of 835°F was reached. The higher molecular-weight ethers, m-bis(m-phenoxyphenoxy)benzene (mmm-5P4E) and m-bis[m-(p-phenoxyphenoxy)phenoxy] benzene (pmmmp-7P6E), had even higher initial decomposition temperatures.

Oxidation Stability

All pure samples of unsubstituted polyphenyl ethers that have been examined have shown outstanding oxidation stability. The first samples of meta-linked ethers that were synthesized had disappointingly low stability but subsequent work has shown that this was due to the presence of less than 10% of an impurity that could not be removed by ordinary purification methods such as distillation or chromatography. Evidence to date indicates that the impurity differs from the main product only by the presence of an oxidatively unstable methyl group. Syntheses which avoid formation of this impurity are under development.

The very high oxidation stability of polyphenyl ether derivatives compared to more conventional lubricant types is shown in Figure 4. In this figure the stable life (time in hours required for the absorption of 0.5 mole of oxygen per 500 g of ether) in the Dornte Oxidation test has been plotted against the test temperature. With most oils, the rate of oxidation roughly doubles for each 18°F (10°C) rise in test temperature. It is evident that presently used oils typified by the ester-based MIL-L-7808C lubricants have very short lives at temperatures above 400°F. Selected alkyl-substituted ethers such as tert-butylated bis(p-phenoxyphenyl) ether and 1-(p-α-cumylphenoxy)- (mixed 2, 3 and 4)-phenoxybenzene are highly resistant to oxidation at temperatures as high as 475-500°F. The unsubstituted ethers are nearly as stable as m-terphenyl and show good oxidation stability at 600°F. This 200°F temperature advantage of unsubstituted ethers over ester lubricants represents over a thousand-fold improvement in oxidation resistance.

Effect of Radiation on the Oxidation Stability of Aromatic Compounds

As is the case for all aromatic compounds, the oxidation resistance of polyphenyl ethers is severely reduced by very high dosages of radiation. The reduction in stability caused by various levels of radiation is shown in Figure 5; m-terphenyl, phenanthrene, triphenyl-p-biphenylylsilane, methyl phenyl silicone (DC 710 fluid) etc., were similarly affected. The samples were irradiated in a nitrogen atmosphere with electrons from a 3Mev Van de Graaff generator and then their oxidation rate was measured in the Dornte oxidation apparatus. Though these aromatic materials loose stability during inadiation, it is evident that they are far less sensitive than aromatic esters or aliphatic esters containing inhibitors.

Dornte (500°F test) oxygen absorption rate curves for bis(p-phenoxyphenyl) ether irradiated to various levels are shown in Figure 6. It can be seen that the oxygen absorption rate for the unirradiated ether is very low and essentially linear. In contrast, all irradiated samples absorbed oxygen rapidly for a short time and then the oxygen absorption slowed to a linear rate somewhat above that of the unirradiated material. The amount of oxygen absorbed during the initial period of rapid oxidation and the slope of the final linear rate both increased considerably with irradiation level. With bis(p-phenoxyphenyl) ether, the initial absorption and final rate became large when irradiated to levels above 5.5×10^{10} ergs/g. Similar oxidation rate curves and upper irradiation limits were found with m-terphenyl, Figure 7.

The initial rapid oxidation of irradiatiated polyphenyl ethers shown in the above tests appears to be largely due to the presence of phenolic degradation products. When bis(p-phenoxyphenyl) ether was irradiated to 1.1×10^{10} ergs/g, approximately 0.8% phenolic materials were formed. At a level of 5.5×10^{10} ergs/g, nearly 7% phenolic compounds were present and at 5.5×10^{11}, approximately 25% of phenolic compounds were indicated. No phenolic materials were found in the m-terphenyl or phenanthrene, but degradation products just as harmful to oxidation stability were produced. The composition of these unstable degradation products is not yet known.

Lubrication Characteristics

Polyphenyl ether derivatives exhibited low wear in one-hour Four-Ball wear tests at 400°F (600 rpm, 1/2-inch diameter 52-100 steel balls). As illustrated in Figure 8, the wear scars of unsubstituted ethers at various loads are very similar to those obtained with di-2-ethylhexyl sebacate and very much lower than the scars obtained with o,o-quaterphenyl. The wear characteristics of bis(p-phenoxyphenyl) ether (pp-4P3E) and bis(m-phenoxyphenyl) ether (mm-4P3E) were essentially identical. Alkyl-substituted ethers such as tert-butylated bis(p-phenoxyphenyl) ether showed even less wear.

Preliminary high-temperature gear tests indicate that the substituted ethers, tert-butylated bis(p-phenoxyphenyl) ether and 1-(p-α-cumylphenoxy)-4-phenoxybenzene have load carrying capacities similar to that of di-2-ethylhexyl sebacate and somewhat greater than those of petroleum oils of equal viscosities. Additional gear and bearing tests are planned.

Synthesis of Meta-Linked Polyphenyl Ethers

Preparation of meta-linked polyphenyl ethers depends on successful synthesis of such itermediates as m-phenoxyphenol, m-bromophenyl phenyl ether and m-dibromobenzene. Several possible routes to some of these compounds are shown in Figure 9. Initial preparations of polyphenyl ethers made using m-phenoxyphenol based on the methyl ether of resorcinol, route A, had very poor oxidation stability. It was found that the instability was due to the presence of a small amount of product that contained methyl groups on the benzene rings. Route B avoided this difficulty and very stable products can be made from the m-phenoxyphenol thus synthesized.

The reaction of various intermediates in the Ullmann ether synthesis to produce bis(m-phenoxyphenyl) ether and m-bis(m-phenoxyphenoxy)benzene are also illustrated in Figure 9.

Summary of the Properties of Promising Polyphenyl Ethers

The properties of promising polyphenyl ethers are compared with those of a typical MIL-L-7808C diester lubricant in Table IV. The thermal and oxidation stability of the polyphenyl ethers is excellent. For applications where the maximum stability is needed, unsubstituted ethers would be the logical choice. The liquid ethers bis(m-phenoxyphenyl) ether and m-bis(m-phenoxyphenoxy)benzene are promising representatives of this class of compounds.

Selected alkyl-substituted ethers are somewhat less stable than the unsubstituted compounds but they should find application where conditions are much too severe for ordinary oils. Ethers such as 1-(p-α-cumylphenoxy)-(mixed 2-, 3 and 4)-phenoxybenzene and tert-butylated bis p-phenoxyphenyl) ether are the best candidates for these applications.

Conclusions and Future Plans

The polyphenyl ethers show great promise for use as lubricants in the presence of radiation at high temperatures. The relatively high-melting para-linked ethers have been most thoroughly studied but initial work indicates that the liquid meta-linked compounds are just as stable. The preparation of the meta derivatives is difficult but very encouraging results have been obtained in the search for practical syntheses.

In the future, evaluation of the meta-linked ethers will be expanded to include performance in actual gear and bearing test rigs.

Table IV. PROPERTIES OF PROMISING POLYPHENYL ETHERS

Compound	Di-2-ethylhexyl Sebacate Based MIL-L-7808C Lubricant	Bis(m-phenoxyphenyl)Ether	m-Bis(m-phenoxyphenoxy)-benzene	1-(p-α-Cumylphenoxy)-(mixed 2-, 3- and 4)-phenoxybenzene	tert-Butylated Bis(phenoxyphenyl)Ether
Abbreviated nomenclature	-	mm - 4P3E	mmm - 5P4E	-	-
Pour Point, °F	- 75	5	40	30	85
Viscosity, cs					
100°F	12.58	60.9	332	284	-
400°F	1.07	1.34	2.04	1.72	3.33
700°F	-	0.47	0.63	0.57	0.83
Flash Point, .F	458	465	540	490	525
Evaporation Loss, %w, 500°F	96	33.3	3.62	19.7	3.8
Small-scale Panel Coke, mg at 800°F	37	0.5	0.2	0.2	1.9
Initial Thermal Decomposition Temperature, °F	575	835	870	700	770
0.5 Mole Dornte Oxidation Time at 500°F, hr	0.3	280	330	40	20

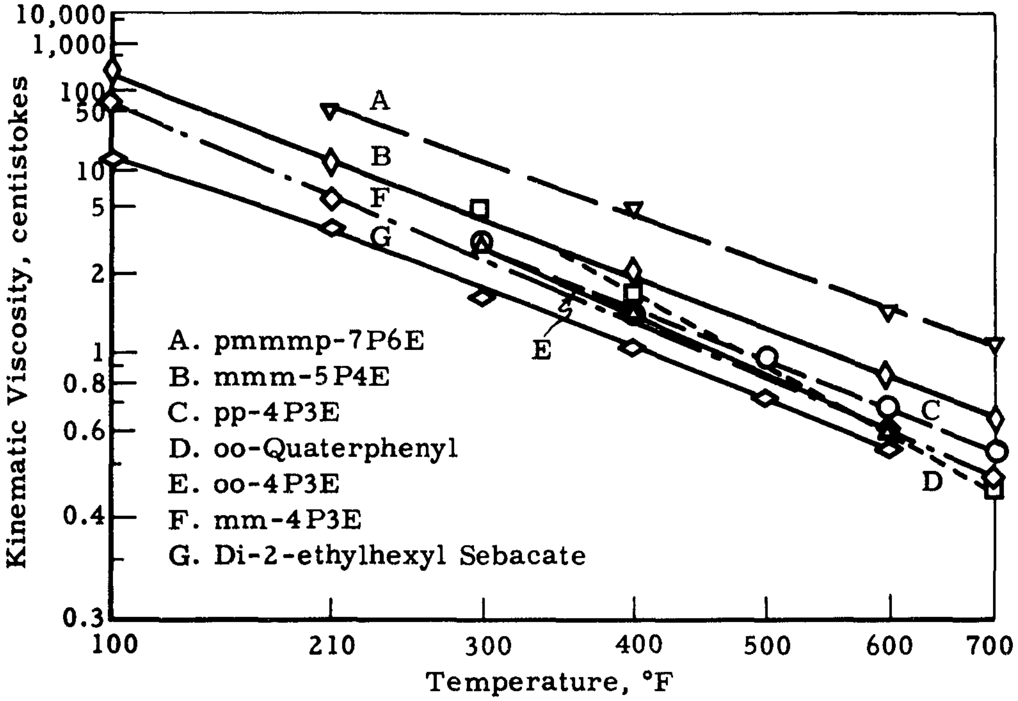


Figure 1. VISCOSITIES OF UNSUBSTITUTED POLYPHENYL ETHERS

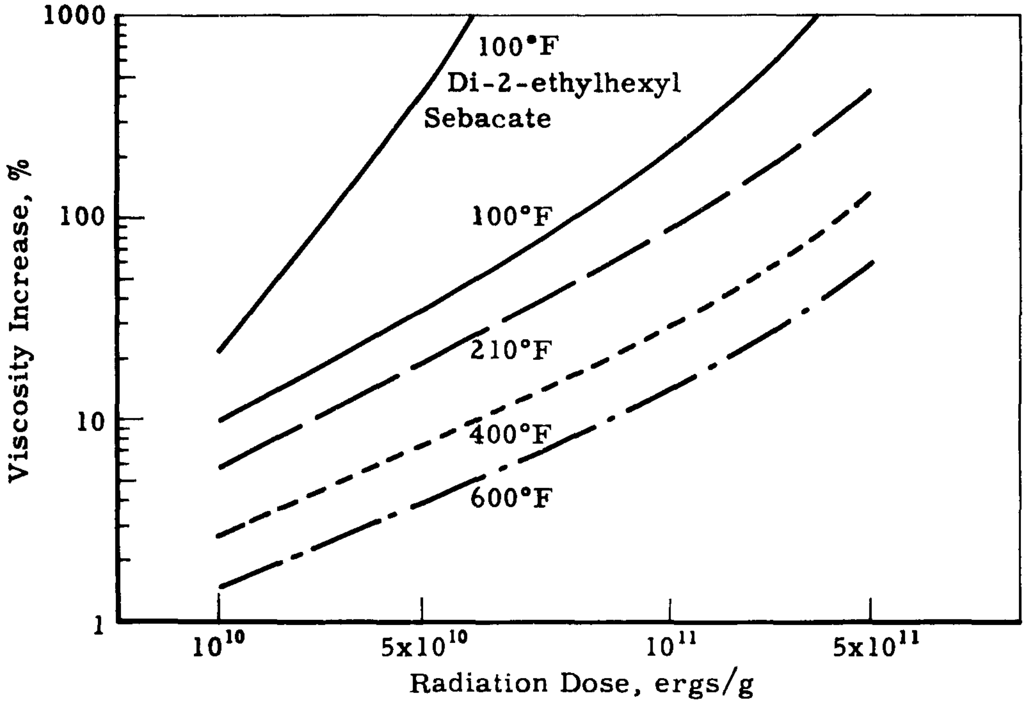


Figure 2. AVERAGE VISCOSITY INCREASE OF POLYPHENYL ETHERS DURING IRRADIATION

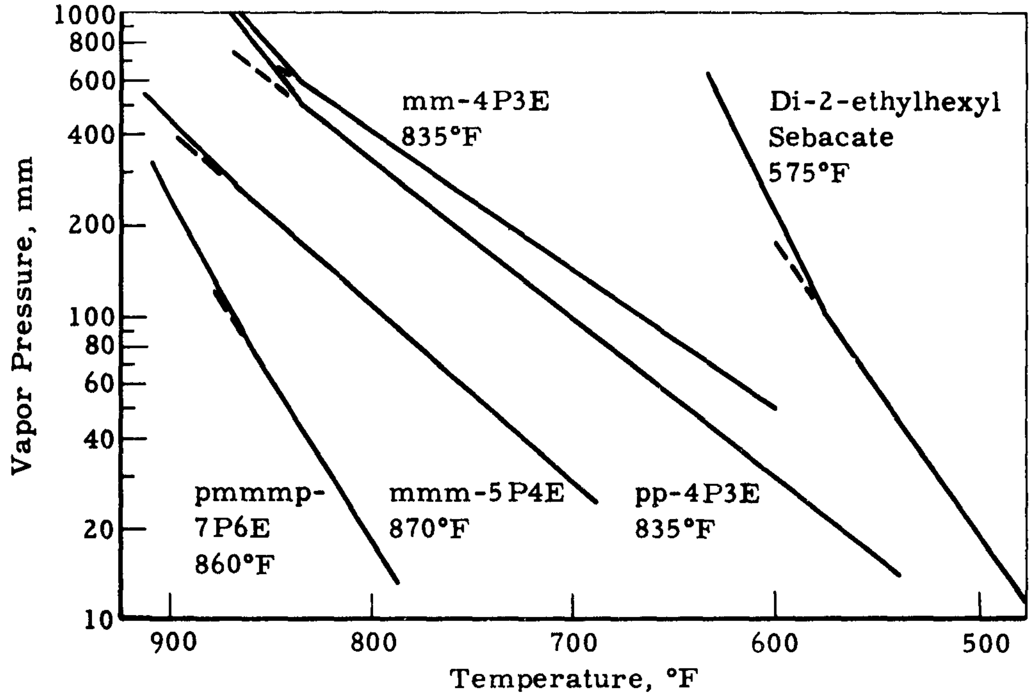


Figure 3. INITIAL DECOMPOSITION TEMPERATURE CURVES FOR VARIOUS POLYPHENYL ETHERS

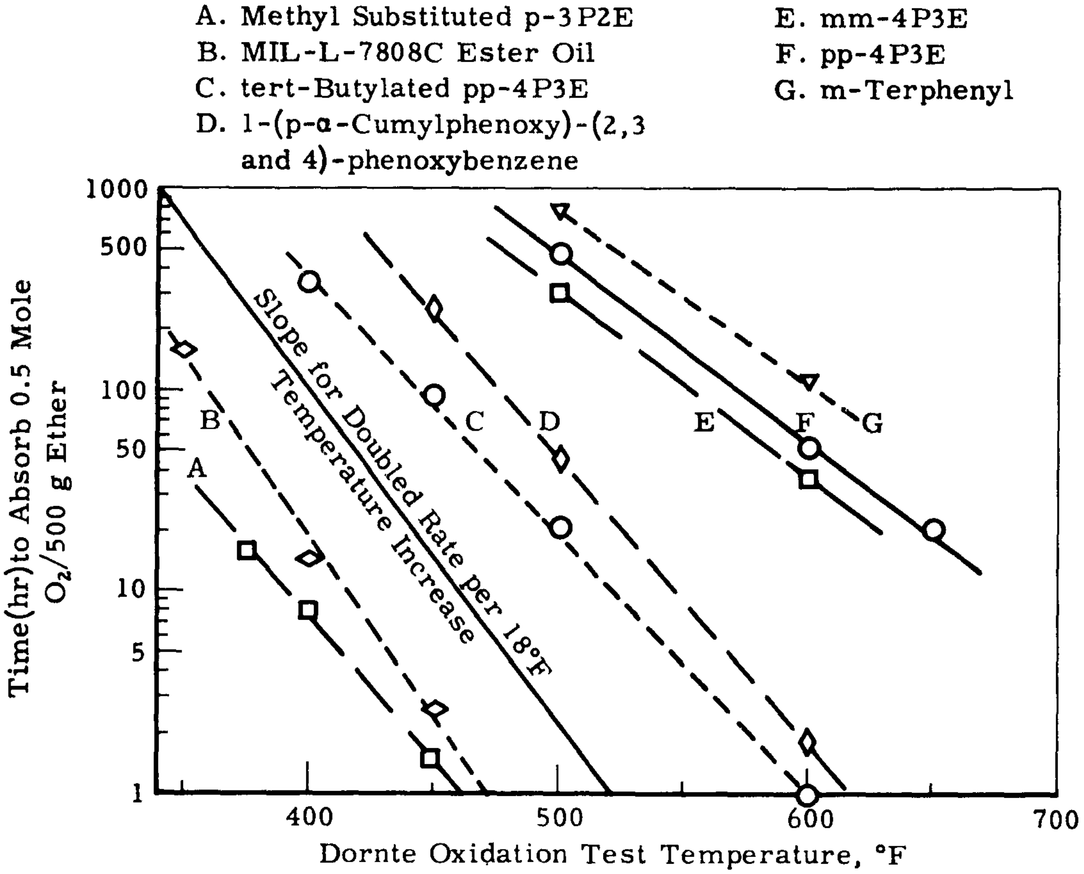


Figure 4. EFFECT OF TEMPERATURE ON THE OXIDATION STABILITY OF POLYPHENYL ETHERS

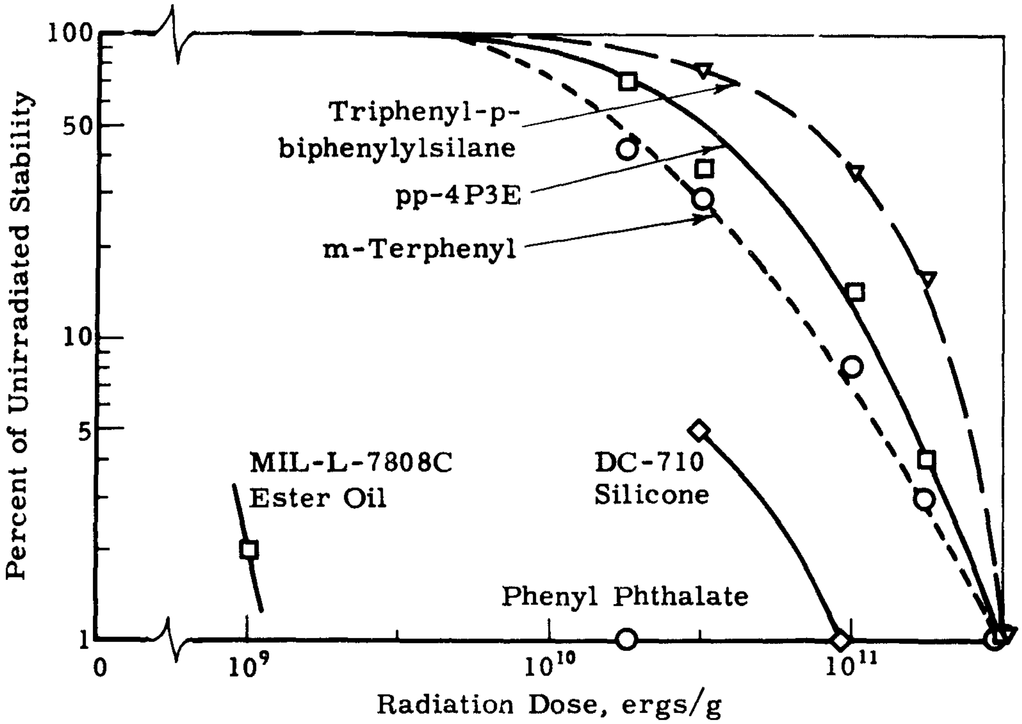


Figure 5. EFFECT OF RADIATION ON THE OXIDATION STABILITY OF VARIOUS MATERIALS

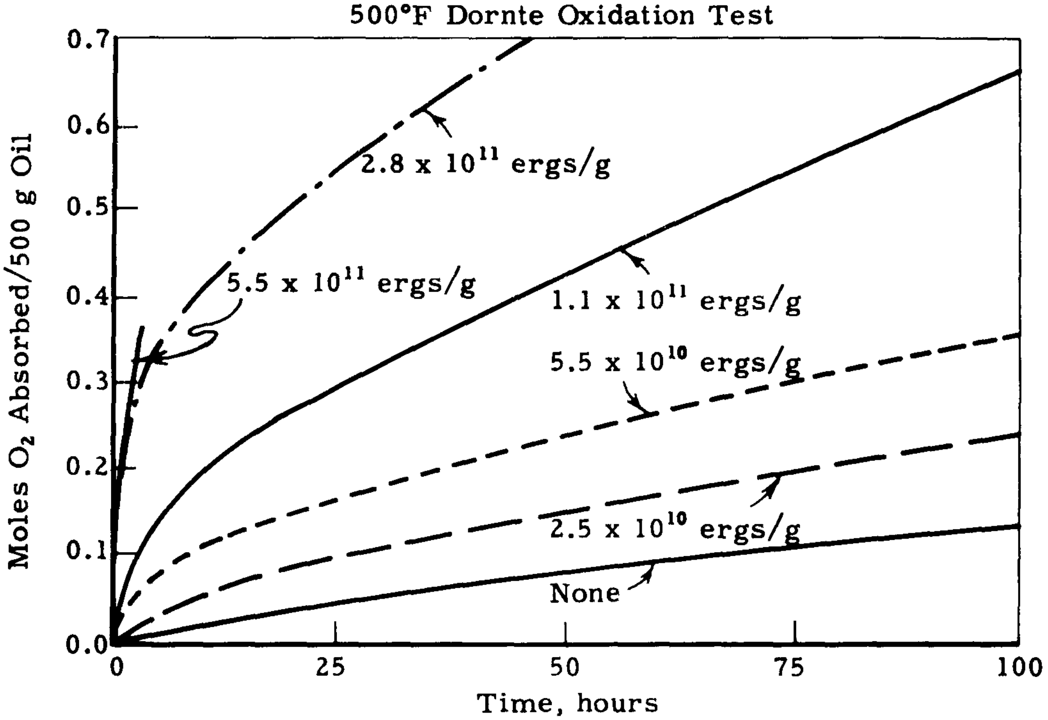


Figure 6. EFFECT OF RADIATION ON THE OXIDATION STABILITY OF BIS (p-PHENOXYPHENYL) ETHER

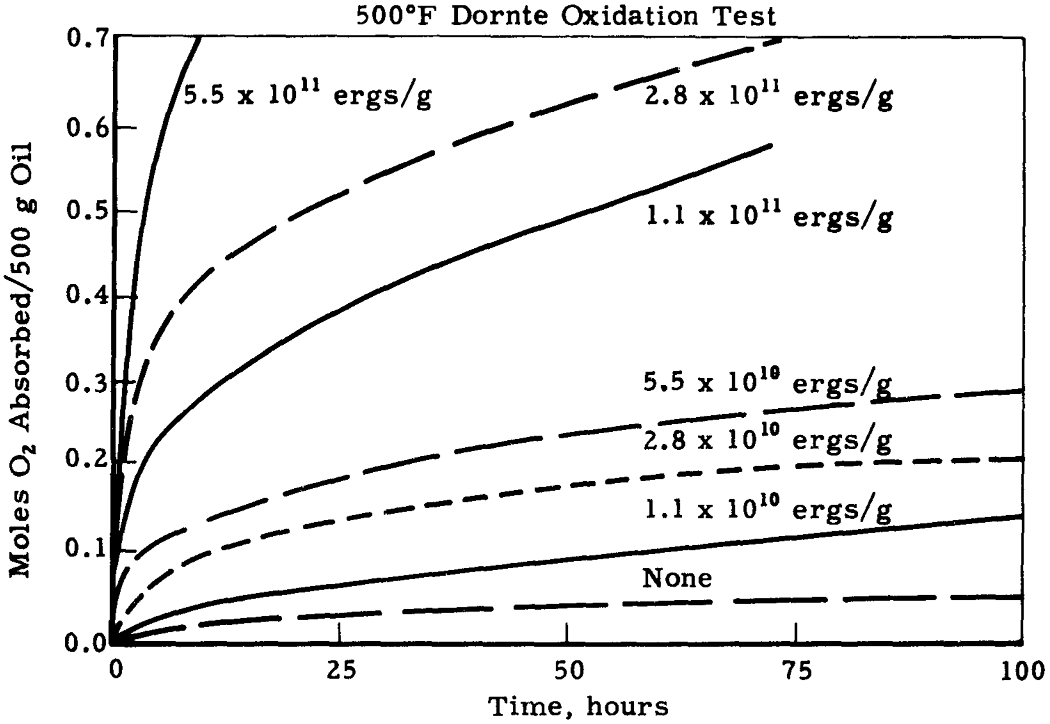


Figure 7. EFFECT OF RADIATION ON THE OXIDATION STABILITY OF m-TERPHENYL

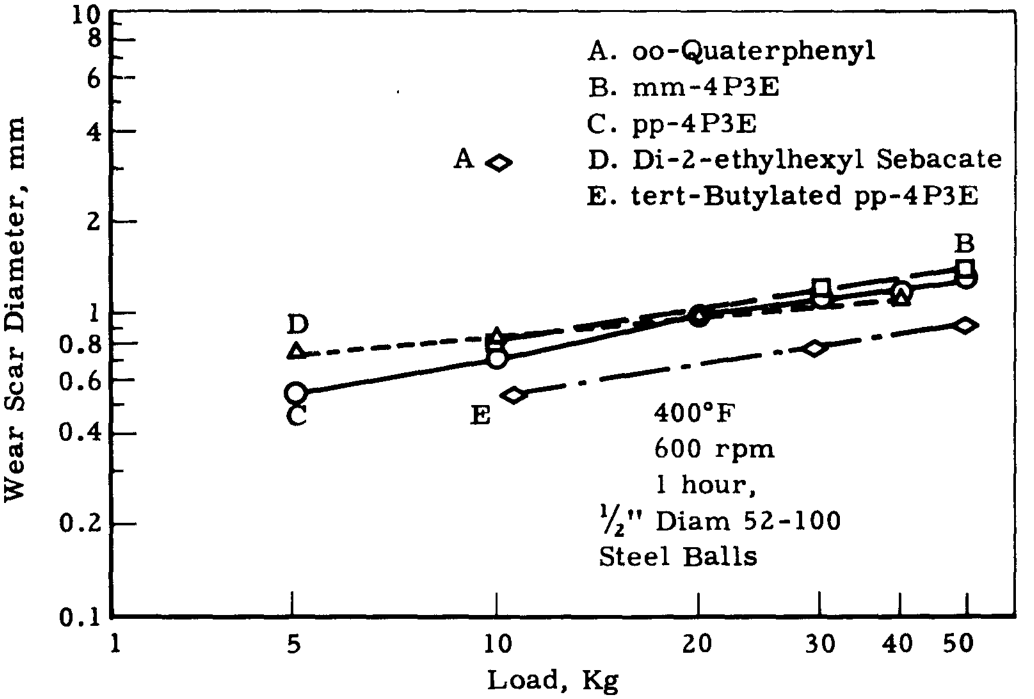


Figure 8. FOUR-BALL WEAR TEST RESULTS WITH POLYPHENYL ETHERS

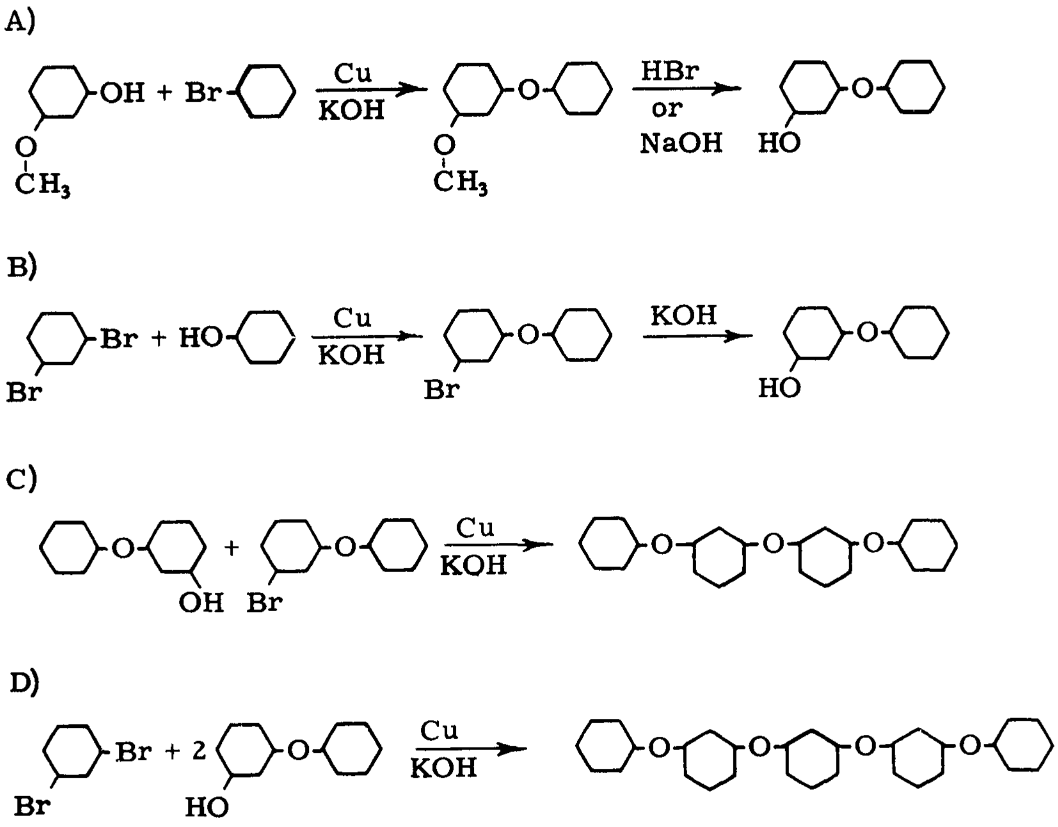


Figure 9. SYNTHESES OF META-LINKED POLYPHENYL ETHERS

ELECTRICAL EFFECTS OF HIGH-INTENSITY IONIZING RADIATION ON NONMETALS

by

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ABSTRACT

It is well-known that nuclear radiation produces permanent damage to electronic components. This damage is associated with the displacement of atoms from their normal sites in crystals and molecules. The advent of very intense sources of ionizing radiation has introduced another problem into electronic circuitry--the transient electrical conductivity induced in otherwise poorly conducting materials. This conductivity is due to the electron excitation produced by the ionizing radiation.

Experiments have been performed to measure the magnitude of these effects The radiation source used was an electron linear accelerator capable of delivering dose rates in excess of 10^8 rad/sec during 10-μsec pulses. The materials which have been studied include resistors, capacitors, and semiconducting diodes.

The apparent resistance of a megohm resistor during the irradiation was less than 2×10^4 ohms. However, this effect was proved to be due primarily to the ionization of the air surrounding the component and its leads. Transient conductivity of a megohm resistor encapsulated in an evacuated container was not detectable in these experiments. However, electrical effects were observed even in this case. These effects were associated with electrons being emitted by the component and its leads during the irradiation (i.e., photoeffect).

Capacitors exhibit the same type of behavior as resistors. The data can be interpreted in terms of a mean trapping time for the carriers which are induced in the dielectric by the radiation. This trapping time in the dielectric of a mica capacitor has been shown to be less than 2×10^{-13} sec. This value indicates that the product of trap density and trap concentration is greater than 2×10^5 cm^{-1}, a quantity which is unexpectedly large.

Rectifying semiconducting junctions are affected drastically by ionizing radiation. Reverse currents as large as 100 ma can be observed during intense radiation, and pulses containing as little as 0.1 rad delivered during 10 μsec have appreciable effects ($>$50 μa reverse current in a 1N91 diode).

These effects can have significant influence on circuits which may be exposed to intense ionizing radiation. Future experiments are planned to study in detail the effects in insulators and semiconductors and to evaluate quantitatively the effect of the surrounding air.

INTRODUCTION

The term "radiation damage" usually refers to effects on materials associated with the displacement of atoms from their usual sites. Such displacements may result in disruption of a crystal lattice or modification of chemical bonds. Depending on the exact mode of damage and the thermal excitation of the atoms (temperature), the effects may anneal, with time constants varying from a small fraction of a second to many years.

Another effect which high-energy radiation has on materials is to excite electrons from their ground states in atoms and crystals into excited states and free-conduction states. This effect is the same as the phenomenon of photoconductivity. In both cases, electrons are excited into states where they are free to move under the influence of applied electric fields. In metals, the number of conduction electrons is normally so very large that available radiation sources will not be able to increase the conductivity appreciably. On the other hand, effects can be observed at the surface of metals, because excitation of electrons to energies greater than the work function can liberate them from the surface. This effect is the same as the photoelectric effect. In semiconducting materials, the normal free electron (or hole) density is small enough that appreciable modifications to the conductivity can be induced by irradiation. The extra carriers induced have lifetimes ranging from fractions of a microsecond to milliseconds, depending on the purity of the material. In insulators, the carriers which can be generated during a short pulse of radiation ($\sim$1 μsec) exceed the normal concentration by many orders of magnitude. However, the mean trapping times are so very short ($< 10^{-10}$ sec) that the equilibrium density of carriers at any moment may be small. In gases, the effect of even small amounts of radiation on conduction is well known. For example, ionization chambers are known to be sensitive to traversal by a single ionizing particle. A number of complications do occur at high ionization rates, particularly in gases, such as air, which contain molecules with a large electron-attachment cross section.

The purpose of the preliminary experiments which are reported in this paper has been to establish the order of magnitude of these various effects. Experiments which are now in progress with a superior irradiation facility will give more accurate quantitative results to support detailed theoretical analysis.

EXPERIMENTAL EQUIPMENT

The preliminary experiments utilized the electron beam of a 7-Mev electron linear accelerator as the ionizing source. This machine, located at the Applied Radiation Corporation, Walnut Creek, California, produces pulses of 10-μsec duration, during which a flux as large as 10^{16} electrons/cm^2-sec can be achieved. In terms of energy deposited, this flux amounts to a dose of approximately 3×10^8 rad/sec, or an ionization rate of approximately 10^{21} electron-ion pairs per second per gram of absorber. Lower intensities can be achieved by moving the sample away from the output window on the accelerator, interposing absorbers, or converting the beam to a bremsstrahlung gamma-ray beam. Neither the energy of the electrons nor the pulse duration are adjustable.

To observe the transient conductivity of a sample, it was placed in a circuit with a series resistance and battery, and the voltage across the component was observed during and after the radiation pulse. The time resolution was limited by the capacitance of the input cable and preamplifier ($\sim$20 μμf).

Some serious problems were encountered during the initial experiments. Because of the proximity of the high-current pulse circuitry in the linear accelerator, it was necessary to provide thorough electromagnetic shielding of the entire electronic system. Furthermore, stray beam electrons which stop in conductors or insulators, including the input cable and the sample being tested, produce a negative signal not due to radiation-induced transient conductivity. It was therefore necessary to provide adequate nuclear-radiation shielding around the cables and amplifiers.

The current experiments are being performed with a 30-Mev electron linear accelerator at General Atomic. It is being operated near 15 Mev, and is capable of continuous adjustment of energy up to 30 Mev, beam current up to 300 ma, pulse length from 0.5 to 5 μsec, and pulse repetition rate up to 720 pulses per second. The electron beam can achieve a flux of 5×10^{18} electrons/cm^2-sec, or a factor of 500 greater than in the experiments reported here. Continuous variability of all beam parameters from the control room is also a very useful feature. The results of these experiments, which are designed to measure quantitatively the effects over a wide intensity range, will be reported in the future.

TRANSIENT CONDUCTIVITY IN SOLID INSULATORS

The initial experiments on the radiation-induced transient conductivity in solid insulators were performed on a half-watt carbon-composition resistor of 1-megohm value and a 100-μμf mica capacitor. The entire surface of the component, as well as the attached leads, was subjected to the electron beam, which has an intensity of up to 2 x 10^{16} electrons/cm^2-sec. During this irradiation, the resistor appeared to drop in value to 2 x 10^4 ohms. Likewise, the mica capacitor appeared to have a leakage resistance of 7 x 10^4 ohms during irradiation.

Subsequent experiments have been performed in which the radiation was collimated to strike the component only, others in which the component was removed but its leads were left in place, and finally, some in which the components were encapsulated inside an evacuated container. These experiments proved that the effect observed previously was due to conduction in the surrounding air, which was also ionized by the radiation source. Actually, when the air contribution is eliminated, the transient resistance of either the megohm resistor or the mica capacitor was greater than a megohm during the same irradiation. From these data, it is possible to place an upper limit on the carrier trapping time in the material. Of the data on a resistor and a capacitor, the limit on the resistance of a capacitor is the more restrictive.

The following estimates are based on a simple mechanism for transient conductivity. The radiation produces carriers (free electrons) at a known rate. These carriers drift in the applied electric field until they are trapped. Only while they drift do they contribute to the transient current. To relate the calculated conductivity to the observed resistance, it is necessary to know the dimensions of the insulator (or dielectric), but these can be inferred from the dimensions of the capacitor.

If it is assumed that carriers are produced at the rate N' per unit volume per second, then the equilibrium concentration is $N'\tau$, where τ is the mean trapping time. If the mobility of the carriers is μ, the resistance is

$$R = \frac{a}{N'\tau q \mu A} ,$$

where A and a are the area and thickness of the dielectric, respectively, and q is the electronic charge. For a capacitor, the ratio of the dimensions equals

$$\frac{a}{A} = \frac{K\epsilon_0}{C} ,$$

where K is the dielectric constant, ϵ_0 is the permitivity of free space (8.85 x 10^{-14} farads/cm), and C is the capacitance.

The mean trapping time, τ, can be evaluated in turn, if one assumes a trap density N, a cross section σ, and an electron thermal velocity v:

$$\tau = \frac{1}{N\sigma v} .$$

Hence

$$R = \frac{K\epsilon_0 N\sigma v}{N' q\mu C} .$$

In the case of the capacitor, the following reasonable values are assumed:

$$K = 10,$$
$$v = 10^7 \text{cm/sec},$$
$$N' = 10^{21}/\text{cm}^3\text{-sec},$$
$$\mu = 100 \text{ cm}^2/\text{volt-sec},$$
$$\sigma = 10^{-15} \text{ cm}^2,$$
$$R > 10^6 \text{ ohms}.$$

Hence

$$N > 2 \times 10^{20} \text{ cm}^{-3} .$$

This concentration appears to be unusually large, but it cannot be disregarded since the other numbers assumed in the calculation could be subject to large errors. Current experiments, which profit from an extra factor of 500 in intensity, should resolve this question.

TRANSIENT REVERSE CONDUCTIVITY ACROSS P-N JUNCTIONS

Ionizing radiation incident on semiconducting material excites electrons from the valence band into the conduction band. At a p-n junction, the concentration of minority carriers can be changed drastically by irradiation, and the rectifying properties of the junction can be altered. Observations on p-n junctions provide a convenient method for studying the behavior of minority carriers during irradiation.

During the experiments the diodes were observed under these conditions:

1. The voltage across the diode was observed by an amplifier with an input impedance of 2 megohms.

2. The diode was biased in the reverse direction through a resistor large enough that the voltage across the diode during irradiation became zero (actually, slightly positive).
3. The diode was biased in the reverse direction through a smaller resistor so that the voltage across the diode always remained negative.

The following simplified theory has been developed to predict the results for these three cases:

The effect of the irradiation is to introduce hole-electron pairs at a rate proportional to the intensity. It is assumed that the extra majority carriers have a negligible effect. It is also assumed that most of the current is carried across the junction by one type of carrier (e.g., holes, to be specific). The quantity K' is defined as the ratio between the rate at which extra holes are produced per unit volume and the normal hole concentration. Hence the holes are being created by the radiation at a rate $K'p_n/\text{cm}^3$-sec, where p_n is the normal density of holes (minority carriers).

When the diode is placed in a high-impedance circuit, the current across the junction is negligibly small and the concentration of minority carriers as a function of time during irradiation is

$$p = p_n\left[1 + \int_0^t K'(t')e^{-(t-t')/\tau}\, dt'\right] ,$$

where τ is the minority-carrier lifetime. The photovoltage V is determined by this concentration:

$$V(t) = \frac{kT}{q} \log \frac{p}{p_n} = \frac{kT}{q} \log \left[1 + \int_0^t K'(t')e^{-(t-t')/\tau}\, dt'\right]$$

$$\text{(after the pulse)} = \frac{kT}{q} \log \left[1 + K_\tau e^{-t/\tau}\right],$$

where

$$K_\tau = \int_0^{t_B} K'(t')e^{t'/\tau}\, dt' \; ;$$

t_B is the beam pulse length.

As long as the excess carrier concentration is large compared to the equilibrium value, the photovoltage decays linearly with a slope

$$\frac{dV}{dt} \approx - \frac{kT}{q\tau} .$$

When the diode is subjected to a constant reverse current during its recovery period, the calculation involves the solution to the time-dependent diffusion equation for a diode with a boundary condition on $\partial p/\partial x$ at the junction. The solution to the equation has been carried out approximately to evaluate the time at which the voltage is zero and becoming negative. This recovery time, t_r, is given by the equation

$$e^{t_r/\tau} \mathrm{erf}\sqrt{t_r/\tau} = K \frac{I_s}{I_R} ,$$

where

$$K = \int_0^{t_B} K'(t')\, dt' ,$$

$I_s = qAp_n\sqrt{D/\tau}$ is the normal reverse saturation current, and I_R is the constant reverse current during the recovery period. It has been assumed in this equation that the positive-voltage condition was established in a short fraction of the time τ.

If the voltage across the diode remains negative so that

$$e^{-qV/kT} \ll 1 ,$$

the current across the junction is determined by the excess carriers. The same diffusion equation is solved with a constant boundary condition that $p_n(x = 0) \approx 0$. The current is then

$$I = I_s\left[1 + K'\tau \ \mathrm{erf}\sqrt{t/\tau}\right]$$

and is independent of the applied voltage.

The phenomena described above can be observed most conveniently on a long-lifetime diode such as 1N91. The recovery time, during which the reverse current is almost constant, is plotted as a function of reverse current in Fig. 1. The minority-carrier lifetime in this diode is 11 μsec as measured by observing the recovery time following a sudden reversal of the voltage across the diode. The lifetime inferred from the semilog plot of Fig. 1 appears to be a function of the reverse current.

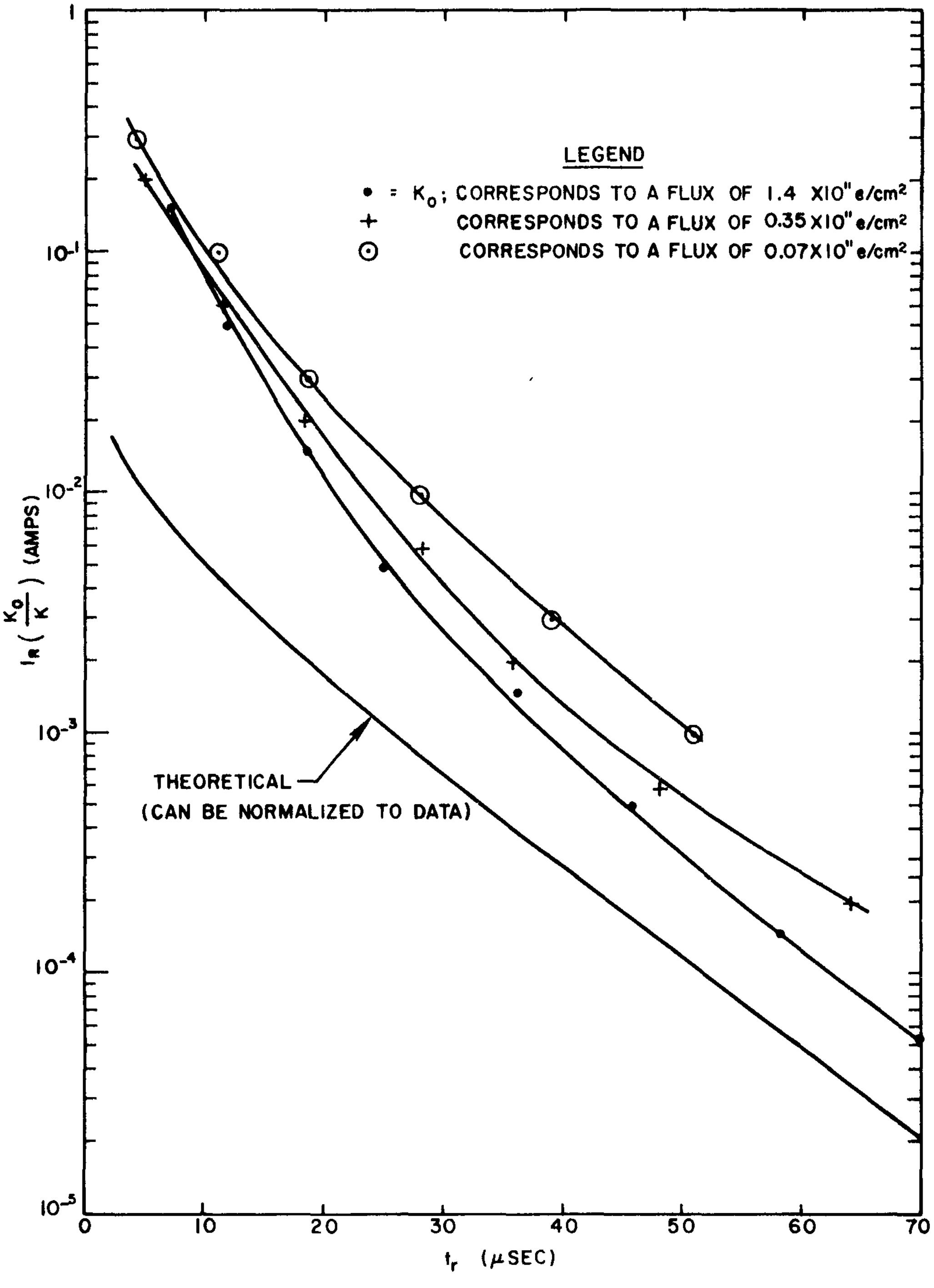

Fig. 1--Observed recovery times for 1N91 diode

Furthermore, if the theory were correct, the curves for the three different radiation intensities should coincide. Apart from these discrepancies, the experimental curves agree qualitatively with the theoretical curve based on a carrier lifetime of 11 μsec.

There are some data on the transient current which flows during irradiation when the series impedance is small enough to allow a negative voltage to remain across the diode. When a 1N91 diode is subjected to a reverse voltage of more than 10 volts during irradiation, the transient current increases with increasing voltage. A typical value of the current is 50 ma during bombardment with 10^{15} electrons/cm^2-sec. The magnitude of this current appears to be proportional to the radiation intensity as predicted.

The observations on the radiation-induced photovoltage indicate that the effective minority-carrier lifetime is not constant during the recovery period, but is somewhat shorter initially. It is thus indicated that the large perturbations caused by irradiation with $\sim 10^{12}$ electrons/cm^2 modifies the ordinary trapping process to enhance the trapping probability. This conclusion would be in agreement with the observations on recovery times, in which the lifetimes calculated from the slope of the curve of recovery time versus reverse current appear to be shorter than those measured by more conventional techniques This observation is also consistent with the Shockley-Reed formulation of trapping phenomena.

PHOTOELECTRIC EJECTION OF ELECTRONS

Some experiments have been performed to measure the conductivity of some ionized gases, including air, but the results of these are somewhat in question and will not be reported. However, during these experiments it has been demonstrated that sizeable currents of electrons can be emitted from metal surfaces placed in an electric field and simultaneously subjected to ionizing radiation. These effects have not yet been studied quantitatively, but they do emphasize that experiments on transient conductivity are beset with difficulties. Even placing a component and its leads in an evacuated container does not necessarily ensure that the observed current went through the component rather than along a bypass. Very careful design of experiments is needed, keeping all of these effects in mind, to measure accurately the transient conductivity in solids.

CONCLUSION

Electronic components and systems which are called upon to function in an environment containing intense ionizing radiation--either as a short pulse or continuously--may malfunction because of the transient conductivity produced by the radiation.

The most sensitive devices are semiconductor rectifying junctions, such as those found in p-n junction diodes and transistors. In both cases reverse currents can increase many orders of magnitude during irradiation. Experiments have been performed during which the damage was still evident after irradiation for a time up to ten times the minority-carrier lifetime.

The next most sensitive part of the electronic circuit is the gas which surrounds the components. Possibly, suitable potting of all metal parts will eliminate effects due to ionization of the surrounding air. Effects due to the photoelectric emission of electrons from surfaces in a vacuum, e.g., vacuum tubes, have not been checked yet.

The magnitude of the transient conductivity in some solid insulators is unexpectedly small and has not been determined quantitatively. Current experiments should produce the desired measurements.

RADIATION EFFECTS ON ELECTRICAL INSULATION

by

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Eight types of insulated, electrical wire were irradiated to a dose of about 1 x 10^{10} ergs/g(C) at temperatures of 15, 55, and 100 C, and relative humidities of 0 and 65 per cent at each temperature in a cobalt-60 gamma source. Electrical resistance was measured before, during, and after irradiation; preirradiation and postirradiation breakdown voltage measurements were made, and the specimens were examined visually for signs of physical deterioration after irradiation.

All insulations exhibited a loss in initial resistance of at least 99 per cent at one or more of the irradiation conditions. Serious deterioration of mechanical properties was observed for all except two polyethylene insulations. In general, best performance, from the standpoint of electrical properties, was obtained under cool, dry conditions. On the average, high temperature had a greater detrimental effect than high humidity. The temperature effect was most pronounced between 15 and 55 C.

For general-purpose use in a radiation field, under a variety of temperature and humidity conditions, polyethylene appears to be superior to the other materials studied. However, under specific controlled temperatures and humidities some of the other materials may be preferred.

INTRODUCTION

A program to study the effects of gamma irradiation on electrical insulation, fuel tank materials, and radome laminates, sponsored by The Lockheed Aircraft Corporation, was conducted by Battelle Memorial Institute. This paper covers the portion of the program dealing with electrical insulation.

A series of six irradiations were made at different environmental conditions, to determine relative effects of radiation, temperature, and humidity upon various insulation.

Eight types of insulated electrical wire were irradiated in a Co-60 gamma source to a dose of about 10^{10} ergs/g(C) at temperatures of 15, 55, and 100 C, and relative humidities of 0 and 65 per cent at each temperature. Electrical resistance was measured before, during, and after irradiation; preirradiation and postirradiation breakdown voltage measurements were made, and specimens were examined visually for signs of physical deterioration after irradiation.

All insulations exhibited a loss in initial resistance of at least 99 per cent at one or more of the irradiation conditions. Serious deterioration of mechanical properties was observed for all except two polyethylene insulations. In general, best performance, from the standpoint of electrical properties, was obtained under cool, dry conditions. On the average, high temperature had a greater detrimental effect than humidity. The temperature effect was most pronounced between 15 and 55 C.

EXPERIMENTAL PROCEDURES

Set-Up

All irradiations of electrical insulation was conducted in Battelle's cobalt-60 gamma source which is located at the bottom of a 14-foot-deep water pool. Approximately 2000 curies were used for these experiments. Wire samples to be irradiated in this source were enclosed in a watertight container with provisions made to bring lead wires to the surface of the pool. The watertight container in final form, as used in these experiments, consisted of an aluminum cylinder about 4 inches in diameter and 12 inches long with a bolt-on cap. A 14 foot piece of 2 inch pipe, through which all lead wires were carried to the pool-side, was attached directly to the cap. The wire samples were wound on a brass tube which was placed in a 1 quart vacuum bottle filler prior to placing in the aluminum cylinder. The heating element and a container for salt solution to maintain constant humidity were placed inside the brass tube. The brass cylinder upon which all samples were wound served as the common terminal for all measurements.

Experiments

Six irradiations were made at total doses approximating 10^{10} ergs/gm(C) (they varied from 7.1×10^{9} to 1.2×10^{12}). The environments for the six irradiations were as follows:

1. 15 C 65 % R. H.
2. 15 C 0 % R. H.
3. 55 C 0 % R. H.
4. 100 C 0 % R. H.
5. 100 C 65 % R. H.
6. 55 C 65 % R. H.

Samples

The effect of radiation on the following insulated electrical wires was investigated:

No. 8 gage wire, MIL-W-7072

No. 16 gage cable, Ty-1-Cl-A

No. 18 gage cable, MIL-W-7139A

No. 16 gage wire, MIL-W-8777

No. 18 gage cable, LAC-1-135B

Suprenant polyethylene

No. 18 gage AWG 36, polypropylene

No. 18 gage AWG 36, polyethylene

Measurements

The effects of radiation were determined by observing electrical and physical characteristics of the insulations as the irradiation progressed. Insulation resistance, breakdown voltage, and visual inspection of the physical properties were the means used to determine degradation of the insulation. Also, in initial experiments, observations were made of radiation-induced voltages and the rectification effect. Measuring equipment used for the experiments was as follows:

Insulation resistance was measured using a General Radio megohmmeter. A Kiethly electrometer was used to measure induced voltage. A Hypot voltage breakdown tester was used for measuring voltage breakdown of the insulation. A Foxboro temperature controller was used to maintain a constant temperature inside the capsule.

For all irradiations, insulation readings were made immediately before and after insertion into the radiation source and periodically thereafter until the end of the irradiation. At every measurement, readings were made both in and out of the field. Voltage breakdown measurements were made at the beginning and end of each irradiation and periodically during the first irradiation. Measurements of induced voltages across the insulation were made during the first irradiation only, as they proved to be of little significance.

Dosimetry measurements were made using a 10-cc, graphite ion chamber and are reported in units of ergs/g(C). The working standard used for calibration of the ion chamber was the copper-modified ferrous sulfate dosimeter. Dosimetry data are based on a G-value of 0.66 for the oxidation of ferrous ion and the relationship that 100 ergs/g absorbed in the dosimeter solution is equal to 90.9 ergs/g(C). The G-value of 0.66 for the copper-modified ferrous sulfate system is equivalent to a G-value of 15.5 for the normal ferrous sulfate system.

RESULTS

Postirradiation Visual Examination

The effects of gamma radiation in combination with temperature and humidity on the physical characteristics of each type of wire as determined by visual examination are presented below. The visual examinations were made after completion of each irradiation.

No. 8 gage wire MIL-W-7072 is an 8-gage stranded conductor with an outer jacket of white woven fabric which is coated with a protective coat of varnishlike material. Underneath the fabric is a white rubberlike sheath. After irradiation the varnish coating is sticky to touch and has turned yellowish. The rubberlike material has turned brown and has lost much of its original flexibility. These effects become much more evident with increasing temperature. Both the fabric and the rubber were almost black for the wires irradiated at 100 C. Any changes due to humidity are not evident visually.

No. 16 gage cable Ty-1-Cl-A has a white fabric outer covering. The next layer of insulation is a gray fibrous material, probably asbestos. Underneath this is a thin layer of a white translucent plastic which appears to be Teflon. Irradiation causes the fabric to deteriorate so that it frays very easily. The asbestos flakes easily when handled. The Teflon was completely deteriorated, and crumbled to a powder when handled. Temperature and moisture had no great effect on the visible physical properties of this wire.

No. 18 gage cable MIL-W-7139-A consists of an outer transparent plastic coating, a light tan fabric layer, several layers of another fabric, and, finally, a white translucent plastic, probably Teflon. After irradiation, the transparent plastic was slightly yellowed and very brittle, and cracked and broke away when the wire was bent. The two fabric coverings were deteriorated so that they frayed and fell apart when touched. The Teflon powders when touched. Some bleaching of the outer fabric is evident. Heat and moisture appear to have no significant additional effect.

No. 16 gage wire MIL-W-8777 consists of a tan fabric covering (probably cotton), a white fabric layer (appears to be silk), and a white rubber insulation. Irradiation causes deterioration of both fabric coverings. They frayed and fell apart easily when handled. The rubber crumbles like soap. It will not withstand bending without cracking. Heat causes darkening of the fabric and decreases the flexibility of the wire. Moisture causes no significant additional effect.

No. 18 gage cable LAC-1-135B consists of an outer transparent plastic coating, a tinned copper shield, another transparent plastic coating, a white fabric layer, and an inner insulation of a white flexible plastic. Both plastic layers turned yellow and became very brittle. The fabric frayed easily. The inner plastic turned brown and hardened somewhat, but is still moderately pliable. At higher irradiation temperatures, increased darkening of the outer coatings was observed. The inner plastic turned almost black and became fairly stiff and hard. The shield corrodes somewhat at the high temperature. Moisture causes no apparent effects.

Suprenant polyethylene wire consists of a tinned copper shield over white polyethylene. Radiation causes relatively little visual change in the polyethylene at low temperatures. However, at high temperature the polyethylene hardened to the point where it cracked slightly if bent double. High temperature produced shield corrosion. Moisture produces no visible difference.

No. 18 gage AWG 36 polypropylene consists of a tinned copper shield and a coating of polypropylene. After irradiation the polypropylene was very brittle and shattered when bent. At high temperature it turned dark brown and crumbled so badly that it would not adhere to the conductor when the shield was pushed back. The shielding was corroded. Moisture had no visible effect.

No. 18 gage AWG 36 polyethylene consists of a tinned copper braid and a clear polyethylene coating. At low temperature the polyethylene was slightly yellowed and somewhat hardened although it remained quite pliable. At high temperature it turned a dark yellow-brown. However, it still remained fairly felxible.

Rectification Effect and Induced Voltage

Measurements made on the samples from the cold-moist run indicate no significant rectification effect due to irradiation. Insulation resistance was measured, using the wire samples only, with the 25-foot lead wires removed, first with the conductor on the positive and then on the negative terminal of the megohm bridge. No. 16 gage cable Ty-1-Cl-A showed a reduction in insulation resistance of 50 per cent and No. 18 gage cable LAC-1-135B showed a reduction of about 35 per cent when the conductor was changed to the negative terminal. Other samples showed no rectification effect.

The measurement of voltages induced across the insulations of the samples showed nothing significant. Readings varied from -0.8 to +9.0 volts, but followed no discernible pattern. Most of the readings were well below 1 volt.

Voltage Breakdown

Heat and moisture appeared to have relatively little effect on the voltage breakdown of the insulations. The one notable exception was polypropylene, which has a very low breakdown after irradiation in the moist condition. At the high temperature it deteriorated so badly that the postirradiation breakdown voltage could not be measured.

Insulation Resistance

Figure I shows the variation of the insulation resistance of a polyethylene sample under various combinations of radiation, temperature, and humidity which is representative of the data for the eight wire types.

The insulation-resistance data does not produce a smooth curve. However, a trend of decreasing resistance as a function of dose is evident. It can also be seen that high temperature has a detrimental effect on the resistance. Moisture shows the greatest damage at moderate temperature.

All wires tested show a degradation of insulation resistance with radiation and heat. The fabric insulations show greater moisture damage than do the plastics such as polyethylene.

Postirradiation-resistance measurements on the insulations irradiated in the cold-moist experiment were continued over a period of 200 hours after termination of the irradiation. Resistance increases, compared with the final out-of-source measurement, of a factor of 20 for MIL-W-8777, a factor of 100 for Suprenant polyethylene, and a factor of 3 for No. 18 gage AWG 36 polyethylene occurred during this period. Changes in all other materials were less than a factor of two.

DISCUSSION AND CONCLUSIONS

In order to draw conclusions about the behavior of the eight wire types under a given radiation dose and various environmental conditions, a statistical analysis of results was performed. The unit of measure used in the analysis was the logarithm of the ratio of insulation resistance after exposure to a radiation dose of about 7.1×10^9 ergs/g(C) to the initial stabilized insulation resistance. The environmental factors considered were temperature (15, 55, and 100 C), humidity (0 and 65 per cent RH), and the wire location at measurement (in the radiation field or out of the radiation field). These factors resulted in 12 different measurements for each of the eight wires, or 96 observations in the entire analysis.

The conclusions from the analysis, applicable to all eight wires, were as follows:

1. There is a strong interaction effect between radiation, temperature, and humidity for all insulations studied. Insulation resistance, at a given radiation dose, is a function of temperature and humidity, and this function is different for each of the wire insulation types. This indicates that any prediction of wire deterioration for a given temperature and humidity depends upon the specific wire in question.

2. Insulation resistance measurements are dependent on the proximity of the wire to the radiation field during measurement. Over all insulations and environments, the mean per cent change from initial with all measurements taken in the radiation field was -79 per cent. The mean per cent change from initial with measurements taken out of the field was -98 per cent. Thus the actual deterioration in insulation resistance due to radiation appears to be greater than measurements taken wholly within the field would indicate. Averaged over all conditions and materials, the magnitude of the transient effect changes by a factor of about 4, whereas the permanent effect changes by a factor of about 50 during the course of the irradiations. This is, of course, to be expected since the transient change, for any given temperature and humidity condition, will depend largely on radiation intensity, with a lesser dependence on the physical deterioration of the material. On the other hand, the permanent change probably arises largely as the result of permanent chemical changes in the material which will increase with increasing dose.

3. Even when compared with the combined effect of radiation, temperature, and humidity, the temperature effect is significant. The significance is mainly due to the difference in deterioration between the 15 and 55 C temperatures. The mean difference in deterioration between the 55 and 100 C temperatures is not significant.

   The mean per cent changes from initial at the three temperatures for all wires at both humidity conditions, measured both in the radiation field and out of it, were as follows:

Temperature, C	Mean Change in Insulation Resistance, per cent
15	-67.4
55	-91.6
100	-94.6

Table I shows the observed per cent deviation in insulation resistance from initial measurement for each wire at each environmental condition, for a radiation dose of approximately 7.1 x 10^9 ergs/g(C). The table shows clearly the nature of the interaction. For example, at 15 C, No. 8 gage wire MIL-W-7072 shows greater deterioration, measured outside the field, for the moist condition than for the dry. This situation is reversed at 55 C. The same observations can be made for No. 16 gage wire MIL-W-8777, No. 18 gage cable LAC-1-135B, No. 18 gage wire polypropylene, and No. 18 gage AWG 36 polyethylene. The remaining wires did not exhibit this behavior.

One fact stands out in an examination of Table I. All the insulation studied lost at least 99 per cent of its initial stabilized insulation resistance at one or more of the environmental conditions. It is also clear that some wires performed better than others at each of the environmental conditions. Thus, at low temperatures, the Suprenant polyethylene and the polypropylene wires exhibited a smaller resistance change than the other specimens. In the intermediate temperature range the No. 18 gage cable LAC-1-135B and the No. 18 gage polyethylene wires appear somewhat superior. At the high temperature, several specimens appear to have actually gained in insulation resistance, although measurement errors may be partly responsible for this phenomenon. Even so, the No. 18 gage cable MIL-W-7139A appears to have been less affected at 100 C than the remaining wires.

Because only one sample of each wire was available for analysis at each environmental condition, it would be almost meaningless, in the statistical sense, to analyze the wires individually. A more comprehensive program with more samples and with multiple measurements would enable one to make more reasonable probability statements about expected wire behavior in the various environments. The present study is more suited to subjective evaluation based on the observed results.

A brief statement of the usefulness of each of these wires under the environmental conditions used in this program is as follows:

No. 8 gage wire MIL-W-7072 has an insulation resistance in excess of 10^{10} ohms before irradiation at 15 C and when dry. When the wire remains cool and dry, a gamma dose in the neighborhood of 10^{10} ergs/g(C) causes a permanent decrease in resistance of about 1 order of magnitude. The total change (transient plus permanent) under these conditions is about 2 orders of magnitude. The presence of moisture causes a decrease of another order magnitude. Heat, combined with moisture and radiation, causes a total decrease of 5 or 6 orders of magnitude. This wire, then, is highly susceptible to combinations of high temperature, moisture, and radiation. It would probably perform satisfactorily in a radiation field for many applications if heat and moisture could be controlled. It would probably be unsatisfactory for high-temperature use even without radiation.

TABLE I. OBSERVED PER CENT DEVIATION FROM INITIAL IN INSULATION RESISTANCE AFTER EXPOSURE TO 7.1 x 10^9 ERGS/G(C)

		Temperature and Humidity					
		15 C		55 C		100 C	
Wire Type	Measurement Field	Dry	Moist	Dry	Moist	Dry	Moist
No. 8 gage wire MIL-W-7072	Out	80.0	97.2	99.8	97.4	99.9	99.3*(a)
	In	72.7	58.3	95.9	85.2	99.7	98.6*
No. 16 gage cable Ty-1-Cl-A	Out	0.0	88.0	80.0	99.0	91.0	186*
	In	9.8	82.7	58.3	94.0	38.3	50.0*
No. 18 gage cable MIL-W-7139A	Out	0.0	97.0	80.0	98.9	70.0	88.0
	In	36.0	93.0	87.5	97.2	36.0	20.0*
No. 16 gage wire MIL-W-8777	Out	0.0	99.2	98.0	97.7	97.7	60.0*
	In	20.0	93.0	39.5	73.6	99.1	120.0*
No. 18 gage cable LAC-1-135B	Out	80.0	99.2	87.3	81.5	95.9	99.1
	In	10.0	90.3	61.4	89.0	96.3	98.7
Suprenant polyethylene	Out	0.0	50.0	85.0	99.6	99.7	99.9
	In	0.0	33.3	57.5	91.1	57.0	98.5
No. 18 gage wire polypropylene	Out	0.0	50.0	96.7	93.0	99.9	98.9
	In	0.0	60.0	92.7	58.3	81.4	89.4
No. 18 gage AWG 36 polyethylene	Out	0.0	93.0	93.0	82.0	99.5	98.2
	In	0.0	50.0	70.0	17.8	60.0	46.3

(a) Asterisk indicates positive deviation; all others are negative.

No. 16 cable Ty-1-Cl-A shows very little permanent change in resistance due to radiation when dry and cool. The transient change under these conditions amounts to a decrease by about 1 order of magnitude. Temperature appears to have little effect. Moisture appears to have a more deleterious effect than either heat or radiation alone. The greatest deterioration was suffered when this wire was irradiated at 55 C and 65 per cent R. H. The final resistance had dropped almost 3 orders of magnitude to about 1 x 10^9 ohms.

No. 18 gage cable MIL-W-7139A shows a maximum decrease of about 2 orders of magnitude in insulation resistance after irradiation. Heat and moisture have no great effect. Serious deterioration of mechanical properties results from irradiation. The insulation will not withstand bending or flexing after irradiation.

No. 16 gage wire MIL-W-8777 suffers about a 2 order of magnitude maximum decrease in insulation resistance when irradiated. Humidity appears to have a more deleterious effect than does heat, at least at temperatures below 55 C. Irradiation, when the wire is dry, does not have great effect on insulation resistance. Again, a serious effect of radiation is the deterioration of mechanical qualities. The insulation crumbles when bent. Heat does affect the flexibility of the insulation.

No. 18 gage cable LAC-1-135B suffers a drop in insulation resistance of about 6 orders of magnitude under the combination of high temperature, moisture, and radiation. Its usefulness in a radiation field is probably limited to cool, dry conditions in applications where the wire is not subject to bending. Radiation embrittles the insulation, and this is aggravated by heat.

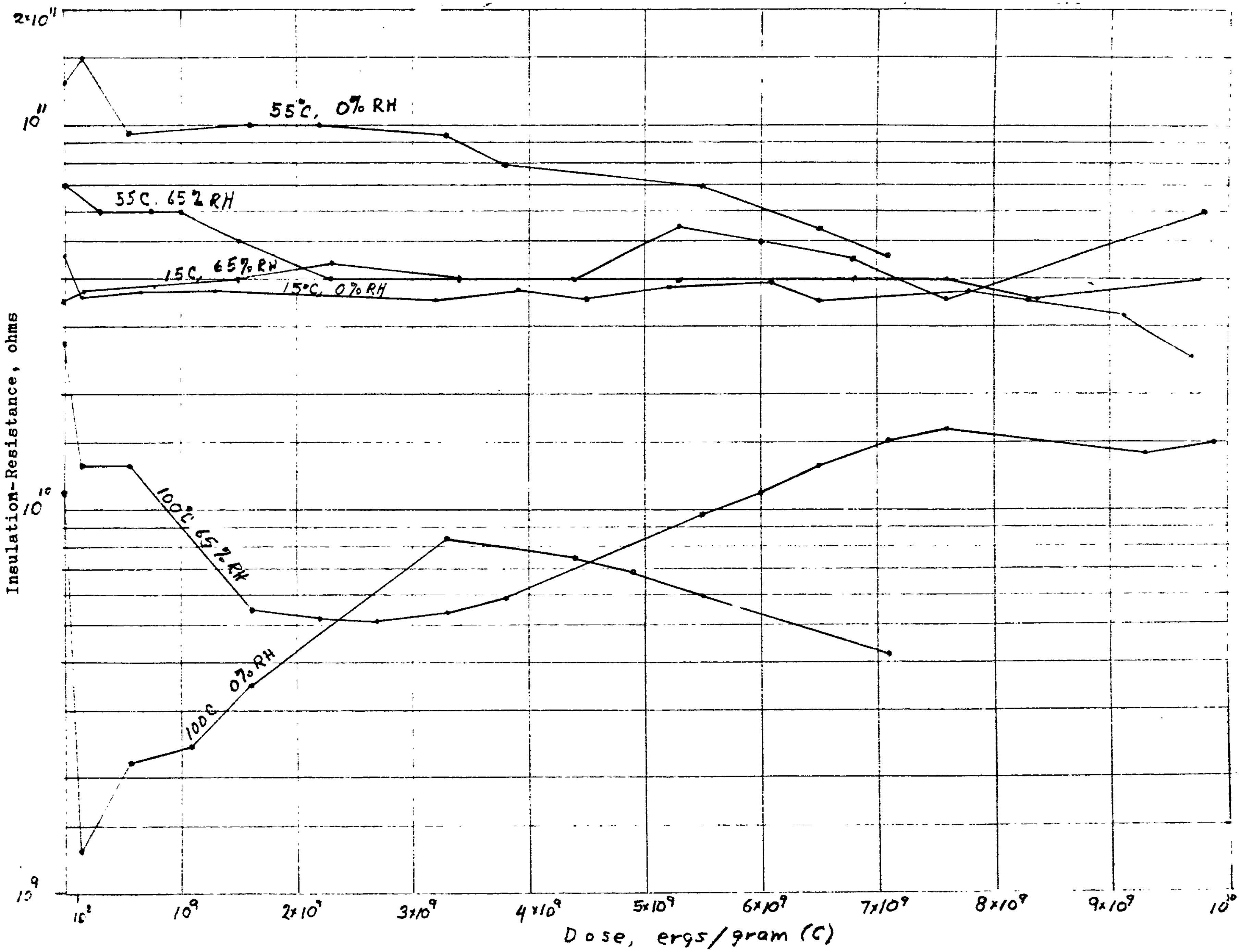
Suprenant polyethylene shows good resistance to radiation, moisture, and heat to 100 C. It remains in good condition mechanically under all environmental conditions studied. The insulation resistance never decreased below 10^9 ohms. Under cool, dry conditions, the resistance change is almost entirely transient in nature. At higher temperatures and/or humidity, permanent changes in resistance become increasingly important.

No. 18 gage AWG 36 polypropylene is unsatisfactory for use in a radiation field. Even at low temperatures and low humidity, it is too brittle for use after irradiation. High-temperature irradiation changes it to a crumbly powder. This serious damage to mechanical properties may depend, to a large degree, on the method of preparation of the polypropylene insulation and may not necessarily exclude all polypropylene from consideration as electrical insulation for use in a radiation field.

No. 18 gage AWG 36 polyethylene remains quite stable in the presence of the combination of heat, moisture, and radiation. Insulation resistance remains about 10^9 ohms at all times. Mechanical properties remain satisfactory, even at high temperatures. The behavior of this material is quite similar to that of the Suprenant polyethylene. These two materials are probably the best choice of those studied for general use in a radiation field where a variety of temperature and humidity conditions is encountered. However, under a given set of controlled temperature and humidity conditions, some of the other materials may be more satisfactory.

The authors wish to express their appreciation to the many people of the Reliability Engineering and Radiation Physics Divisions at Battelle and of Lockheed Aircraft Corporation for their assistance on this paper.

Figure 1. Insulation Resistance of Polyethylene Under Effect of Radiaioon, Heat, and Moisture



A STUDY OF RADIATION EFFECTS ON FUEL TANK SEALANTS AND BLADDER CELL MATERIAL

by

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The effects of exposure to gamma irradiation were studied on two commercial thiokol based sealants and one high-temperature bladder cell material. Samples were tested dry in their original cured state then, after exposure to 140° F, immersed in JP-4 fuel for periods equivalent to those required to reach the three radiation doses used. After gamma irradiation at 140° F, they were immersed in JP-4 fuel to radiation doses of 9.3×10^8, 3.5×10^9, and 9.9×10^9 ergs/gm (carbon). The sealants showed about 10% degradation at the intermediate dose level and serious damage at the highest dose level. The bladder cell material apparently withstood a dose of 9.9×10^9 ergs/gm (carbon) at 140° F in JP-4 without great damage.

While awaiting completion of the nuclear testing facilities at Air Force Plant No. 67, the Lockheed Nuclear Products Branch subcontracted under a prime Air Force contract to Battelle Memorial Institute of Columbus, Ohio, an experimental radiation effects program. This program consisted of studies pertaining to radiation effects on electrical insulation, fuel tank sealants and bladder cell material, and radome laminates in various environments.

This paper treats with the sealants and bladder cell phase of the program. Prior knowledge indicated that organic materials are subject to severe damage from nuclear radiation; however, little work had been done in the field of effects of radiation in combination with conventional environmental parameters such as heat and exposure to organic solvent-type liquids. Actually, these environments are extremely important in considerations concerning design problems in nuclear-powered aircraft. At the Battelle cobalt-60 gamma facility, conventional commercial materials were tested under these added environments.

EXPERIMENTAL WORK

The following materials were selected for the investigation:

1. PRC-1422 Type B-2, Products Research Corporation, a thiokol base, sodium and potassium dichromate accelerated sealant
2. Presstite 1-221, Presstite-Keystone Corporation, a thiokol base, cumene hydroperoxide accelerated sealant
3. BTC-6 high-temperature bladder cell material, Goodyear Tire and Rubber Company, a 350° F Buna N - nylon fabric - nylon film rubber sandwich fuel cell material.

Item 2 was eventually eliminated from the program because of its inability to develop a "tight" cure. The Presstite Corporation later reported it to be an experimental material.

Irradiations were conducted statically; and the physical properties tested before and after irradiation were ultimate tensile strength, ultimate elongation, and hardness (on sealants only). Dose measurements, made by using a 10-cc graphite ion chamber, are reported in ergs/gram (carbon). The working standard used for calibration of the ion chamber was a copper-modified ferrous sulfate dosimeter. The dosimetry data are based on a G-value (the number of ferrous ions oxidized per 100 ev of energy absorbed in the water solution) of 0.66 for the oxidation of ferrous ion, and the relationship that 100 ergs/gram absorbed in the dosimeter solution is equal to 90.9 ergs/gram absorbed in carbon. The G-value of 0.66 for the copper-modified ferrous sulfate system is equivalent to a G-value of 15.5 for the normal ferrous sulfate solution. A flux map is shown in Figure 1.

SPECIMEN PREPARATION

Each of the sealants was compounded according to instructions on the can; that is, 7.5 parts PRC-1422-B-2 with 1 part curing agent and 10 parts Presstite 1-221 with 1 part curing component. The curing agent and the base sealant were combined on a three-roll paint mill. Sealants were then molded into sheets approximately 1/8 inch thick and cured at room temperature for 24 hours, followed by 48 hours at 120° F. The molded sheets were aged a minimum of three weeks prior to testing; and, prior to aging, 1-inch-wide by 5-inch-long tensile bars were cut for use in the test program. Sets of at least five specimens of each sealant were treated as follows:

1. One set, uncoated - maintained at room temperature
2. One set, coated - maintained at room temperature

3. One set, coated - in JP-4 fuel at 140° F for periods corresponding to exposure

4. One set, coated - in JP-4 fuel irradiated at various dosages

The coating used on the sealants was Buna N sealant overcoat, fill and drain Gelac Type EPS-4031 material to conform to Gelac 5-781 specification. Coating was accomplished by dipping, and samples were mechanically removed from the Buna N solution at a withdrawal rate of 2 inches per minute.

It was not necessary, of course, to prepare the Goodyear bladder-cell material, nor did it have to be coated. Standard dumbbell specimens were cut from all materials for tensile-strength and elongation measurements.

EXPOSURE CONDITIONS

The exposure of specimens to three different cobalt-60 (gamma) radiation doses and of control specimens under the pertinent environmental conditions was conducted as follows:

1. Specimens suspended in JP-4 fuel at 140° F; irradiated to (a) 9.3×10^8, (b) 3.5×10^9, and (c) 9.9×10^9 ergs/g (C)

2. Control specimens suspended in JP-4 fuel at 140° F, but not irradiated

3. Room-temperature control specimens not immersed in fuel or exposed to radiation

Exposure to 140° F JP-4 fuel and to 140° F fuel plus irradiation necessitated certain preparation for specimen handling and exposure.

SPECIMEN BOXES

Two specimen boxes were required, one to submerge in the cobalt-60 pool and the other to hold specimens in fuel as controls. In each case, the boxes were filled with JP-4 fuel and maintained at a temperature of 140° F. To simulate aircraft structural materials, the boxes were built of aluminum; but in order to use the cobalt-60 source swimming pool type, it was necessary to have a stainless steel outer box surrounding the aluminum container. The annulus between the two boxes provided the necessary thermal insulation. The details of construction are shown in Figure 2.

The temperature in the box was regulated by means of a Foxboro controller, and the voltage input to the heaters was controlled by a variac so that a failure of the controller in the on position would not result in an extreme buildup in temperature in the box.

The second box was required for maintaining specimens in fuel at 140° F as controls for the irradiated specimens. In this case, an aluminum box identical to the one just described was used. Controls for this box were identical to the ones used for the submerged equipment.

IRRADIATION TESTS

Sealant and bladder-cell strips were suspended in the aluminum boxes, which were then sealed. The effectiveness of the seal was determined by pressurizing the container and checking for leaks under water. The boxes were then filled with JP-4 fuel, with the vent tube used as an inlet. The filled "cell" to be irradiated was lowered between two rows of cobalt-60 rods parallel to the front and back of the box, and the control cell or box was placed in service at the same time. After a predetermined period of irradiation, the samples were removed and permitted to dry out at room temperature. Exposure time (in fuel) of the nonirradiated test specimens was identical with that of the cobalt-60 exposed samples.

The dried 1-inch by 5-inch strips were cut into tensile dumbbells. These specimens were then pulled on a Baldwin-Southwark tester at a jaw-separation rate of two inches per minute. The data for samples exposed to three different radiation doses and for fuel-immersed and dry exposed controls are reported as ultimate tensile strength and elongation at break. Shore hardness measurements were made as an A_2 scale, with a double-thickness sample (1/4 inch).

Irradiation of specimens was carried out to three levels:

1. 9.3×10^8 ergs/g (C) at a dose rate of 1.3×10^7 ergs/g-hr (C)
2. 3.5×10^9 ergs/g (C) at a dose rate of 1.5×10^7 ergs/g-hr (C)
3. 9.9×10^9 ergs/g (C) at a dose rate of 1.9×10^7 ergs/g-hr (C)

RESULTS

The following general observations were made on PRC-1422 sealant specimens. Data are shown in Table I.

1. The reduction in tensile strength at the lowest radiation dose is of the order of 10 per cent. Elongation values show no change, and hardness is reduced by 10 per cent. Specimens showed no visual evidence of degradation.
2. At the intermediate radiation dose, tensile strength is reduced by about 25 per cent. Elongation values are reduced by 13 per cent and hardness is reduced by some 16 per cent. As in the case of low-dose tests, these specimens did not show visual evidence of degradation.

3. The sealant specimens subjected to highest radiation doses - 9.9×10^9 ergs/g (C) - were badly pitted and were swelled because of penetration of fuel through the Buna N overcoat. It was necessary therefore to vacuum-dry the exposed strips to remove the fuel prior to making physical property measurements. Tensile strength of these specimens showed a reduction of about 68 per cent. Elongation at break and hardness were reduced by 54 and 23 per cent, respectively.

Figure 3 shows specimens irradiated to the maximum dose in fuel at 140° F, control specimens exposed to 140° F fuel but not irradiated, and specimens held at room temperature and not exposed to fuel. Two complete sets of samples are shown. The light-colored strips represent the Presstite sealant, which was not tested at other levels of radiation because of the character of the material. The darker strips represent PRC-1422-B-2 sealant. The effect of the high level of radiation may be seen readily in the blistered samples. These "bubbles" contained liquid fuel and represent a separation of the Buna N coating from the base sealant.

The effect of maximum irradiation in 140° F fuel on the Presstite 1-221 sealant may be seen in Table II. These results are reported here for general interest even though the test was not carried through all three levels of radiation. Initial values for tensile strength, elongation, and hardness are subnormal. In spite of this, the degradation is extreme - 68 per cent reduction in tensile strength, 64 per cent reduction in elongation, and 37 per cent reduction in Shore A_2 hardness.

There was no visual evidence of change in the Goodyear bladder-cell material BTC-6, even at the maximum radiation dose of 9.9×10^9 ergs/g (C), as shown in Figure 3. The following observations were made on measured changes in physical properties:

1. At the three radiation doses - low, medium, and high-tensile strength values decreased 16, 18, and 22 per cent, respectively.

2. Changes in elongation values are not significant, since values for control specimens on which changes were based varied considerably. This variation is probably due to the character of the fabric at the point where tests were made.

Test data are shown in Table III.

CONCLUSIONS

In regard to the PRC commercial sealant material, changes in physical properties are not serious through the intermediate radiation dose (applied to specimens in 140° F JP-4 fuel) of 3.5×10^9 ergs/g (C). No visible change in sealant character can be observed up to this same dose. On the other hand, properties of the sealant are seriously impaired at a radiation dosage of 9.9×10^9 ergs/g (C).

One rather important factor was not determined in these tests. That was the effect of radiation on the adhesion of sealants to an aluminum alloy surface. Since the performance of these products depends to a large extent on this property, it is recommended that determinations of this type be made.

Radiation dosages through 9.9×10^9 ergs/g (C) apparently do not seriously impair the physical properties of Goodyear bladder-cell material BTC-6, nor is the product visibly changed by this exposure while immersed in 140° F fuel.

DESCRIPTION OF COMPONENT PARTS SHOWN IN FIGURE 1

A. Outer stainless steel box. Cover is 1/8-inch stainless steel plate.

B. Inner aluminum box; 2-inch depth. Cover is of same construction but 1 inch in depth.

C. Ceramic insulated, two-conductor electrical lead encased in a copper tube. A flexible, rubber-sheathed lead was connected to this about 3 feet from the box.

D. Chromalox strip heater (110 v, 400 w) attached to bottom of aluminum box.

E. Vent tube. Flexible Tygon tubing was attached to this stainless steel nipple to dissipate any vapor coming from the heated fuel. It also acted as a safety valve in case fuel should overheat through electrical control failure.

F. Thermocouple; ceramic insulated.

G. Pressure tube. One end of flexible Tygon tubing was attached to the stainless steel tube, the other end to a tank of nitrogen. A constant nitrogen pressure of 15 psig was maintained in the annular space between boxes at all times during irradiation. This was done for two reasons: (1) to minimize danger of explosion in case of JP-4 leakage to space between inner and outer boxes containing open heater terminals, and (2) to keep a positive pressure inside the box greater than the 6-psi pressure of the water in the cobalt-60 pool.

H. Milled slot. A 1/32-inch by 1/4-inch slot was milled in each half of the aluminum box. A 1/8-inch polyethylene gasket was used as a seal in this slot.

I. Milled slot. A 1/16-inch by 1/4-inch slot was milled in the stainless steel box. No slot was used in the cover plate. A 1/8-inch polyethylene gasket was used as the sealing element.

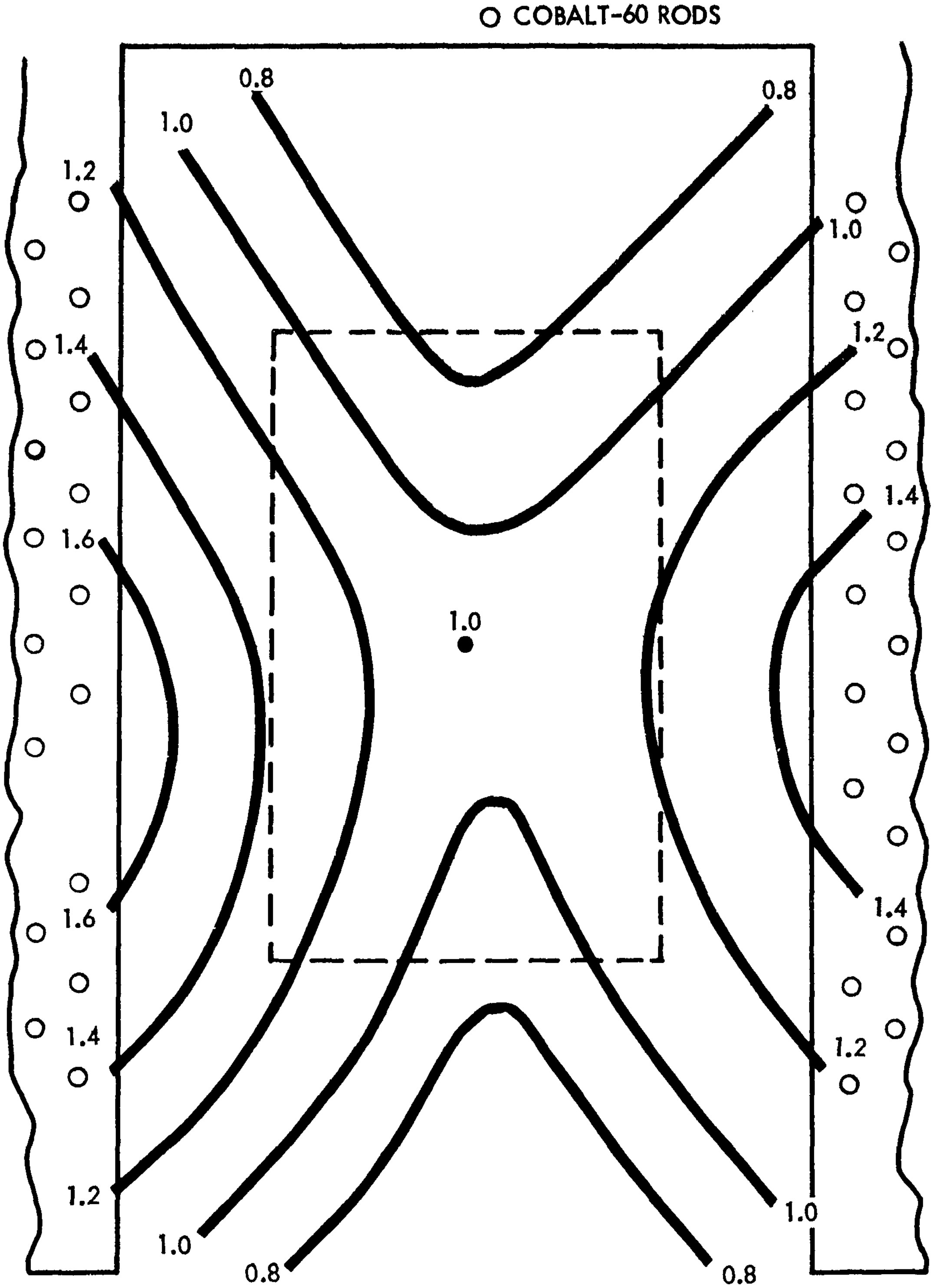

FIG. 1 FLUX MAP OF BATTELLE COBALT-60 POOL, RELATIVE INTENSITY

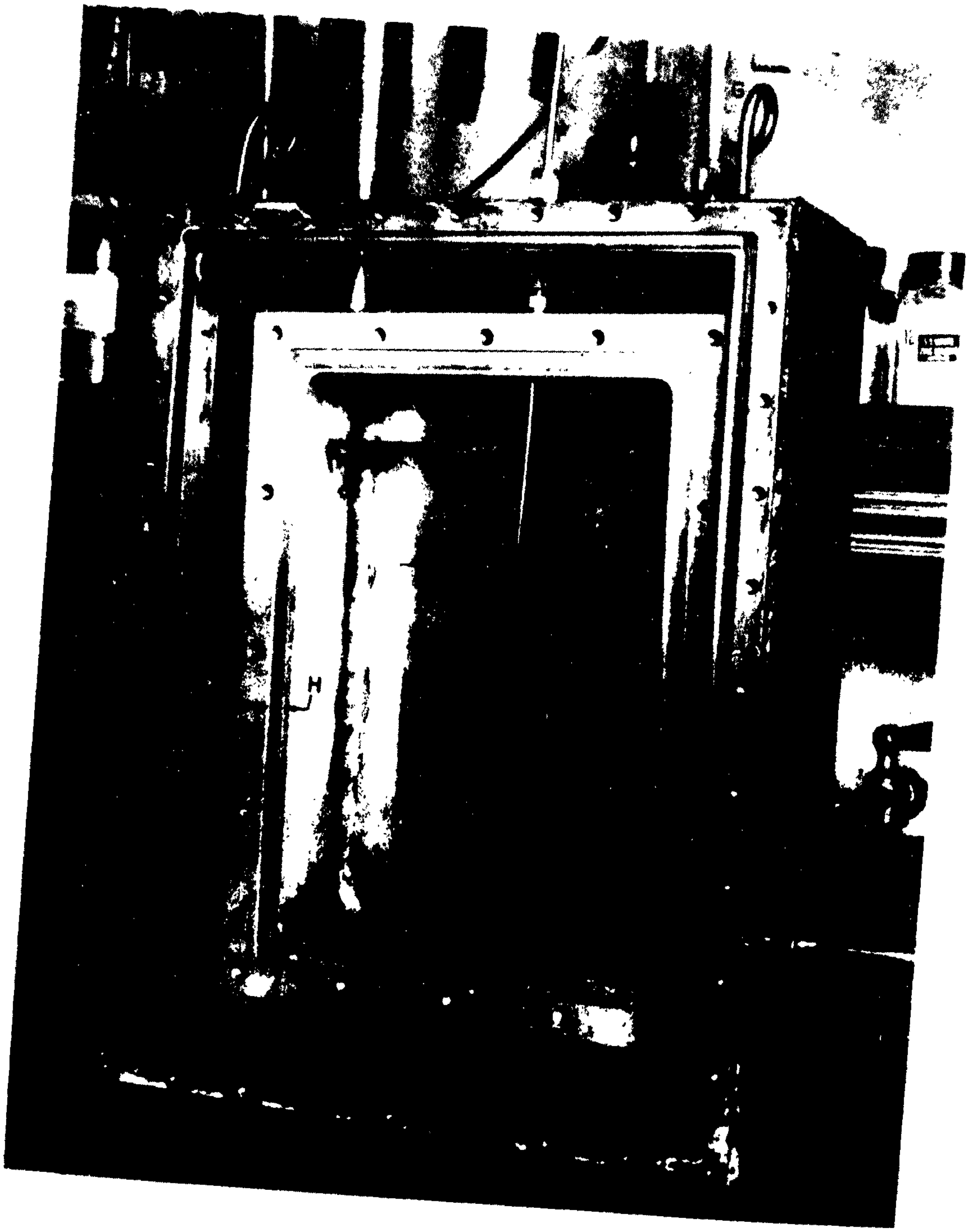

FIG. 2 SAMPLE IRRADIATION SPECIMEN BOX

FIG. 3 COMPARISON OF IRRADIATED AND NON IRRADIATED SAMPLES

TABLE I

PHYSICAL PROPERTIES OF PRC-1422-B-2 SEALANT BEFORE AND AFTER EXPOSURE TO VARIOUS GAMMA RADIATION DOSAGES

	ORIGINAL SPECIMENS (ROOM TEMPERATURE-DRY SPECIMENS)		CONTROL SPECIMENS (BUNA N COATED - 140°F IN JP-4 FUEL-NOT IRRADIATED)			IRRADIATED SPECIMENS (140°F IN JP-4 FUEL)		
						RUN I	RUN 2	RUN 3
SPECIMEN	UNCOATED	BUNA N COATED	RUN I	RUN 2	RUN 3	$9.3 \times 10^{9(a)}$	$3.5 \times 10^{9(a)}$	$9.9 \times 10^{9(a)}$
1	504	451	424	371	379	292	304	144
2	667	480	457	346	494	326	299	156
3	519	533	386	334	467	350	329	147
4	477	491	390	461	500	350	299	145
5	570	491	405	471		402	303	133
6	479	427	418	500		377	330	
7	454	425		456		388		
8	506	414		480		404		
AVERAGE TENSILE STRENGTH, psi	522	464	413	427	460	361	311	145
AVERAGE ELONGATION, PER CENT	290	245	250	260	240	250	226	110
AVERAGE SHORE A_2 HARDNESS	64	64	60	54	60	56	45	46

(a) RADIATION DOSAGES IN ergs/g(C).

TABLE II
PHYSICAL PROPERTIES OF PRESSTITE I-221 SEALANT (a) BEFORE AND AFTER EXPOSURE TO GAMMA RADIATION

SPECIMEN	ORIGINAL SPECIMENS (ROOM TEMPERATURE - DRY SPECIMENS)		CONTROL SPECIMENS (BUNA N COATED - 140°F IN JP-4 FUEL - NOT IRRADIATED)	IRRADIATED SPECIMENS (140°F IN JP-4 FUEL) DOSAGE - 9.9×10^9 erg/g(C)
	UNCOATED	BUNA N COATED		
1	194	198	232	67
2	205	195	248	70
3	227	205	216	82
4	222	208	242	75
5	192	202	255	83
AVERAGE TENSILE STRENGTH, psi	208	201	238	75
AVERAGE ELONGATION, PER CENT	650	650	530	190
AVERAGE SHORE A_2 HARDNESS	36	34	34	

(a) WORK WITH THIS SEALANT DISCONTINUED AT LOCKHEED'S SUGGESTION DUE TO LACK OF "TIGHT" CURE. PRESSTITE LATER REPORTED THIS TO BE AN EXPERIMENTAL SEALANT COMPOUND+

TABLE III
PHYSICAL PROPERTIES OF GOODYEAR BLADDER CELL MATERIAL BTC-6 BEFORE AND AFTER EXPOSURE TO VARIOUS GAMMA RADIATION DOSAGES

	ORIGINAL SPECIMENS (ROOM TEMPERATURE - DRY SPECIMENS)	CONTROL SPECIMENS (BUNA N FABRIC - 140° F IN JP-4 FUEL - NOT IRRADIATED)			IRRADIATED SPECIMENS (140°F IN JP-4 FUEL)		
					Run 1	Run 2	Run 3
		Run 1	Run 2	Run 3	9.3×10^{8}(a)	3.46×10^{9}(a)	9.91×10^{9} (a)
	6738	6870	6462	7061	5860	4962	5357
	7340	6950	6163	6220	6210	5429	5089
	7487	6530	6230	6265	6460	5140	5089
	6388	7020	6620	6430	4950	4830	4877
	7161	7040	6370	6115	5330	5375	4735
	6535					5280	
	6740						
	6250						
	6640						
AVERAGE TENSILE STRENGTH, psi	6808	6882	6369	6418	5762	5169	5029
AVERAGE ELONGATION PER CENT	40	25	40	40	25	37	40

(a) RADIATION DOSAGES IN ERGS/G (C).

THE EFFECT OF ELECTRON RADIATION ON THE COMPLEX DYNAMIC MODULUS OF POLYSTYRENE AND HIGH-DENSITY POLYETHYLENE*

by

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Measurements of the elastic modulus and mechanical loss at 5 to 10 kcps were made on nonirradiated and 5-Mev-electron-irradiated specimens of polystyrene and high-density polyethylene over a temperature range from 80° to 320°K. Specimens were irradiated at liquid-nitrogen and room temperatures to doses of up to 7×10^7 rads. Considerable dependence of the modulus on irradiation temperature was noted in polyethylene. The polystyrene specimens exhibited marked modification of the internal friction spectrum under room-temperature irradiation. These changes in the dynamic modulus are discussed in terms of early-stage cross-linking mechanisms.

INTRODUCTION

The bombardment of organic high polymers with gamma-rays, electrons, protons, neutrons, etc., is known to considerably alter many of their mechanical properties. Furthermore, the degree of alteration is dependent, for the most part, on the total energy absorbed per unit mass of the polymer,[1,2] not on the type of radiation. The molecular mechanisms responsible for the changes in properties appear to be broadly classed[3] as "cross-linking" between adjacent polymer chains, unsaturation of organic bonds, and breaking, or scission, of the main skeletal chain itself.

Most, if not all, of the published literature[4,5] on the mechanical effects of the irradiation of organic high polymers has dealt with irradiations carried out at room temperature or above. The present investigation is based on an attempt to control the development of molecular rearrangement subsequent to the passage of the disturbing radiation by irradiating at low temperatures, at which both reaction and migration rates should be lowered. Comparison is then made with specimens irradiated at room temperature.

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*This work was performed under arrangements with Convair—Fort Worth, A Division of General Dynamics Corporation, under Air Force Contract AF33-600-32054.

Much information can be gained about the nature of molecular motions in solids by examining their mechanical-dispersion behavior. Reported below is a mechanical-dispersion study of some of the structural changes induced in the polymers polystyrene and high-density polyethylene by irradiation at 100° and 300°K, with 2 to 7×10^7 rads of 5-Mev electrons.

EXPERIMENTAL PROCEDURE AND MATERIALS

The mechanical-dispersion measurements were made by a resonant-bar method, using the longitudinal mode of excitation. The frequency was varied over a limited range (3,000 to 15,000 cps) by exciting harmonics. The temperature was varied by adjusting the thermal contact of the resonant apparatus with a nitrogen bath, giving a temperature range of 80° to 320°K. The apparatus was so designed as to permit simultaneous determination of the length and resonant frequency of the specimens at all temperatures, thus making possible accurate determination of Young's modulus as a function of temperature. The mechanical energy loss, Q^{-1}, was measured by displaying the output of an electromagnetic transducer on a chart recorder and sweeping the frequency; the frequency width at the half-power point of the recorded curve divided by the resonant frequency gave the measure of the energy loss. The low-temperature irradiations were carried out in the mechanical-dispersion apparatus by maintaining a flow of liquid nitrogen past the specimen.

The electron irradiations were performed using the Applied Radiation Corporation's linear accelerator at Walnut Creek, California. Electrons of 5-Mev energy monitored by cobalt-glass chips were used for the irradiations.

A number of separate investigations on dummy specimens were performed to determine the temperature rise inside the specimens during bombardment. Carbon resistors embedded along the axis of the dummy specimens served as thermal elements. In no case, at the power levels used, did the internal temperature rise 5°K above the bath temperature.

The specimens used were rod shaped, 3/16 in. in diameter, and 6-1/2 in. long. The average density of ten specimens of high-density polyethylene at 292.2°K before irradiation was 0.9631 ±0.0024 g/cm^3. The density at 292.2°K after the 300°K irradiation was 0.9587 ±0.0024 g/cm^3; and the density at 292.2°K after 100°K irradiation was 0.9620 ±0.0024 g/cm^3. The unirradiated polystyrene density was 1.1835 ±0.0050 g/cm^3 measured at 295°K.

EXPERIMENTAL RESULTS

The results in this section will be discussed in terms of the formalism of linear relaxation theory; i.e., it will be assumed that the mechanical-dispersion relations of Zener[6] hold:

$$Q^{-1} = \Delta_0 \frac{\omega \tau}{1 + (\omega\tau)^2} \tag{1}$$

$$\frac{\Delta M}{M} = \Delta_0 \frac{1}{1 + (\omega\tau)^2} \tag{2}$$

$$\tau = \tau_0 \, e^{H/KT} \tag{3}$$

where

$$\Delta_0 \ll 1 , \tag{4}$$

where Q^{-1} is a measure of the energy loss in each cycle of oscillation, Δ_0 is the "relaxation strength," ω (sec^{-1}) is the angular frequency of oscillation, τ_0 (sec) is the "natural thermal" period, H (ergs) is the barrier activation energy, T (°K) is the temperature, K (ergs deg^{-1}) is Boltzmann's constant, and $\Delta M/M$ is the modulus defect, i.e., the fractional change in Young's modulus due only to the activation of the relaxation mechanism. Zener's formulation assumes, in general, that such quantities as $\Delta M/M$ are $\ll 1$. It is realized that in such a complex molecular system as exists in the organic high-polymer solids, it is not unreasonable that strong nonlinear relaxation behavior may exist and thus invalidate this type of formulation. However, the linear theory is certainly the simplest and therefore deserves first consideration.

Consider first the polystyrene data, shown in Figs. 1, 2, and 3. As can be seen in Fig. 1, for unirradiated material, there are peaks in the loss curve at 120 ±2°K and at 267 ±3°K for frequencies in the neighborhood of 5500 cps, and hints of peaks forming at both lower and higher temperatures. Figure 2 shows the corresponding variation of Young's modulus with temperature. To a first approximation, there appears to be only a slow linear variation of the modulus with temperature. The data is sufficiently precise, however, to warrant the taking of differences from a best straight line through all the points. These fractional differences in Young's modulus, $\Delta M/M$, are shown in Fig. 3. Note that in Fig. 3, $\Delta M/M$ for the unirradiated specimen drops sharply at 122 ±1°K and again at 250 ±5°K; also, the end of a drop is seen below 122°K, and the beginning of another above 250°K.

If the processes taking place in the vicinity of 120°K and 260°K are simple linear relaxation phenomena, Eqs. (1) and (2) imply that the maximum value of the modulus defect, $(\Delta M/M)_m$, and the maximum energy loss, $(Q^{-1})_m$, should be related by

$$(\Delta M/M)_m = 2(Q^{-1})_m , \tag{5}$$

and that the modulus drop and the loss peak should occur at the same temperature. Equation (5) is satisfied by all the polystyrene data to well within a factor of 2. Thus, the linear relaxation relations (1) through (4) are approximately satisfied.

By measuring the peak position at higher harmonics, an estimate of the activation energy corresponding to these peaks can be made. The peak at 120°K has H = 0.20 ±0.02 ev/atom, while the peak at 267°K has

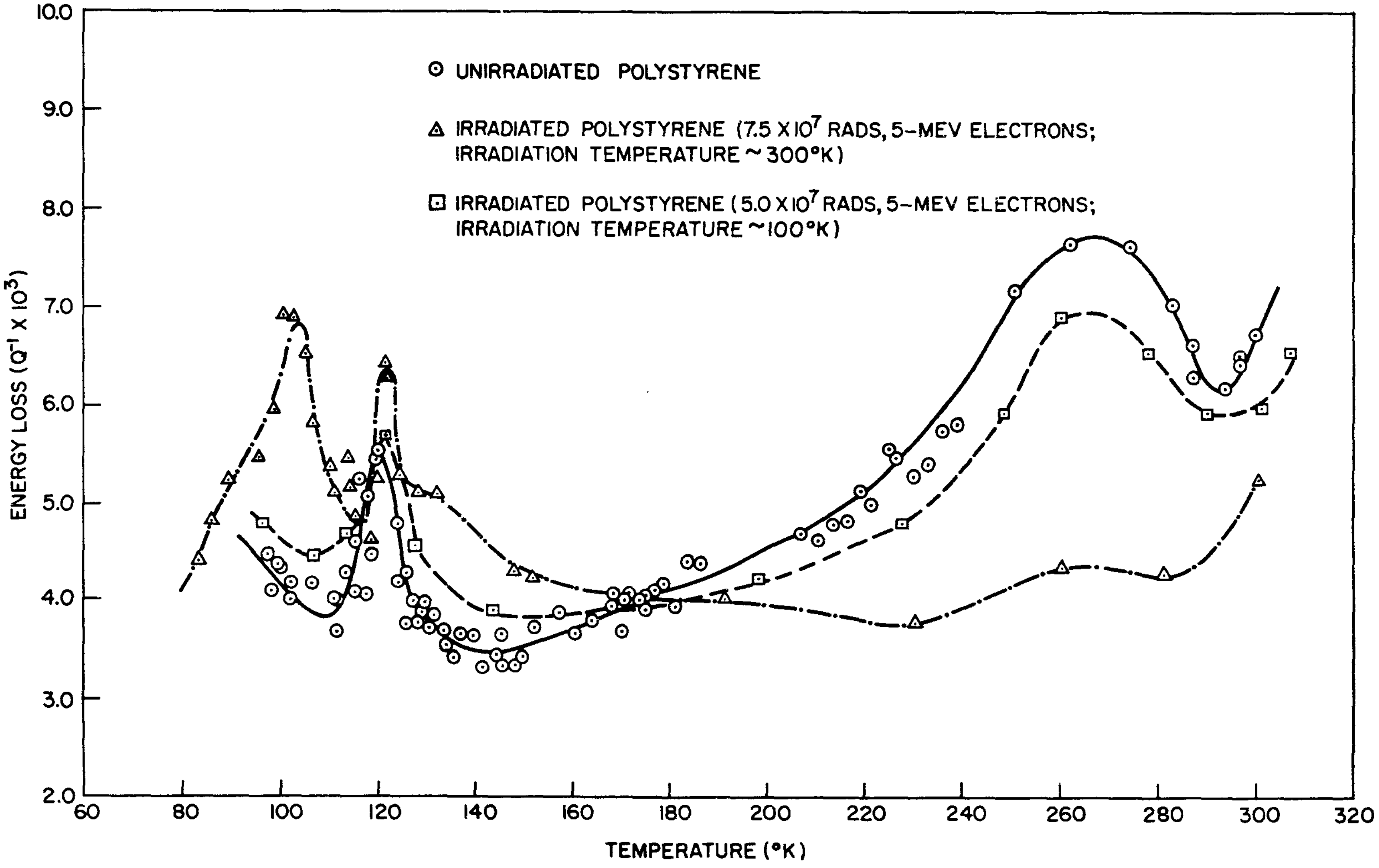

Fig. 1--Energy loss, Q^{-1}, in unirradiated and irradiated polystyrene as a function of temperature

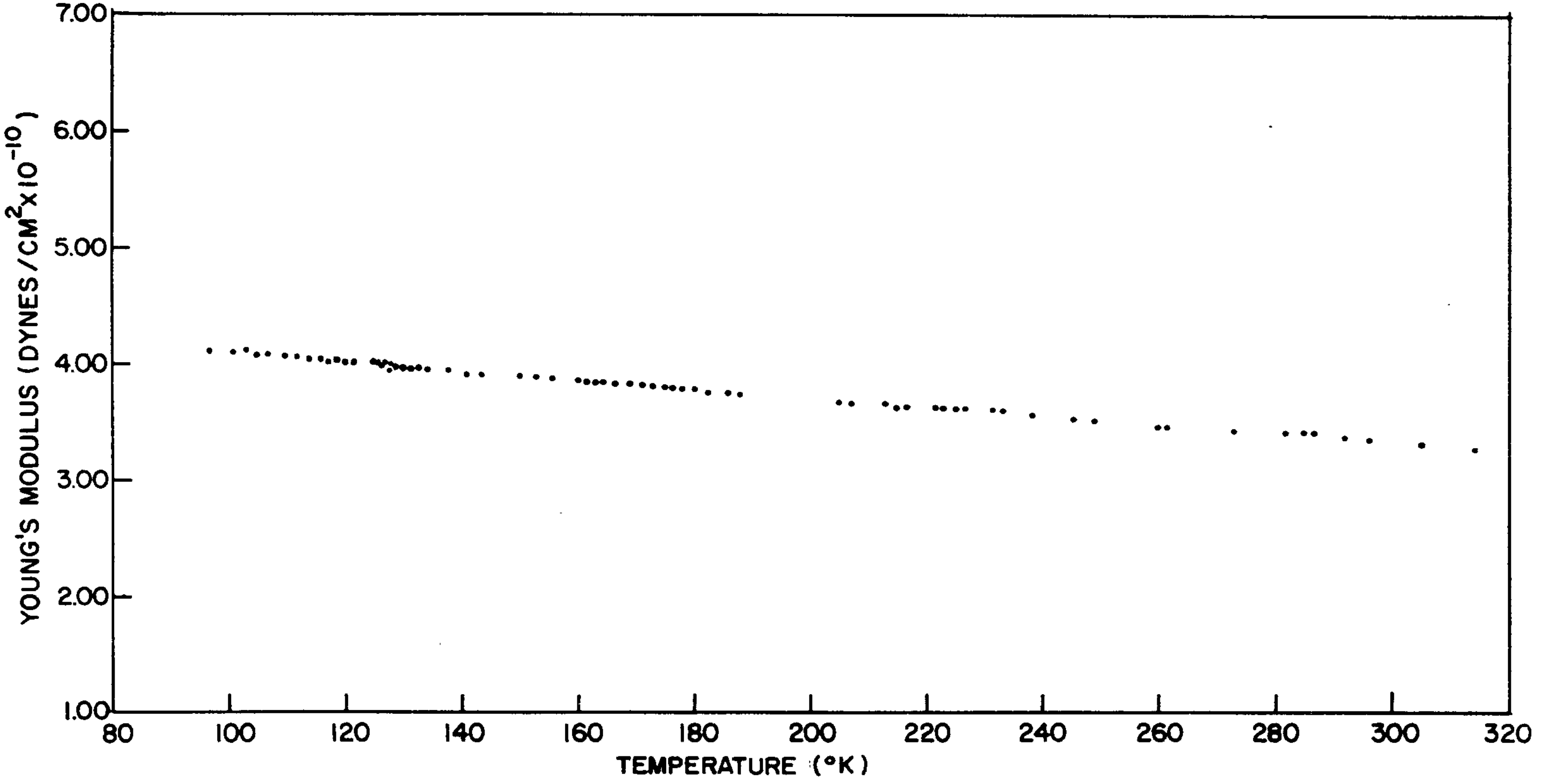

Fig. 2--Young's modulus, M, of unirradiated polystyrene as a function of temperature

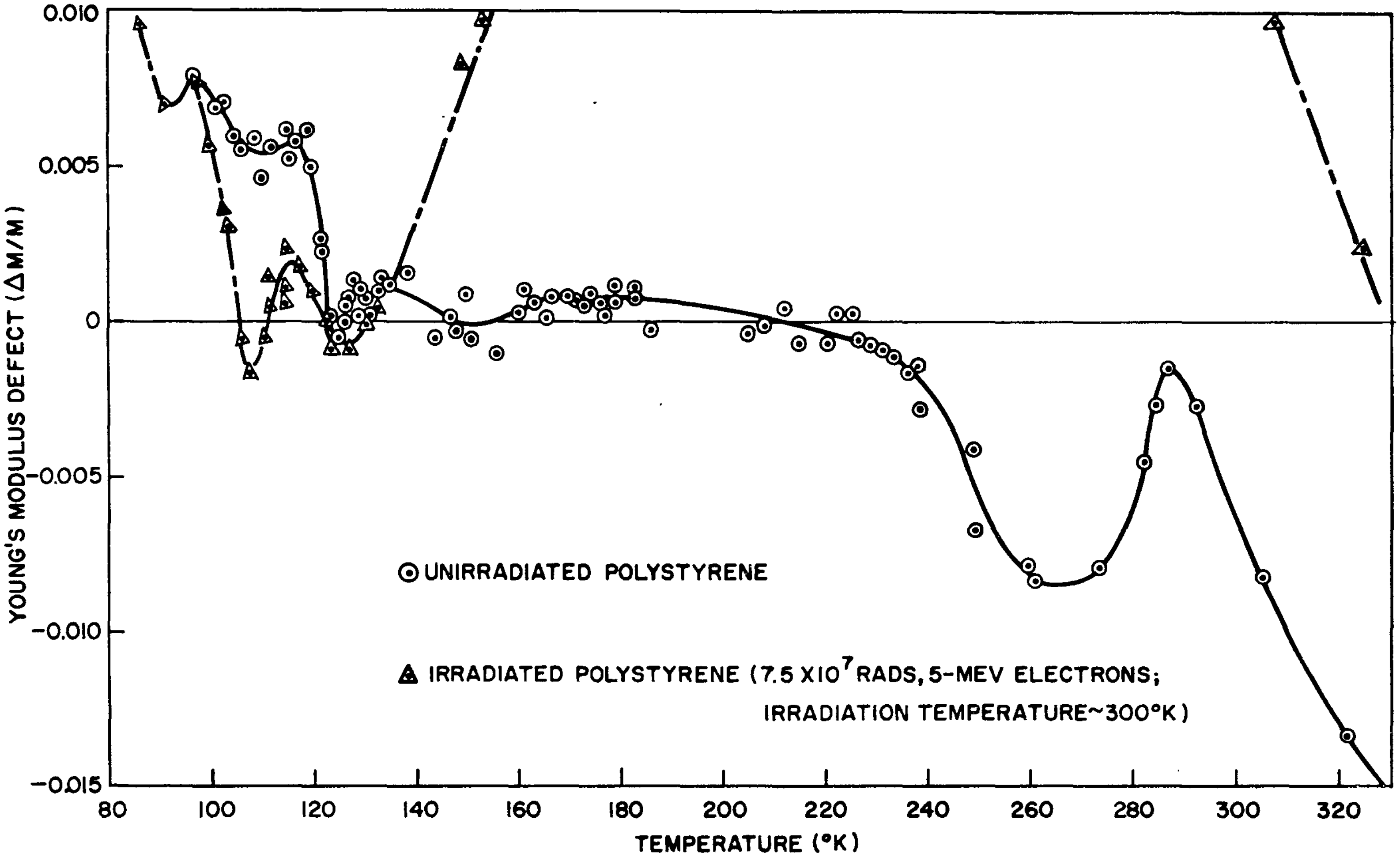

Fig. 3--Young's modulus defect, ΔM/M, of unirradiated and irradiated polystyrene as a function of temperature

FIGURE 7

RUBBER MODULUS VS RADIATION DOSE

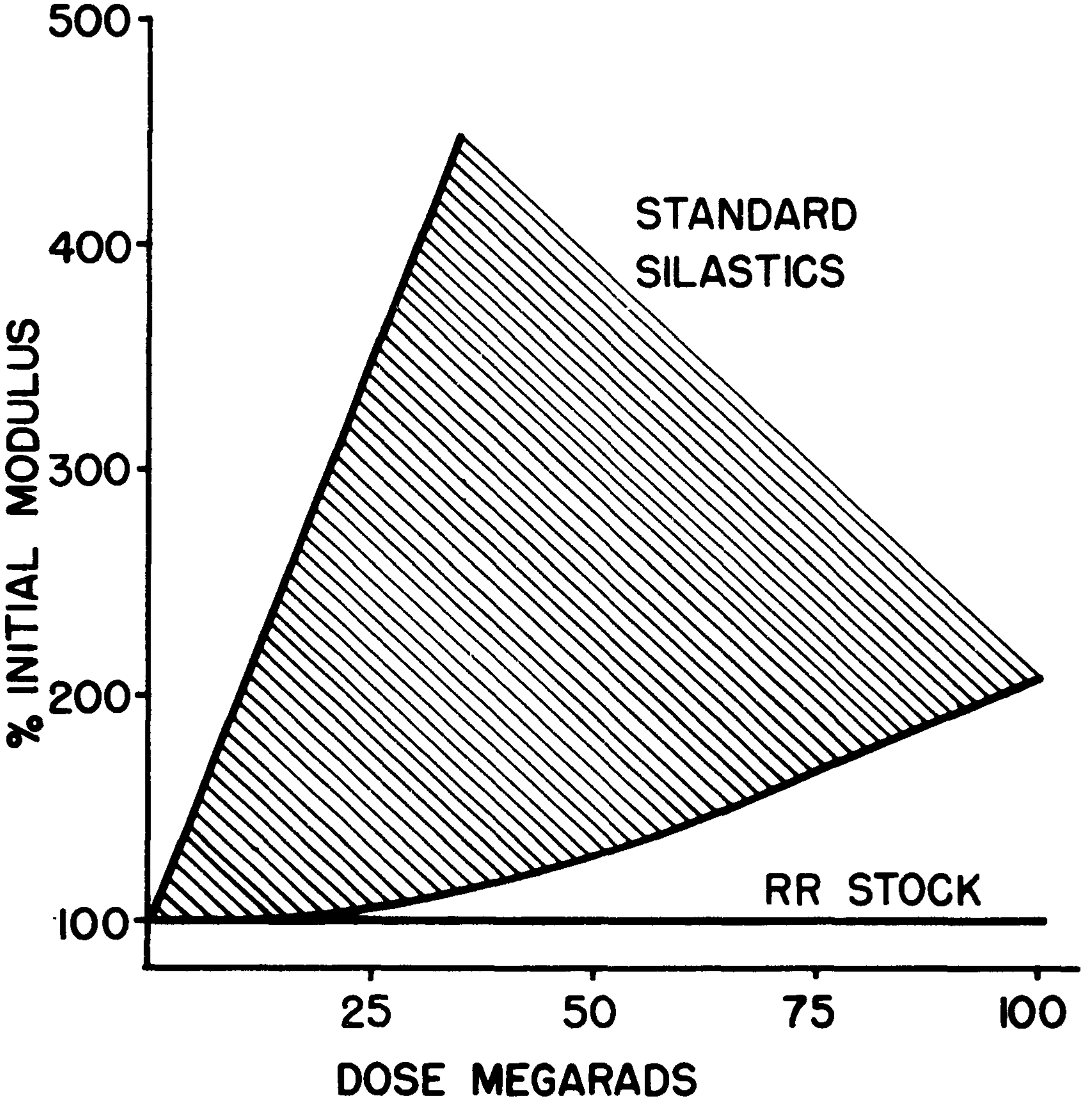

FIGURE 8

RADIATION EFFECTS AT 200° C

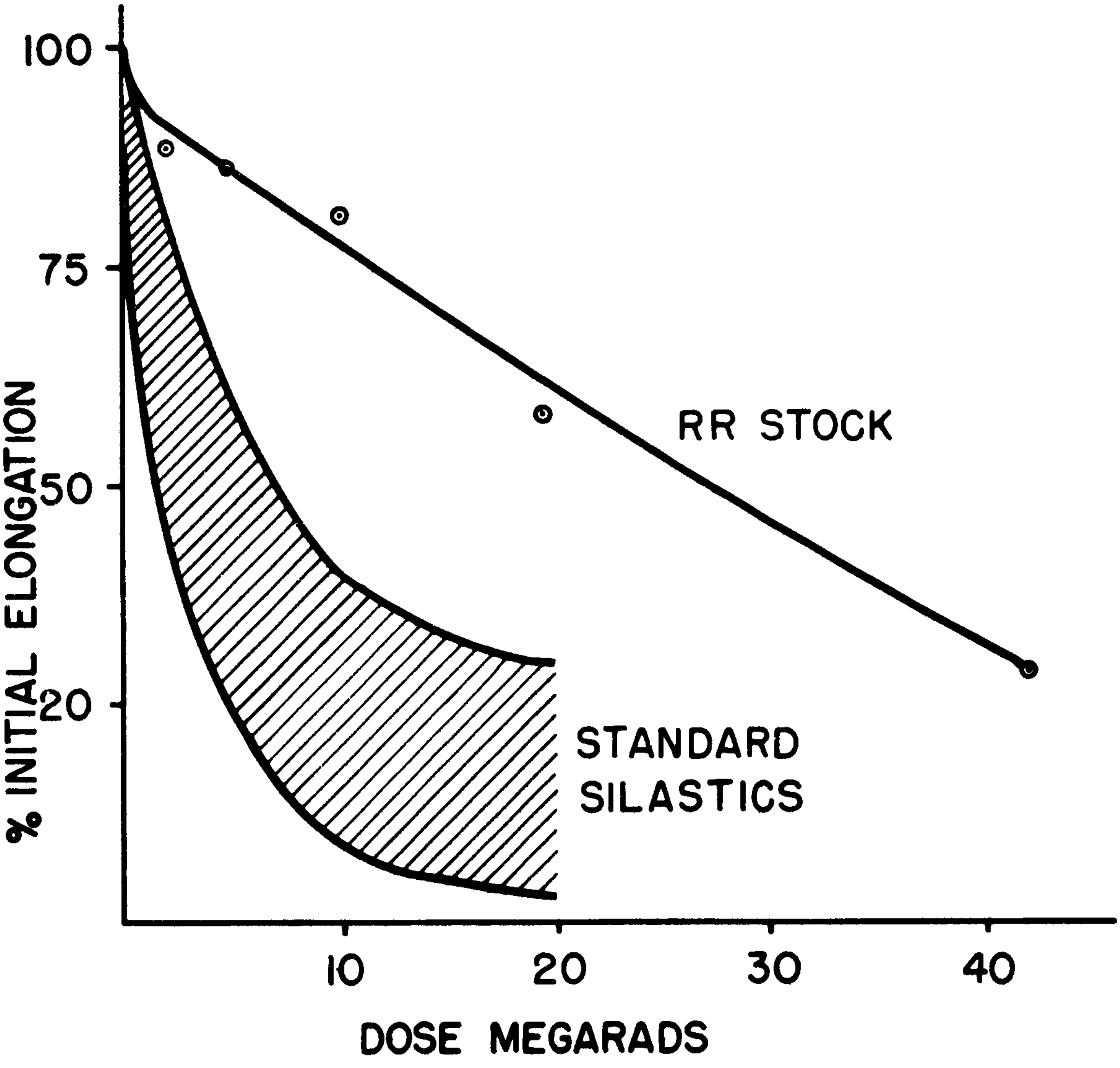

TABLE I

EFFECT OF ELECTRON FRACTION ON GAS EVOLUTION

EXPERIMENTAL FLUIDS

	$G_{\text{NON-COND}}$	e_{METHYL}
I $(C_6H_5)_4(CH_3)_2Si_2O$	0.0034	0.0826
II $(C_6H_5)_5(CH_3)_3Si_3O_2$	0.0202	0.093
III $(C_6H_5)_4(CH_3)_4Si_3O_2$	0.0355	0.140
IV $(C_6H_5)_4(CH_3)_6Si_4O_3$	0.0702	0.195
V $(C_6H_5)_4(CH_3)_8Si_5O_4$	0.147	0.245

TABLE 2

EFFECT OF ELECTRON FRACTION ON GAS EVOLUTION

STANDARD SILOXANES

	$G_{\text{NON-COND}}$	e_{METHYL}
VI $[(CH_3)_2SiO]_4$	2.01	0.45
DOW CORNING 550 FLUID	0.30	0.29
DOW CORNING 710 FLUID	0.07	0.195

TABLE 3

EFFECTS OF RADIATION ON RESIN-GLASS LAMINATES

	FLEXURAL STRENGTH PSI	
RESIN	ORIGINAL	AFTER 10^9 RADS
TESTED 25°C		
2106	41,406	36,300
2105	40,700	26,500
TESTED 250°C		
2106	14,700	17,600
2105	4,180	9,970

TABLE 4

EFFECTS OF RADIATION ON RESIN-GLASS TAPES

	DIELECTRIC STRENGTH VPM	
	ORIGINAL	AFTER 10^9 RADS
XR-5561 ON GLASS	1560	1230

TABLE 5

ELASTOMER CHANGE IN ELONGATION AFTER 90 MEGARADS

ELASTOMER	% CHANGE
HIGH PHENYL SILICONE (D.C.)	-1.8
NATURAL RUBBER*	-12.
BROMINATED ISOBUTYLENE-ISOPRENE	-12.8
ISOCYANATE URETHANE	-30.
ACRYLONITRILE-STYRENE	-36.
POLYVINYL CHLORIDE	-44.
ETHYLENE	-50.
BUTADIENE ACRYLONITRILE	-55.
LS-53 SILICONE (D.C.)	-78.
NEOPRENE	-78.
METHYL VINYL SILICONE (D.C.)	-80.
NATURAL RUBBER	-82.
VINYLIDENE FLUORIDE-HEXAFLUOROPROPYLENE	-84
DIMETHYL SILICONE (D.C.)	-90.

→NO ANTI-RAD ADDITIVES IN D.C. FORMULATIONS←

*INCLUDES SPECIAL ANTI-RAD

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TABLE 6

RADIATION EFFECTS OF HIGH TEMPERATURE IRRADIATION

ELASTOMER	$\frac{\Delta \text{MODULUS}}{\Delta \text{DOSE}}$ 25°C	200°C
R.R. STOCK	0	5.0
2068	3.9	—
LS-53	0.48	14.1
916	5.05	14.4
2048	6.2	21.2
7-170	8.6	—
152	8.9	—
2071	9.0	34.1
80	9.8	60.1
675	12.2	26.5
S-2201	—	48.1

TESTED AT 25°C

TABLE 7

RR STOCK PROPERTIES 25°C IRRADIATION

DOSE MEGARADS	TENSILE PSI	ELONGATION %	MODULUS PSI
0	605	120	190
50	592	130	185
100	550	118	190
200	450	100	205
594	400	55	380

TESTED AT 25°C

TABLE 8

RR STOCK PROPERTIES 200°C IRRADIATION

DOSE	TENSILE PSI	ELONGATION %	MODULUS PSI
0	736	241	144
5	749	207	184
10	720	197	192
19.2	684	137	262
42.6	547	57	480

TESTED AT 25°C

RADIATION RESISTANT SILICONES

By

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Silicones as a class cover a wide range of polymer compositions within which are newer materials of outstanding radiation resistance. These take the form of fluids, greases, resins and rubbers. Inherently, silicones are thermally stable and this is reflected in excellent performance for some polymers in the combined environments of radiation and high temperature. Comments in the literature which classify silicones as poor in radiation resistance are based on observations covering only a limited area of the total field with concentration on a few of the less stable polymers.

Inherent in each silicone polymer is a dependence upon the stability and flexibility of the siloxane backbone. The organic groups substituted on such a chain modify this stability and flexibility. It is possible, for example, to use sufficiently large alkyl groups as to lose all of the inherent siloxane stability and revert to that of a simple branched hydrocarbon. Practically, one retains most of this stability if only methyl and phenyl groups are used. The greatest flexibility is retained if one uses only methyl groups, but such polymers are poor in radiation resistance. As has long been known, the incorporation of phenyl substituents raises radiation stability. In hydrocarbon systems this usually ends in the preparation of high melting aromatic solids. The chief advantage of the silicone family with regard to radiation resistance is the ability to introduce large amounts of phenyl substitution without losing the flexibility inherent in the siloxane backbone. One may prepare fluids, greases, flexible resins and rubbers free of the aromatic crystalline character of organic compounds, but with the inherent radiation resistance of high phenyl content polymers.

The inherent thermal stability of these high phenyl radiation resistant silicones is important. It is becoming increasingly apparent that materials will be needed to withstand the combined effects of radiation and high temperatures. Our preliminary studies in this area of simultaneous exposure are promising.

FLUIDS

The radiation resistance of fluids was studied by measuring quantitatively the gases evolved upon irradiation. This yields sharper distinctions and is less time consuming than carrying the exposure to ultimate gelation. The amount of gas is proportional to the number of bonds broken and so the G_{gas} values, moles of gas per 100 electron volts, are related to the number of degradative events. Data for a series of phenyl and methyl substituted siloxanes are listed in Table I.

The gas obtained had a condensable fraction which remained relatively constant within the series. This and the gas composition indicated that such gases were derived from the phenyl groups whose concentration was held relatively constant within the series. The non-condensable gases varied directly with the concentration of methyl groups. The parameter ϵ methyl listed in the last column of Table I is a number defined by Burton[1] as,

$$\epsilon \text{ methyl} = \frac{\Sigma \text{all electrons in methyl groups}}{\Sigma \text{all electrons}}$$

In these sums all electrons are counted, not just those in valence positions.

Similar gas data for more standard materials are listed in Table 2.

The correlation between $G_{non\text{-}condensable}$ and ϵ methyl from both tables is quite good. This may best be noted in Figure 1 where log $G_{non\text{-}condensable}$ is plotted against ϵ methyl.

The range of stability exhibited by these fluids is large. The least stable all methyl fluid produces more than 100 times the amount of gas produced by the most stable high phenyl fluid shown. One might judge silicones as poor in radiation resistance if one had experience only with all methyl fluids. The high phenyl fluids, however, are comparable to organic polymers of high aromatic content.

The one point which falls below the curve is for a material which is a crystalline solid. All the others are fluids. One might guess that the mechanism of radiation damage in a solid is different from that in a liquid. This is confirmed by dissolving the solid in the next higher liquid member. Data for such a solution fall on the straight line.

GREASES

The radiation stability of these fluids was also indicated by the behavior of greases formulated from them. Two fluids from Figure 1 were compounded into greases using copper phthalocyanine as a thickening agent. These greases were exposed in covered tin plated steel cans to gamma radiation from Co^{60}. As a measure of radiation damage one obtained data on the changes in micro penetrometer at various dose levels as in Figure 2.

Damage first is noted by a thinning (rising penetrometer) followed by a pronounced hardening (falling penetrometer). This process is much faster in the grease formulated from the fluid with the higher electron fraction for methyl - the less radiation stable fluid produces a less stable grease.

In addition to the effect of the stability of the fluid one must also consider the influence of the nature of the thickening agent. A series of greases were prepared with 710 fluid, ϵ methyl = .195 and were radiated in tin plated steel cans by gamma rays from Co^{60}. The damage as noted by changes in pentrometer with varying doses may be noted in Figure 3.

The filler has a very marked effect on grease stability and of those tested aryl urea and copper phthalocyanine are outstanding.

One must also consider the initial molecular weight of the fluid since radiation serves to cross link high molecular weight fluids to a gel point sooner than low molecular weight liquids. This effect may be noted in Figure 4.

Despite the higher electron fraction for methyl (0.245) the lower molecular weight fluid (750) is damaged no more rapidly than the liquid of lower ϵ methyl (0.195) but higher molecular weight (1250). In essence the two opposing influences have effectively canceled each other.

In summary, for greases and fluids the electron fraction for methyl in a silicone material predicts the amount of gas evolved from a fluid and the relative rate of hardening of a grease when exposed to gamma radiation from Co^{60}. This is exclusive of the factors of filler and molecular weight.

RESINS

Silicone resins are inherently radiation stable because of their high phenyl content and lower sensitivity to additional cross linking. The data of Table 3 show that laminates prepared from typical silicone resins do lose some strength after an exposure of 10^9 reps (0.83×10^{11} ergs/gm carbon) of gamma radiation from Co^{60}.

Actually the strength at a high temperature is increased by the additional cross linking from radiation.

Dielectric properties are also slightly lowered by the same 10^9 rep exposure as may be noted in Table 4.

Electrically or structurally silicone resins would be quite acceptable after this high dose of radiation.

RUBBERS

Rubbers are among the most sensitive engineering materials since they are of high molecular weight and thereby are affected by slight changes in cross linking level. Elongation is markedly affected by radiation and one might rate a series of rubbers as to their radiation resistance by the dose required to lower the elongation to 50%. Figure 5 shows such data for a series of silicone rubbers of varying ϵ aliphatic. These were silica filled rubbers cured by conventional peroxides. High phenyl content, reflected by low $\epsilon_{aliphatic}$, produces rubbers which require more than five times as much radiation as is needed to produce equivalent damage in conventional dimethylpolysiloxanes, $\epsilon_{aliphatic} = 0.45$. Subsequently it will be shown that the most resistant rubber of Figure 5 is comparable to the best combination of anti rad and natural rubber in room temperature radiation exposure and is outstanding in a combined radiation and high temperature environment (200°C).

To show the unusual properties of the radiation resistant stock one might compare the retention of initial elongation with the spectrum of properties attainable with commercial silicone rubber stocks as in Figure 6.

Natural rubber devoid of a special anti-rad is also shown in this figure to indicate that many silicone rubbers are comparable. At one time we had hopes that the incorporation of anti rads might improve silicone rubbers as they have natural rubber. A survey of more than 90 compounds used by others as anti rads has failed to yield a single compound which will improve commercial silicone rubbers in their resistance to radiation at room temperature. Some measurements give promise that anti rads may be found which will improve the radiation resistance of the high phenyl stock significantly.

The behavior of modulus (Modulus = $\frac{\text{Tension (psi)}}{\alpha - 1/\alpha^2}$ at α = 1.5) for standard stocks and the radiation resistant rubber is shown in Figure 7. Again it is clear from the unchanged modulus that the radiation resistant stock is scarcely affected by 100 x 10^6 rads (10^{10} ergs/gm carbon).

A comparison with other elastomers is possible from data of J. W. Born[2] and Harrington[3]. In Table 5 the retention of elongation after 90 megarads is shown for various elastomers listed in order of decreasing stability.

The radiation resistant stock compares favorably with the combination of natural rubber and best anti rad. It may be possible to improve the resistance of the high phenyl stock by the use of special anti rads.

The real test of rubber-like materials is found in the combined environment of radiation and high temperatures. Our own experiences show that the effects of the two environments are not simply additive. The combined environment is invariably more severe than one would expect. Figure 8 shows data for the change in elongation with dose of gamma rays from Co^{60} in a temperature environment of 200°C. Such a temperature, while quite damaging to organic rubbers, only slowly affects most silicone rubbers.

The simultaneous environment is quite damaging for the standard silicone rubber formulations, but the radiation resistant stock is outstanding in its performance.

Another way of showing the effects of radiation alone and of the combined environments is from measurements of modulus which yield slope values ΔModulus/ΔDose from the change in modulus with dose. The data for standard stocks and the radiation resistant rubber are summarized for room temperature and 200°C radiation exposures in Table 6.

Since modulus values are proportional to the number of cross links in a rubber, these slope figures are measures of the relative ease of forming cross links by radiation.

While comparisons have been made of the properties of the radiation resistant rubber with other rubbers under a variety of conditions, no actual properties have been listed. Since these values are often desired for engineering design, such data are summarized for the room temperature radiation in Table 7.

While the initial properties of the rubber are not all that one might desire, it should be remembered that this is a new composition with a limited compounding history. With added experience with this new material one may expect reasonable improvements in physical properties.

Similar data for the combined environment are summarized in Table 8.

The initial properties of this particular formulation are considerably better than those of the sample in Table 7.

Some preliminary experiments with this stock at high temperatures indicate that its performance in the combined environments may be improved by the use of anti rads.

In summary, silicones as a class cover a wide range of polymer compositions among which are materials of outstanding radiation resistance. Perhaps, more important, some of these polymers give promise of excellent performance in combined environments of radiation and high temperatures.

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FIGURE I

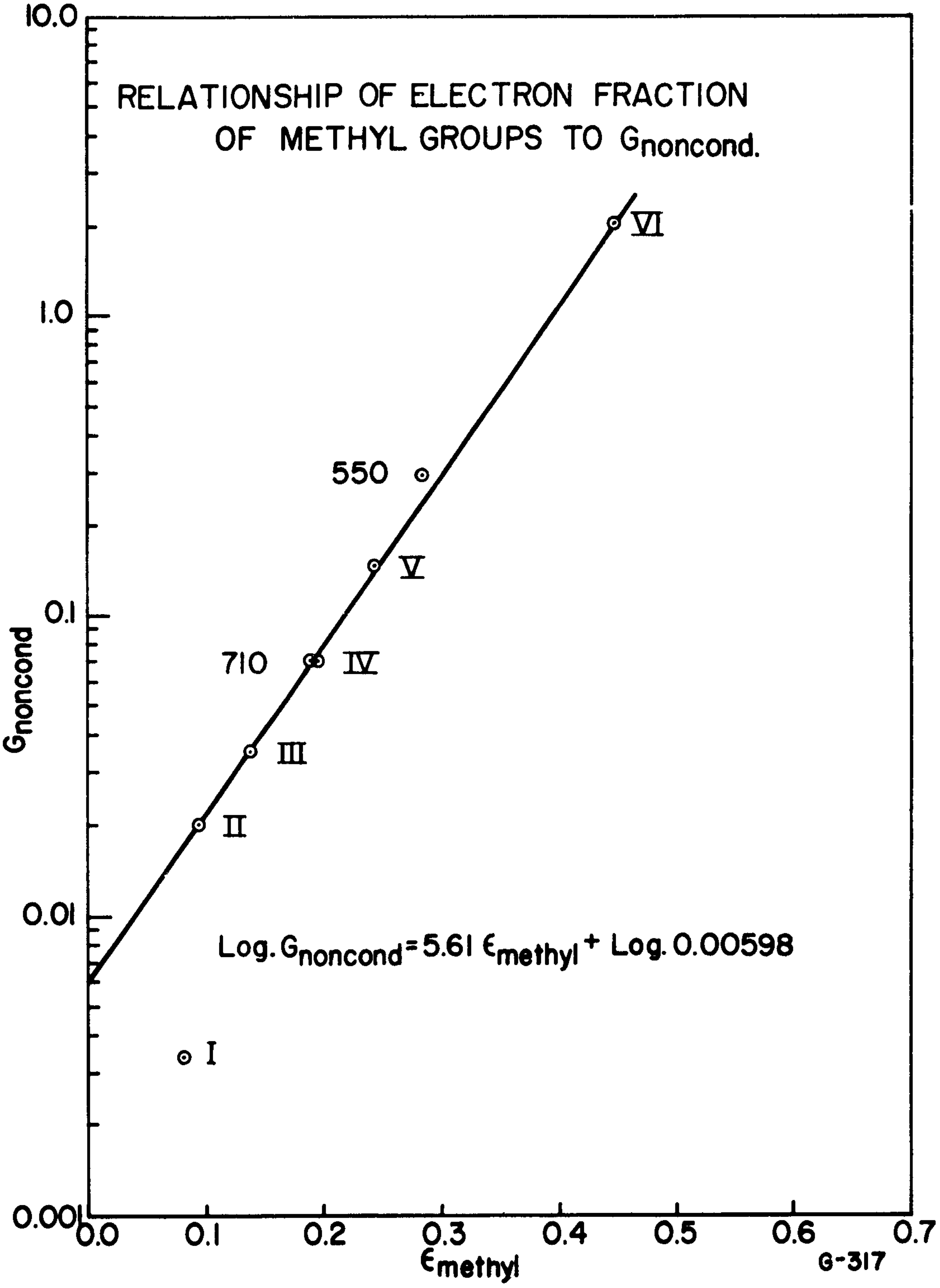

RELATIONSHIP OF ELECTRON FRACTION OF METHYL GROUPS TO $G_{noncond.}$
10.0
1.0
0.1
0.01
0.001
$G_{noncond}$
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
ϵ_{methyl}
VI
550
V
710
IV
III
II
I
$\text{Log.} G_{noncond} = 5.61\, \epsilon_{methyl} + \text{Log.}\, 0.00598$
G-317

FIGURE 2

EFFECT OF ELECTRON FRACTION ON
GREASE STABILITY TO RADIATION

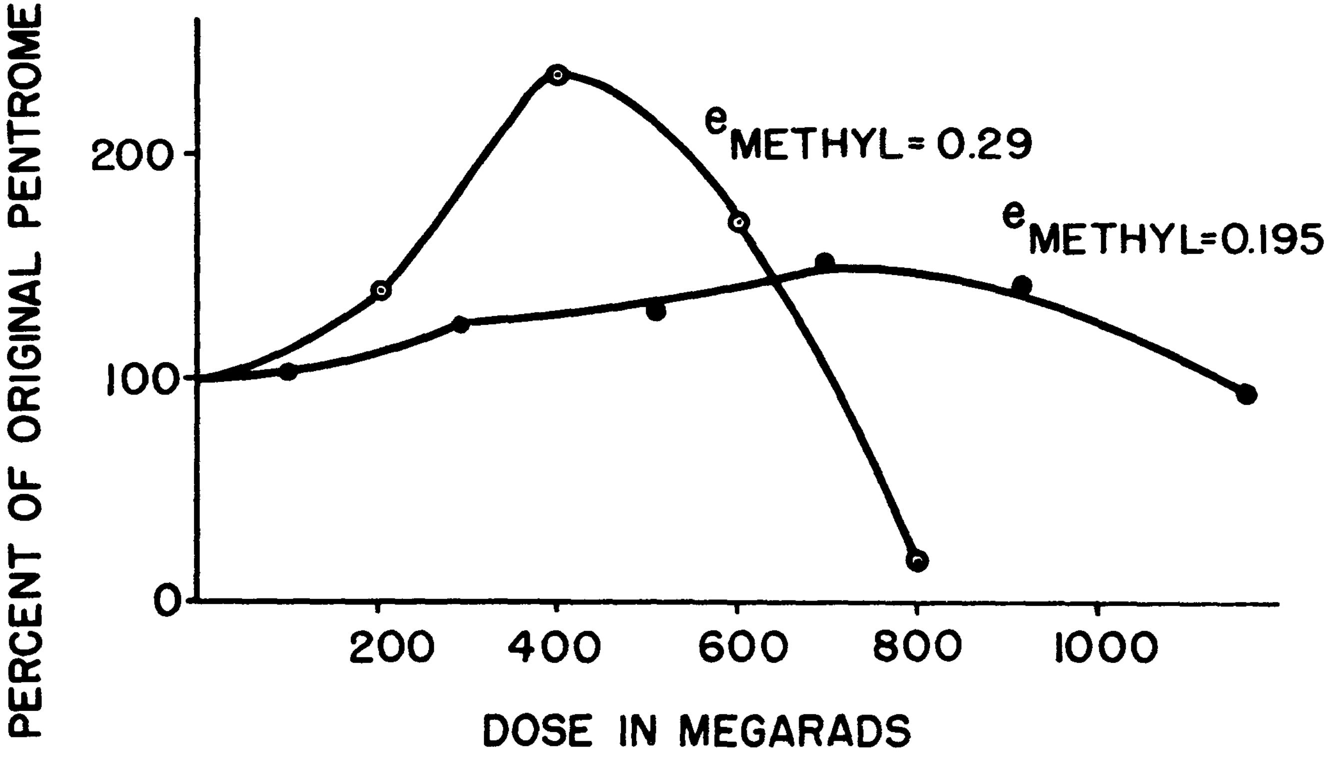
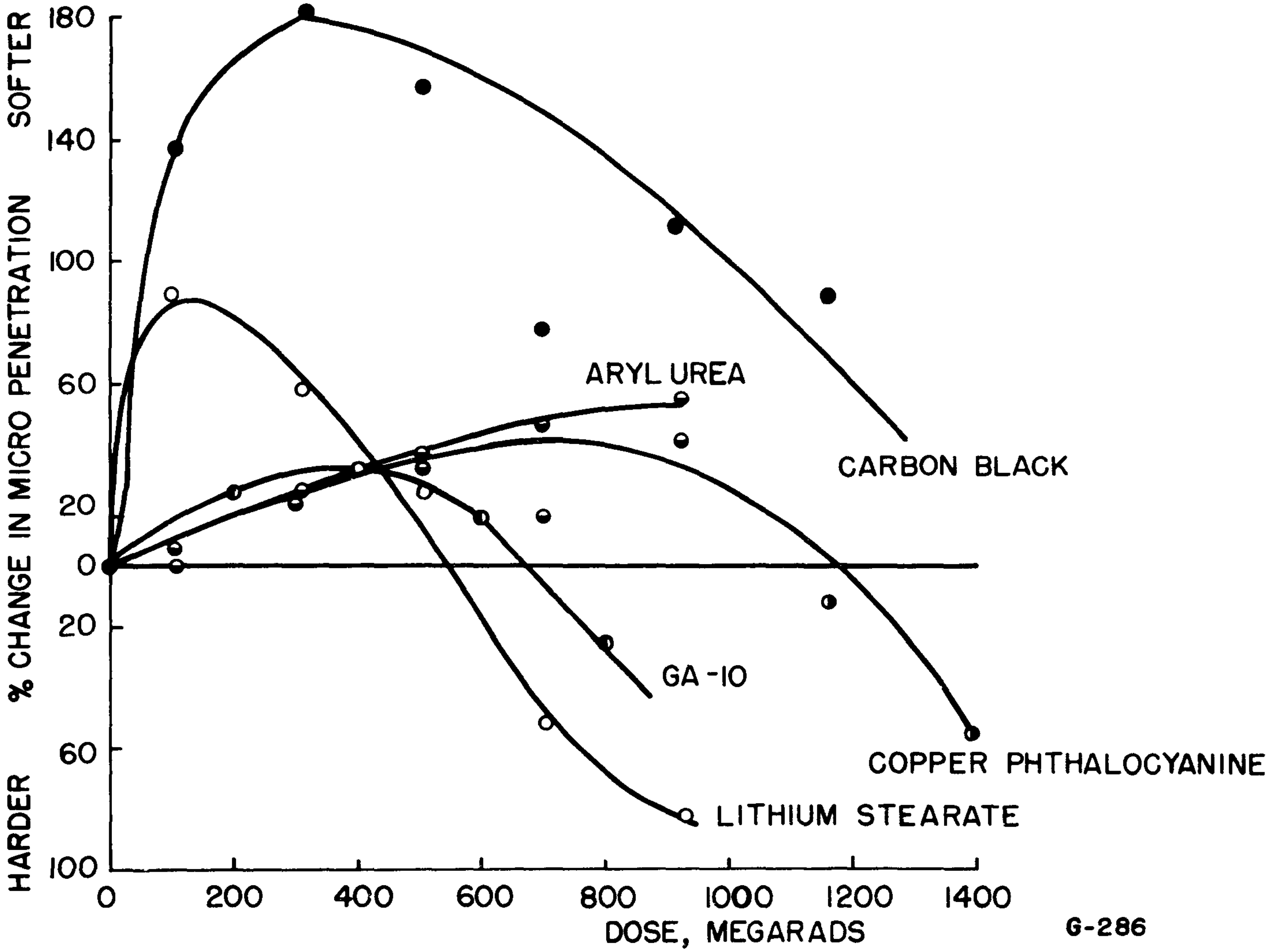


FIGURE 3

FILLER EFFECT ON RADIATION RESISTANCE



G-286

FIGURE 4

EFFECT OF MOLECULAR WEIGHT AND ELECTRON FRACTION ON GREASE STABILITY TO RADIATION

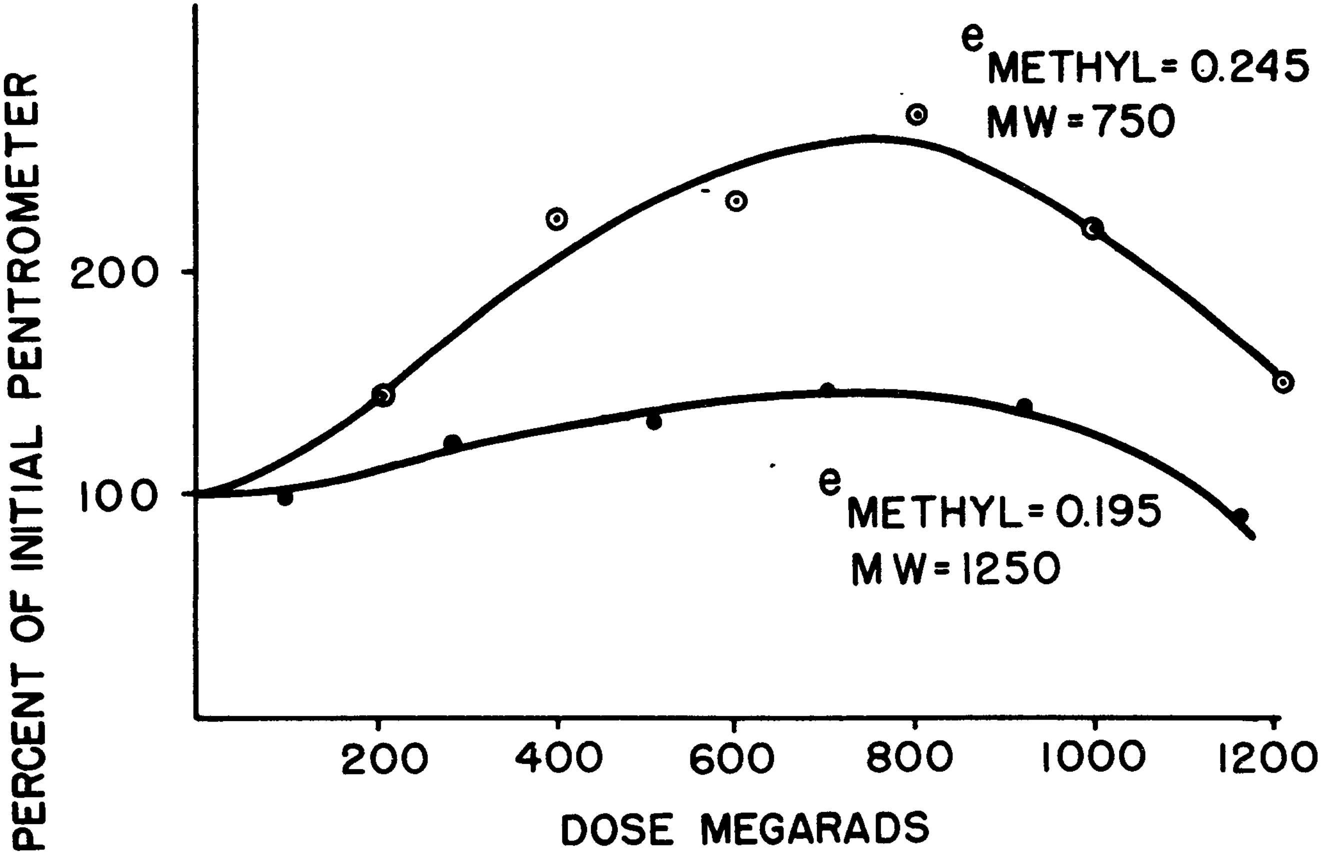


FIGURE 5

EFFECT OF ELECTRON FRACTION ON RUBBER STABILITY TO RADIATION

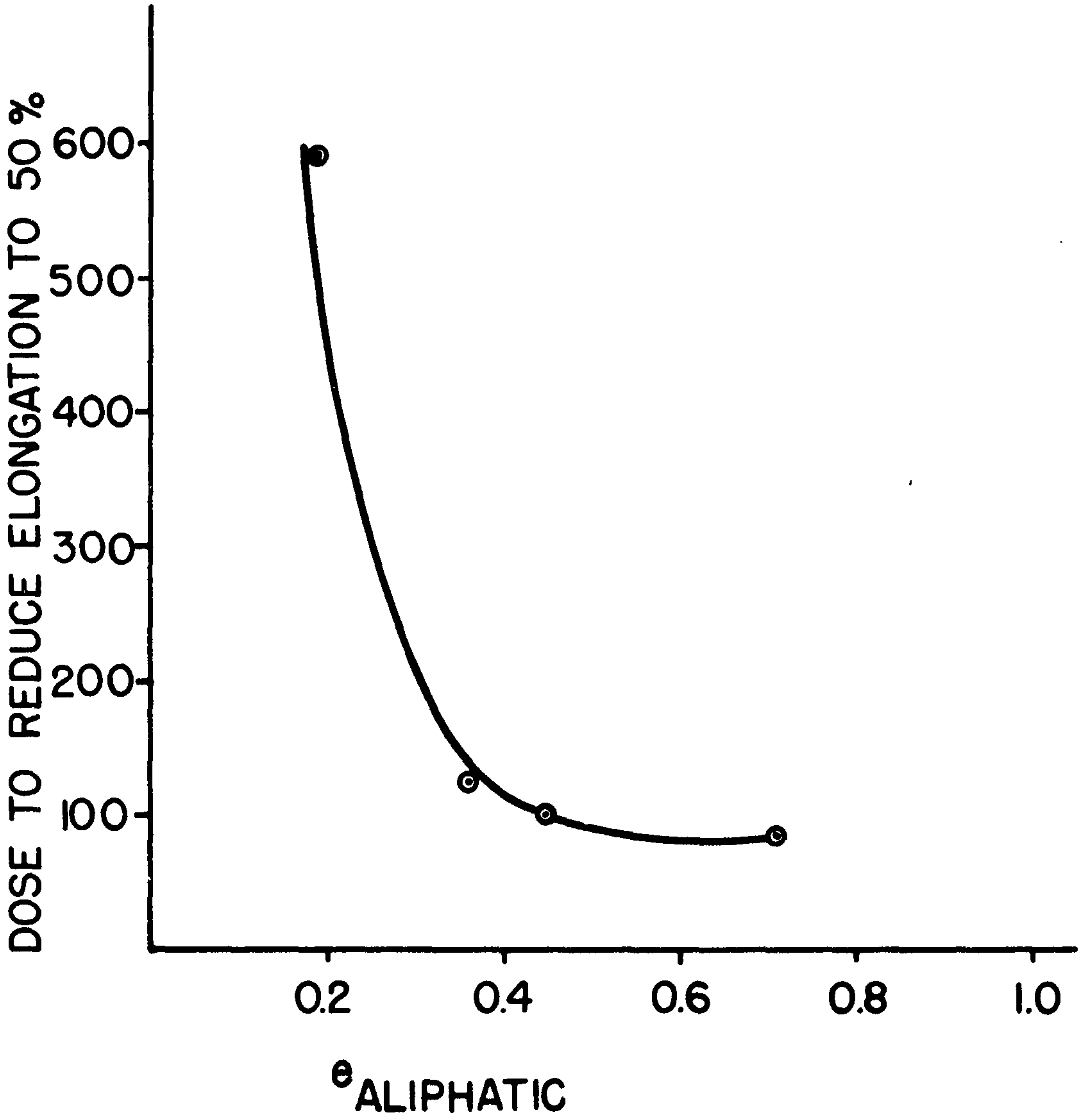
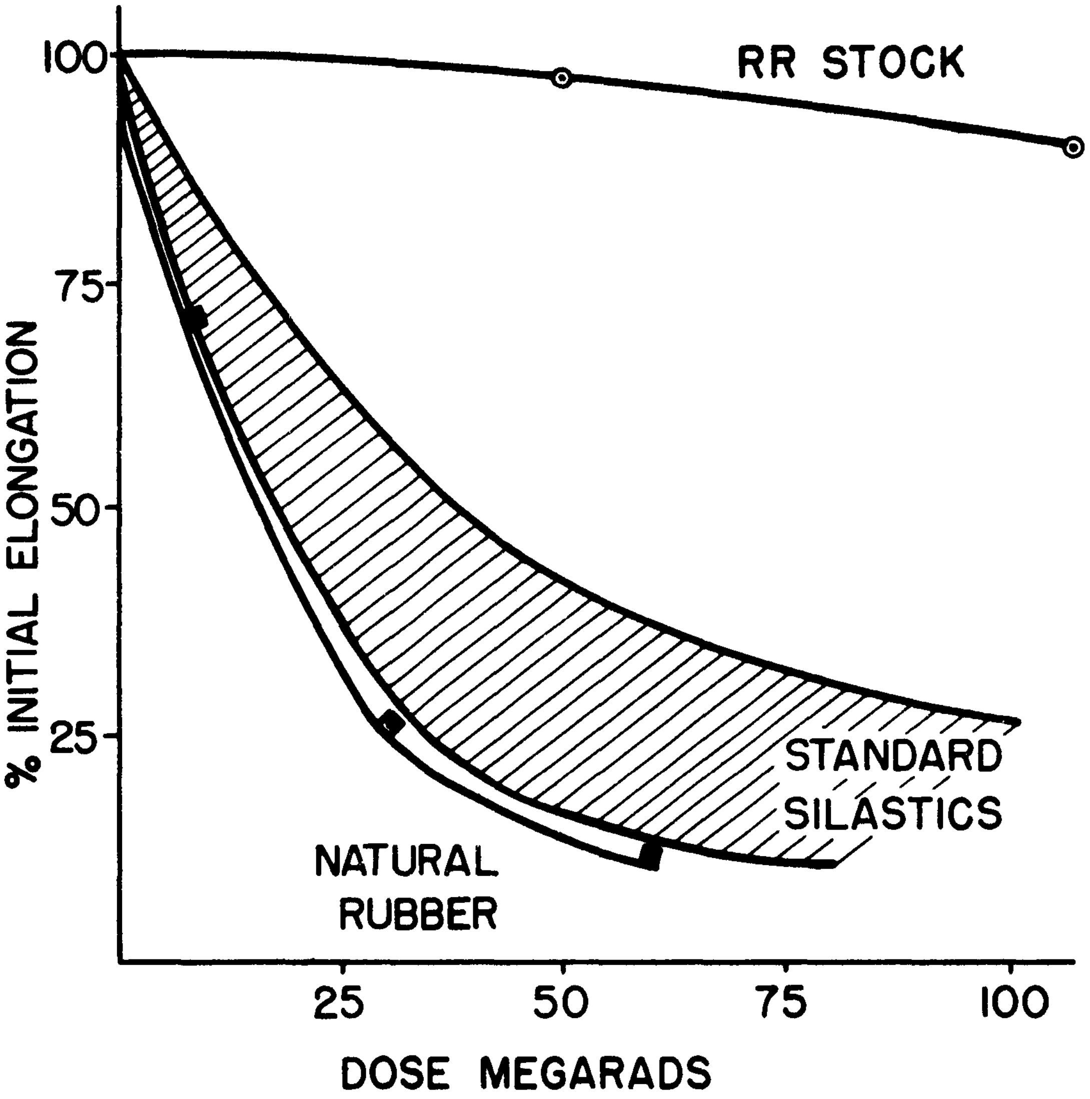


FIGURE 6

RUBBER ELONGATION VS RADIATION DOSE



$H = 0.49 \pm 0.02$ ev/atom. Both of these values of the activation energy make τ_0 of the order of 10^{-13} sec, which is about the period of atomic thermal motion.

If the polystyrene specimen is now irradiated at about 300°K, with 7×10^7 rads of 5-Mev electrons, it appears that the peak believed to exist below 90°K has shifted to lie now at about 104 ± 2°K, while the old peak near 120°K has not shifted, and the peak near 265°K has all but disappeared (see Fig. 1). There still appears to be an indication of a peak beyond 310°K.

Note that the irradiation at low temperature with 5×10^7 rads of 5-Mev electrons produced results much more similar to those of the unirradiated case.

Turning now to the high-density polyethylene data shown in Figs. 4 and 5, it is at once evident that the modulus defect that results as the large energy-loss peak is traversed does not satisfy the requirement that it be small compared with unity, and it most certainly does not satisfy relation (5).

By varying the frequency, one can produce a shift in the peak at 185°K, measured at 7000 cps, that corresponds to an activation energy of 0.30 ± 0.03 ev/atom; and τ_0 once again is of the order of 10^{-13} sec. According to current literature,[7,8] this peak should correspond to the so-called gamma peak, with the beta peak starting to form beyond 300°K.

Irradiation at 300°K with 7×10^7 rads of 5-Mev electrons produced a decrease in Young's modulus at low temperatures, but a slight increase at room temperature. Irradiation at 100°K with a small dose (2×10^7 rads) produced only a very slight decrease at low temperature and about the same increase at room temperature as was found with the 300°K irradiation.

CONCLUSIONS

Considering the dispersion data as a whole, it would seem that the irradiation temperature definitely influences the details of the radiation-damage mechanism. One can also conclude that low-temperature irradiation generally retards the magnitude of the radiation-induced changes.

The polyethylene data are focused on the behavior of the gamma peak; this peak is believed[9] to be caused by methyl-group twisting motions responding to a stress applied to the whole chain. Since these motions would probably be strongly restricted in the close-packed regions of the polyethylene crystallites, it is thought that the barrier region with $H = 0.30$ ev is populated only by relatively free segments of the polymer chain between crystallites. Upon irradiation, the cross-linking of adjacent chains can produce enough distortion around the cross-linked points to disturb the close packing in the crystallites, thereby increasing the amount of "free" lengths of chain and hence lowering the modulus at nitrogen temperatures, as well as the room-temperature density, by a method not connected with relaxation. At the same time, this mechanism qualitatively accounts for the rise in modulus at room temperatures, because the structure has more cross-links to stiffen the structure at the high temperatures. The low-temperature data might indicate that the amount of distortion caused by cross-linking within the crystallites

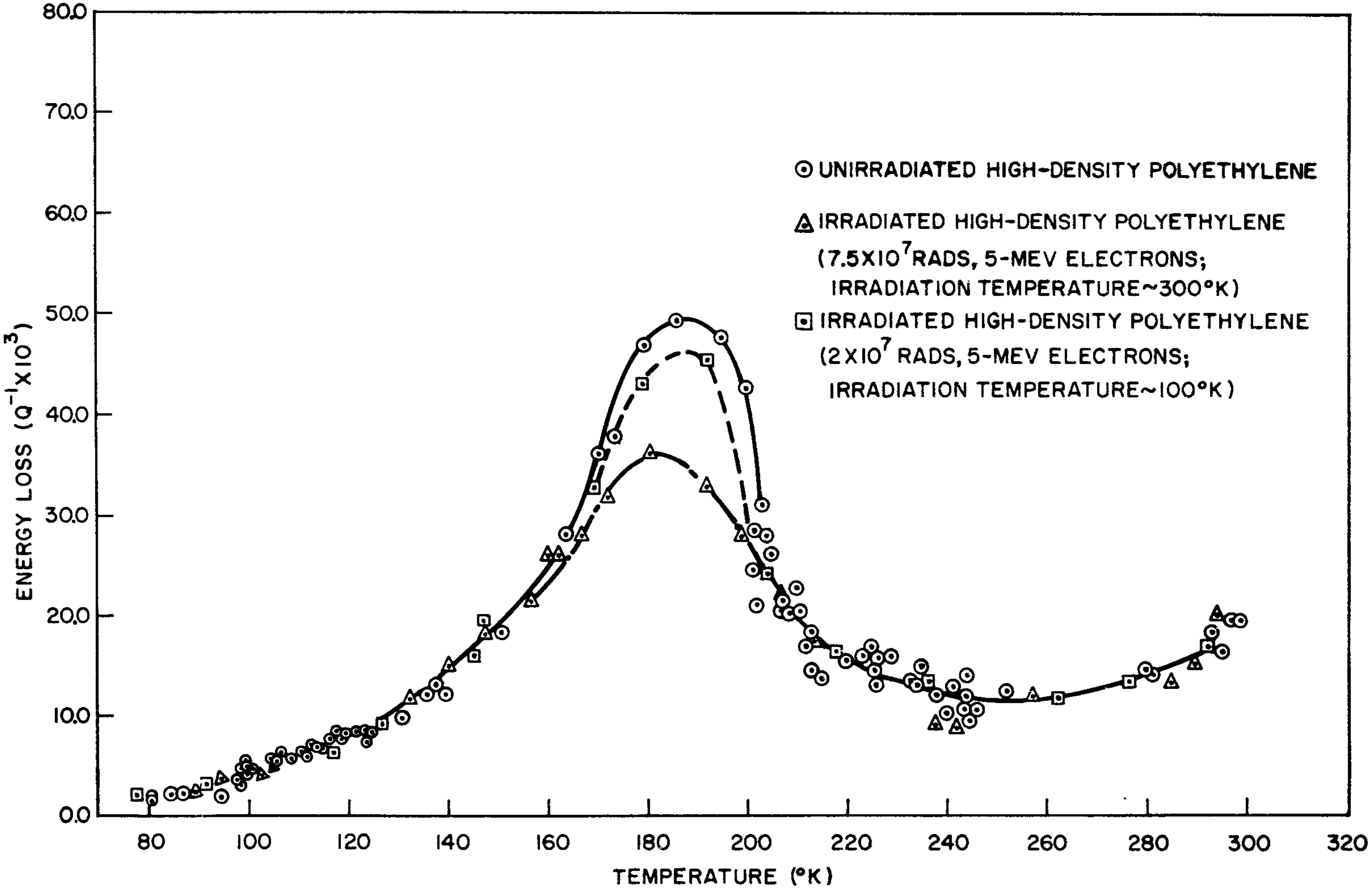


Fig. 4--Energy loss, Q^{-1}, on unirradiated and irradiated polyethylene as a function of temperature

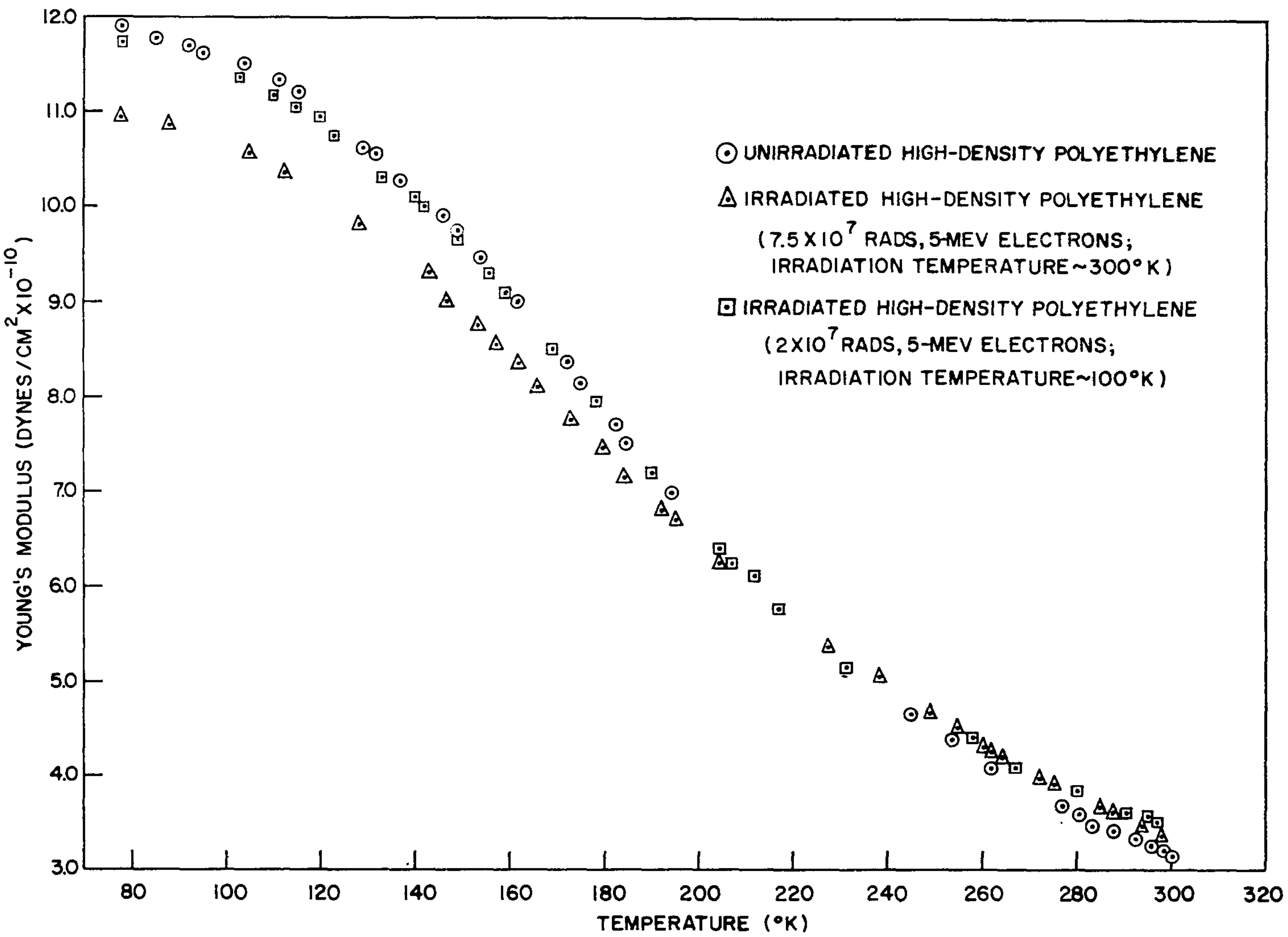


Fig. 5--Young's modulus, M, of unirradiated and irradiated polyethylene as a function of temperature

is less when the chains are cross-linked at low temperature; this speculation is also consistent with the room-temperature density measurements made on the low-temperature irradiated specimens.

The polystyrene data show that in the early stages of damage at least three significant molecular changes result: (1) A low-energy barrier corresponding to the peak below 90°K is shifted to 104°K. Energetically, this corresponds to a change in barrier height of perhaps from 0.13 to 0.18 ev, assuming that $\tau_0 \approx 10^{-13}$ sec for all the low-temperature peaks. (2) The barrier at 120°K (0.20 ev) remains unchanged, while the relaxation strength, or number of configurations at that barrier height, is perhaps increased. (3) The barrier at 260° to 270°K probably remains unchanged in height, but the number of configurations at that height is definitely reduced. It also must be born in mind that polystyrene structurally resembles glass more closely than does a partially crystalline polymer like polyethylene. It is interesting, therefore, to compare the "deformation losses" discussed by Volger[10] in glass with the polystyrene low-temperature peaks. The deformation losses are characterized by quite low (0.05- to 0.2-ev) activation energies, as well as by having $\tau_0 = 10^{-13}$ sec. It has been speculated that they are caused by slight reorientations of certain metallic ions under the influence of lattice deformation. The low energies are believed to arise from the relatively open random skeletal structure possessed by glass. Perhaps in similar fashion the low-temperature peaks in polystyrene can be accounted for by reorientation of molecular groups (e.g., of benzene rings). Radiation-induced defects (e.g., active hydrogen) could create or induce such additional bonding as would hinder the easy motion of such a group, thereby raising its energy barrier.

One of the most difficult problems in obtaining information from low-temperature measurements is to decide whether the major effect of the low temperature is to slow the diffusion of the defect, or to slow its reaction rate, or both; in any case, one must first find a good measure of the irradiation effect.

Since the polystyrene results indicate that one is dealing here with a fairly good linear relaxation mechanism and that this mechanism is certainly being influenced by irradiation and irradiation temperature, it is felt that more detailed low-temperature investigations of this polymer should be fruitful in uncovering the atomic details of the damage event. Hand in hand with such a mechanical investigation should be an investigation of the existence and actions of free hydrogen and other free radicals by electron spin resonance methods; this type of investigation is currently under way at General Atomic.

ACKNOWLEDGMENTS

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RADIATION EFFECTS ON ORGANO-SILICONS

by

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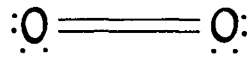
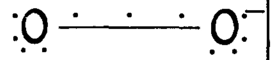
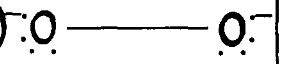
The paper discusses the heat, radiation, and oxidative stability of silicon materials. A stepwise energy reduction mechanism for oxygen is proposed that allows molecular oxygen to be changed to atomic oxygen in 30-40 Kcal increments rather than in steps of 96 Kcal. The mechanism helps explain the relative ease of oxidation of silicon materials and the products formed at relatively low temperatures.

In this discussion an attempt will be made to explain the behavior of a polymethylsiloxane material in an environment comparable to that anticipated for a nuclear-powered aircraft. Thus, by necessity, the organo-silicon material will have to be evaluated in the presence of air (oxygen), at elevated temperatures, and in a nuclear radiation field.

Atkins et al.[1] heated a polymethylsiloxane in air and studied the rates at which formic acid and formaldehyde were produced at 175°, 200° and 225°C. They found the polymethylsiloxane to be comparatively stable at 175°C; the rate of breakdown at 225°C was twice that at 200°C, at which temperature the breakdown was slow. Without any oxygen in the system, the polymethylsiloxane materials were reported to be stable to approximately 400°C.

Pauling[3] describes the different excited states of the oxygen molecule. The excited states are summarized in Table I. It can be observed from Table I that there is very little difference in the bond strengths of molecular oxygen in the double bond form and the single bond two-three-electron excited form (A and B). With the breaking of one of the three-electron bonds (B to C), the bond strength decreases by more than one-third. The next excited state (D) reduces the bond energy to a value less than 40 percent of the original. The bond distances of the different excited states substantiate the differences in their bond strengths. The final product, as shown in (E), is the extremely reactive atomic oxygen sometimes referred to as nascent or free radical oxygen.

BOND STRENGTHS AND DISTANCES FOR O_2

STRUCTURE	NAME	BOND STRENGTH (Kcal / Mole)	MOLECULAR DISTANCE (A°)
(A) 	MOLECULAR	96	1.10
(B) 	SINGLE BOND PLUS 2 THREE-ELECTRON BONDS	96	1.10
(C) 	SUPEROXIDE	57.2 TO 74	1.24
(D) 	PEROXIDE	35	1.32
(E) 	ATOMIC		

With the aid of the Arrhenius equation, $K = S\exp(-\Delta H/RT)$, an estimation of the temperature required to break a bond can be obtained (k is the log of the dissociation constant, S is a constant 10^{13}, ΔH is the heat of activation of the bond, R is the gas constant 1.987, T is the temperature in degrees Kelvin.). An application of a first order reaction using this equation is shown in Figure 1. Here the log of the dissociation constant is plotted against the heat of activation. The temperature lines give an approximation of the rates of reaction at any value of the heat activation. Assuming the pyrolytic breakdown of the polymethylsiloxane to be a first-order reaction, and plotting the temperature lines for 175°, 200° and 225°C, as used by Atkins et al., it is possible to observe the differences in decomposition half-lives. At 175°C the half-life was found to be 33 days (790 hours), at 200°C, it was 70 hours; and at 225°C, it was six hours. These results indicate that the oxidative change takes place at approximately the 40 Kcal per mole energy level. This is considerably less than the 400°C temperatures or 60 Kcal per mole required for pyrolysis of the polymethylsiloxane in the absence of air.

In general, oxygen can react with the polymethylsiloxanes in one of two ways; as a radical scavenger; or, as a free radical, both in the molecular or atomic form. In Table II an attempt has been made to illustrate the radical scavenger type of reactions. These reactions require the (Si-C) or the (C-H) bond to be broken before the oxygen can link the two free radical fragments together. This can hardly be the dominant mechanism, as the temperatures, in most cases, are not high enough to result in an appreciable bond separation.

Table III illustrates oxygen as a free radical. In these reactions the oxygen, as a free radical in a higher energy state, can remove a hydrogen from a methyl group, forming the hydroperoxide radical and a methylene radical attached to the polymer. The hydrogen is removed from methyl groups until the oxygen is reduced to water. Formulas 1 through 4 show that each superoxide form of molecular oxygen is potentially capable of forming four methylene radicals on the polymethylsiloxane polymer. The methylene radical previously formed can then react with the molecular oxygen to form a peroxide-free radical. Because of the electronegativity of the two oxygens attached to the carbon (methylene group), the electron density between the silicon and the carbon is shifted away from the silicon atom, causing the (Si-C) bond to be weakened. The bond strength of the (Si-C) bond decreases from 68 Kcal per mole to a value of approximately 40 Kcal per mole. This corresponds to a temperature of approximately 200°C. When the bond breaks, formic acid and a silicon free radical attached to the polymer are formed.

EFFECT OF LOG K ON HEAT OF ACTIVATION

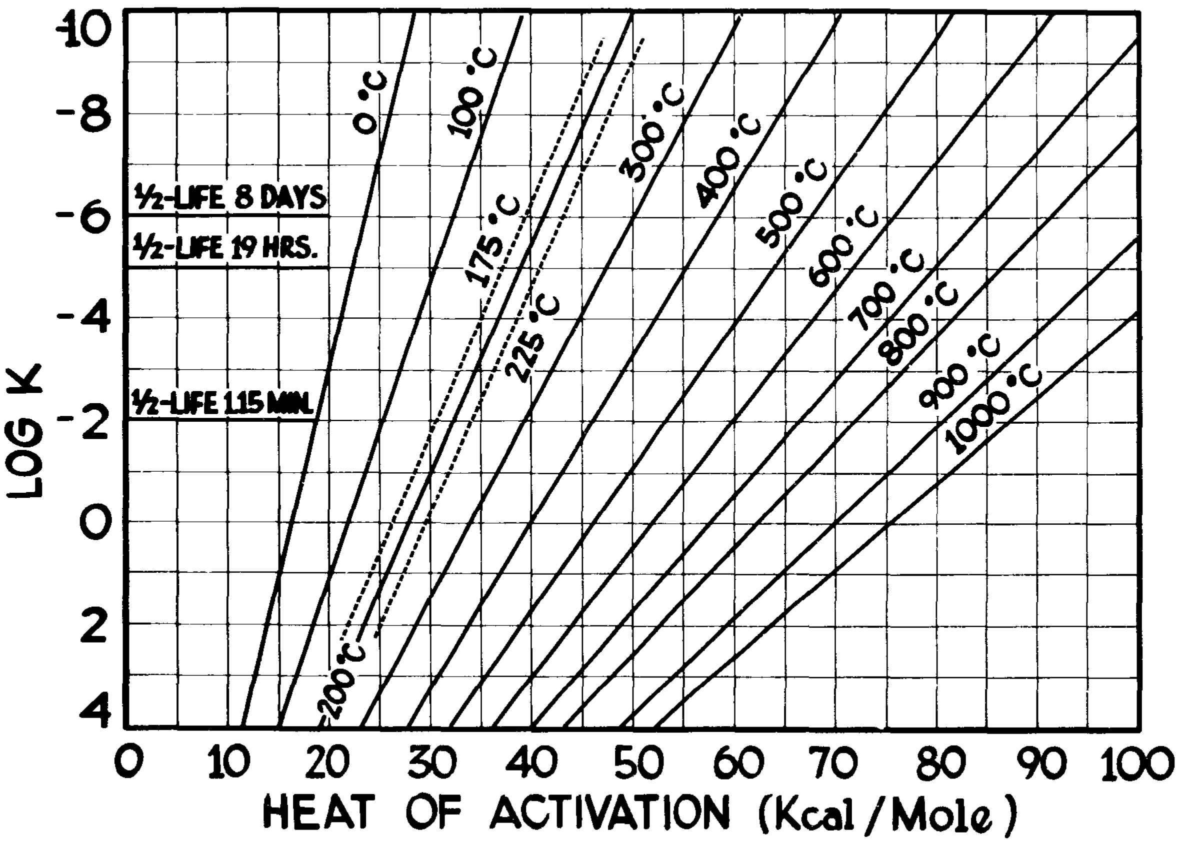


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FIGURE 1

FREE RADICAL SCAVENGER REACTIONS FOR O_2

1. $CH_3Si(OR)_2CH_3 \longrightarrow CH_3(OR)_2Si^* + CH_3^*$

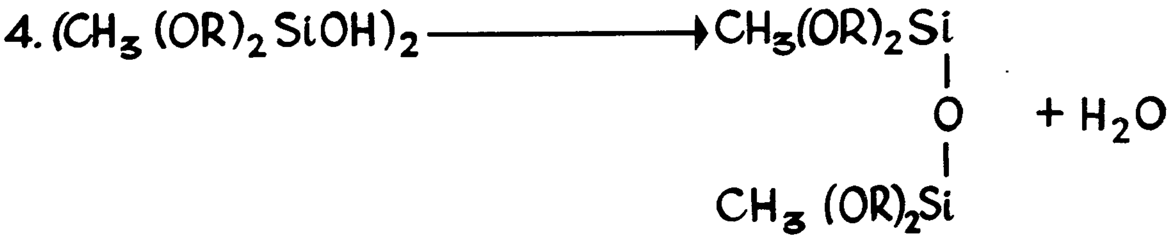
   68 Kcal (Si–C), FREE RADICAL

2. $CH_3(OR)_2Si^* + CH_3^* \xrightarrow{\text{OXYGEN}} CH_3(OR)_2Si\,O{-}O{-}CH_3$

   PEROXIDE LINKAGE, 35 Kcal TO BREAK BOND.

3. $CH_3(OR)_2Si{-}O{-}OCH_3 \longrightarrow CH_3(OR)_2SiOH + CH_2O$

   FORMALDEHYDE



4. $(CH_3(OR)_2SiOH)_2 \longrightarrow CH_3(OR)_2Si{-}O{-}Si(OR)_2CH_3 + H_2O$

   CROSS LINKING

TAB. II

FREE RADICAL REACTIONS FOR O_2

$$1.\ CH_3(OR)_2SiCH_3 \xrightarrow[\text{OXYGEN}]{\text{SUPEROXIDE}} CH_3(OR)_2SiCH_2^* + \underset{\text{HYDROPEROXIDE}}{HO_2}$$

$$2.\ CH_3(OR)_2SiCH_3 \xrightarrow{HO_2} CH_3(OR)_2SiCH_2^* + \underset{\text{HYDROGEN PEROXIDE}}{H_2O_2}$$

$$3.\ CH_3(OR)_2SiCH_3 \xrightarrow{H_2O_2} CH_3(OR)_2SiCH_2^* + \underset{\text{HYDROXY RADICAL}}{OH} + H_2O$$

$$4.\ CH_3(OR)_2SiCH_3 \xrightarrow{OH} CH_3(OR)_2SiCH_2^* + H_2O$$

$$5.\ CH_3(OR)_2SiCH_2 \xrightarrow[\text{OXYGEN}]{\text{MOLECULAR}} CH_3(OR)SiCH_2OO^*$$

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TAB. III

FREE RADICAL REACTIONS FOR O_2 (Cont'd)

6. $CH_3(OR)_2SiCH_2OO^* \xrightarrow{\text{REARRANGEMENT}} CH_3(OR)_2Si^* \underset{\text{FORMIC ACID}}{HCOOH}$

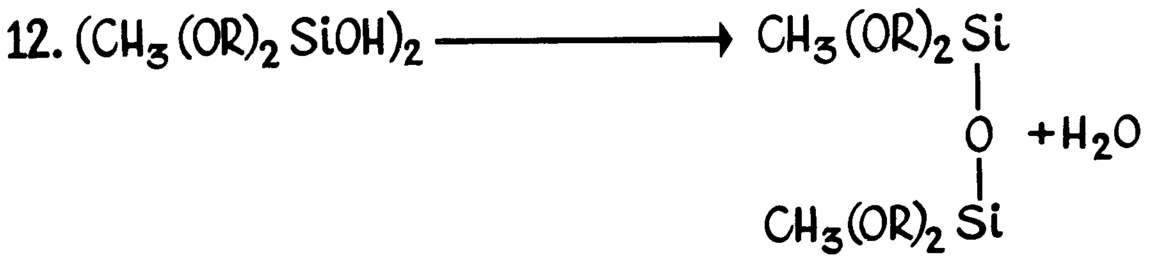
7. $CH_3(OR)_2Si^* \xrightarrow[\text{OXYGEN}]{\text{MOLECULAR}} CH_3(OR)_2SiOO^*$

8. $CH_3(OR)_2SiOO^* \xrightarrow{CH_3(OR)_2SiCH_3} CH_3(OR)_2SiOOH + CH_3(OR)_2SiCH_2^*$

9. $CH_3(OR)_2SiOOH \xrightarrow[\text{PEROXIDE BOND}]{\text{35 Kcal/mole}} CH_3(OR)_2SiO^* + {}^*OH$

10. $CH_3(OR)_2SiO^* \xrightarrow{CH_3(OR)_2SiCH_3} CH_3(OR)SiOH + CH_3(OR)_2SiCH_2^*$

11. $CH_3(OR)_2SiCH_3 \xrightarrow{{}^*OH} CH_3(OR)_2SiCH_2^* + H_2O$

12.


$$(CH_3(OR)_2SiOH)_2 \longrightarrow \begin{array}{c} CH_3(OR)_2Si \\ | \\ O \\ | \\ CH_3(OR)_2Si \end{array} + H_2O$$

Another molecule of oxygen then becomes attached to the silicon free radical, forming the silicon peroxide free radical. The latter free radical can then remove a hydrogen from a methyl group, to form the silicon hydrogen peroxide and another methylene free radical on the polymer. The silicon peroxide breaks at the oxygen (peroxide) bond, forming the hydroxyl radical and the silicon-oxygen free radical. The energy necessary to break the peroxide oxygen is 34 Kcal per mole. The silicon-oxygen free radical can remove a hydrogen from a methyl group, thus forming a hydroxy group on the silicon and another methylene radical attached to the polymer. The hydroxyl radical can remove a hydrogen from a methyl group forming water and another methylene radical attached to the polymer. The silicon-hydroxyl groups can condense to form the silicon-oxygen-silicon crosslink and a molecule of water.

Therefore each methylene radical that is formed can react with molecular oxygen to produce three additional methylene radicals, one molecule of formic acid, one molecule of water and one hydroxyl group attached to the silicon or one-half of a (Si-O-Si) crosslink.

When a polymethylsiloxane material is irradiated, all of the chemical bonds are susceptible to being broken. The irradiation of the fluids in the absence of oxygen produces hydrogen, methane and methane polymers.[2,4] These tests have shown that the (Si-C) and (C-H) bonds are vulnerable.

With molecular oxygen in a radiation system, strong oxidizing reagents are formed. This can result from the reaction of oxygen combining with atomic hydrogen to form hydroperoxide (HO_2), from the breaking of the molecular oxygen ($O = O$) bond to form atomic oxygen and ozone. Since one of the products of oxidation is water, hydroxyl radicals can be expected. The hydrogen from the radiation breakdown of water can unite with oxygen to form additional hydroperoxide. The methylene radical (RCH_2*) which results from the break of the (C-H) bond, can be oxidized to form a peroxide radical. With temperatures below the thermal rupturing point of the (Si-C) bond (as shown in Table III), this radical can acquire a hydrogen from a methyl group, forming a methylene-hydrogen peroxide and another methylene radical. The rate at which the peroxide oxygen or the silicon-carbon bonds will break will be temperature-dependent if the polymethylsiloxane material follows the pattern observed for several different types of organic fluids.

The radical scavenger reactions as shown in Table II become more important in a radiation field because of the increase in the number of bond breaks. Since not all of the radiation-produced free radical fragments formed by the bond cleavage will return to their original bond site, or be scavengered by the oxygen, a number of methyl radicals will be oxidized to formaldehyde. This may be visualized as follows:

$$CH_3{*} + O_2 \longrightarrow CH_3OO{*}$$

$$CH_3OO{*} + RCH_3 \longrightarrow CH_3OOH + RCH_2{*}$$

$$CH_3OOH \longrightarrow CH_2O + H_2O$$

Table IV summarizes the effects of the combined environments upon a polymethylsiloxane material. The common free radicals formed for all combinations are the $RCH_2{*}$ and the $R{*}$. The presence of oxygen forms the silicon-oxygen-silicon cross-linking along with the oxidative products of methane.

The relative amounts of the different products are unknown, but more than likely these will depend upon the oxygen concentration and diffusibility, the temperature during the test, and the type and energy of the radiation used for the experiment.

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RADIATION, OXYGEN & HEAT EFFECTS ON POLYMETHYLSILOXANE MATERIAL

ENVIRONMENT	FREE RADICALS	LINKAGES	FINAL PRODUCT
HEAT + OXYGEN	$\underline{RCH_2^*}$, $\underline{R^*}$ OH, H_2O_2, HO_2 O_2^*	$\underline{Si\text{-}O\text{-}Si}$	$\underline{CH_2O}$, $\underline{CHOOH}$ H_2O
RADIATION+OXYGEN	$\underline{RCH_2^*}$, $\underline{R^*}$, H^*, CH_3^*, HO_2 H_2O_2, OH^*, O_2^* O	$\underline{Si\text{-}O\text{-}Si}$	$\underline{CH_2O}$, $\underline{CHOOH}$ RCH_2OOH, H_2O
RADIATION + HEAT	$\underline{RCH_2^*}$, $\underline{R^*}$ CH_3^*, H^*	$Si\text{-}C\text{-}Si$ $Si\text{-}C\text{-}C\text{-}Si$	H_2, CH_4
RADIATION+OXYGEN + HEAT	$\underline{RCH_2^*}$, $\underline{R^*}$ H^*, CH_3^*, HO_2, H_2O_2 OH^*, O_2^*, O	$\underline{Si\text{-}O\text{-}Si}$	$\underline{CH_2O}$, $\underline{CHOOH}$ H_2O

NPC 7488

TAB IV

NATIONAL BUREAU OF STANDARDS REPORT

6126

RADIATION CHEMISTRY OF FLUOROCARBON POLYMERS AND MONOMERS

by

L. A. Wall, R. E. Florin, and D. W. Brown

National Bureau of Standards
Washington 25, D. C.

to

WRIGHT AIR DEVELOPMENT CENTER
Wright-Patterson Air Force Base, Ohio

September 1, 1958

National Bureau of Standards
U. S. DEPARTMENT OF COMMERCE

0706-11-3890 September 1, 1958 6126

RADIATION CHEMISTRY OF FLUOROCARBON POLYMERS AND MONOMERS

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Report to be presented at the

RADIATION EFFECTS SYMPOSIUM
Atlanta, Georgia
October 28-30, 1958

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Washington 25, D. C.

The changes in polymers irradiated with Co^{60} gamma rays were studied with reference to formation of gas molecules, crosslinking, and scission in air and in vacuum, as evidenced by mechanical properties such as "zero-strength-time" and free-radical accumulation and disappearance as shown by electron spin resonance. The polymers studied were: Teflon, Teflon 100X, Kel F, Kel F elastomer, Viton A, and trifluoroethylene. These polymers show great differences in radiation stability depending upon environment and constitution. The molecule hexafluorobenzene showed outstanding radiation stability, approximately comparable to benzene, and would be a promising basis for the preparation of resistant polymers. Mixtures with added hydrocarbon materials were somewhat less stable. It appears that radicals in Teflon build up approximately linearly, at least up to a dose of 72 megr, and disappear very slowly in vacuum, while in a perfluoropropene-tetrafluoroethylene copolymer the radical concentration shows signs of leveling off at 50 megr and probably declines somewhat in two days.

Fluorocarbon polymers are useful under severe conditions of high temperature, solvents, and corrosive environments, but according to previous reports they are very sensitive to radiation. Since there is relatively little information available on this latter subject it is desirable to have a better understanding of the behavior of the various commercial and the potentially commercial fluorocarbon products in radiation fields. The reported information is almost exculsively about Teflon. It may be somewhat misleading if extended to the whole class of fluorocarbon products because the molecules of Teflon appear to have exceptionally low intermolecular forces, and thus technically useful polymers are required to have very high molecular weights with consequent great sensitivity to radiation damage.

Occasionally sensitivity to radiation is useful; thus radiation has been used to prepare graft copolymer on a base of Teflon,[1] and is reported to bring about the crosslinking of a perfluoropropene-vinylidene fluoride copolymers to a tough rubbery product.[2] Methods for crosslinking fluorocarbon polymers in general would increase their usefulness. In addition to the present range of fluorocarbon polymers available commercially or on a pilot plant scale, there are at least two types of fluorocarbon structure of which one may expect a different order of radiation resistance, the perfluoroaromatic ring and the perfluorotriazine ring. So far, only exploratory polymers have been disclosed using these aromatic and quasi-aromatic systems; examples are a polyphenyl of low molecular weight[3] and several perfluoroamidine copolymers.[4]

This article summarizes the results to date of a program for studying the effect of radiation upon fluorocarbon polymers and simpler molecules at high and low temperatures. Radiations have been done mainly with a 2000-Curie Cobalt-60 source, with radiation fields of the order of 0.6×10^6 R/hour. Temperatures from 4° K to about 500° C are available. Chief reliance has been placed upon mass spectrometry for the determination of volatile products and solution viscosity and mechanical properties such as "zero-strength-time" (ZST)[5] for indicating the molecular weight and amount of crosslinking. Electron spin resonance (e.s.r.) has also thrown some light on the numbers and kinds of free radicals present.

The work is divided into two fields by differences of technique and object: (a) irradiation of fluorocarbon polymers and (b) radiation chemistry of small molecules, with emphasis on perfluoroaromatic structures.

POLYMERS

Teflon.- There is considerable literature on radiation damage of Teflon. The material has been listed as easily damaged,[6] losing all strength at about 2.5×10^8 R. A limited study of Teflon under Co^{60} γ-radiation showed reduction of a thousand-fold after 10^6 R.[7] When irradiated in the presence of water and air, the yield of ionic fluoride is about 0.2 atoms/100 e.v.[8] The volatile products include CF_4.[9] The electron spin resonance spectrum is known to cover a region of about 210 gauss at about 9000 megacycles, and to contain 7 or 8 partially resolved peaks; it is also stated that the resonance has a life of many months. The pattern is changed by reaction with molecular oxygen. There is disagreement over precise features of the spectrum.[10,11]

In the present study the yields of the volatiles are shown in Table 1. Carbon tetrafluoride was present but not especially prominent. The yields of CO_2 and SiF_4 suggest an attack of corrosive fluorocarbon fragments upon the glass. Probably no monomer is produced, a mass spectrometer peak at mass 100 (the molecular weight of C_2F_4) being attributable to larger molecules. Besides the fluorocarbon molecules reported, there is also formed some material which can be sublimed, perhaps fluorocarbons of the C_{20}-C_{40} range. The effect of post heating is small.

Radicals appear to build up linearly in the solid, with no apparent falling off over a period of 184 hours in which 64.0×10^{20} e.v./g were absorbed. There is some uncertainty about the scale of the original measurements, but five months later the radicals still remaining were equivalent to a yield of 0.197 radicals per 100 e.v. (Figs. 1 and 3).

Teflon 100X.- This new copolymer of C_2F_4 and C_3F_6 is chemically much like Teflon, but decomposes at somewhat lower temperatures, and also softens at much lower temperatures so that it can be molded in conventional equipment around 300° C. Upon irradiation in air the mechanical deterioration is extreme; strips for ZST cannot be handled much above 10 megr dose (Fig. 4, curve 1). In vacuum the deterioration is much slower and seems to be preceded by an anomalous slight rise (Fig. 4, curve 2). A rise would usually indicate crosslinking, but with this polymer it is very hard to imagine a reasonable mechanism for the formation of crosslinks. Comparison of samples in air and vacuum shows that at the existing combination of dose rate (about 0.6 megr/hr) and strip thickness (60 mil), the air diffuses into the interior of the strip rapidly enough to sustain the characteristic monotonic chain scission.

The e.s.r. spectrum of the Teflon 100X is different from that of Teflon; the system of peaks is more poorly resolved but still distinguishable (Fig. 2). Figure 6 shows the rate of buildup of radicals estimated by e.s.r. The yield of trapped radicals is considerable, about 1.1 radical per 100 e.v. There is some evidence that the rate of decay of radical concentration is detectable in a few days, and thus more rapid than for Teflon.

Polytrifluoroethylene.- The yield of volatiles is shown in Table 2. The SiF_4 due to corrosive fluorine compounds is important; the precursor is no doubt HF liberated from the polymer. Recent publications[12] indicate that CF_2CFH polymerizes with frequent head-to-head arrangements, and thus with -CHFCHF- groups in the chain is able to give up HF easily.

Kel-F.- The ZST and the molecular weight as a function of dose are shown in Table III, also Figure 5, curves 3 and 4. No e.s.r. signal was found in a sample irradiated and measured at 25° C. Obviously chain scission dominates.

A very rough calculation based on published relations connecting ZST, solution viscosity, and osmotic molecular weight,[5,13] leads to a preliminary estimate G (chain scissions) = 1.7 scissions/100 e.v. This may be compared with an apparent G (F atoms) = 7/100 e.v. derived from early literature data.[14]

Kel-F Elastomer 5500.- The ZST determinations show that Kel-F elastomer 5500 undergoes chain scission rather rapidly (Fig. 4, curve 5).

Kel-F Elastomer 3700.- Kel-F elastomer 3700 crosslinks rapidly at doses below 11 megr. Ultimately, however, (at 15 megr) degradation begins to dominate and the ZST decreases (Fig. 4, curve 6). Once the crosslinked network has formed, the ZST sample no longer undergoes the highly reproducible failure by viscous flow but fails instead by transverse fracture, with a very large random error. The new behavior remains even though the ZST later decreases to low values. The Kel-F elastomer has abundant sites for crosslinking by HF (or HCl) elimination. For a very short interval Kel-F elastomer 5500 also crosslinks.

Viton A.- The copolymer of C_3F_6 and CF_2CH_2 crosslinks very early (Fig. 7), the ZST (at 114° C) rising to inconveniently high values before a dose of 1.2 megr both in vacuo and in air. This agrees approximately with other work[2] on crosslinking by radiation. Post heating (100° C for 30 minutes) had little effect. Very long irradiation time in vacuo (200 megr) weakened the samples somewhat, but the ZST remained unobservably high.

SMALL MOLECULES

The irradiation of small molecules including hexafluorobenzene, benzene, perfluoroheptane, and their mixtures has made use of three kinds of containers : (1) small thick-walled capillary tubes, (2) nickel capsules joined via a nickel capillary section to small Kovar seals, and (3) small Monel bombs bearing bellows valves. They have various advantages and also objectionable features. The all-glass apparatus (1) is certainly vacuum-tight and sturdy, but probably reactive chemically and hard to open for quantitative examination of gaseous products. It has been used so far for mixtures at 218°C. The nickel capsules (2) are very fragile but can be made vacuum-tight. Most of the surface of the capsule is unreactive, but long-lived products such as hydrogen fluoride can slowly diffuse to the glass tubing end and react there. Analytically this turns out to be an advantage as the SiF_4 formed is easily separated from the main body of less volatile material and determined quantitatively in the mass spectrometer. Unfortunately the special glass at the Kovar seal zone is especially vulnerable to attack; thus the production of large amounts of hydrogen fluoride causes early failure. These capsules with Kovar seals are limited to a few atmospheres pressure at most, and therefore to temperatures well below 100° C for the liquids studied here. The small Monel bombs (3) are unreactive, strong, and easily inspected without destruction after use, but can be expected to leak slowly at the valve over long periods of time. They have been used for studies under hydrogen pressure and would also probably be satisfactory for high temperature use.

Hexafluorobenzene.- Pure hexafluorobenzene appears to resist radiation in a way reminiscent of benzene itself (Tables IV and V, first column; Fig. 8). The yield of "polymer" (non-volatile material of uncertain structure) is about 1.3 C_6F_6 units/100 e.v. absorbed at 218°, about the same as that of benzene at this temperature, and at 20° C it is 1.7 C_6F_6 units/100 e.v. as against 0.93 units (of C_6H_6) for benzene.[15,16] The amount of corrosive fluorine (appearing as SiF_4) is low at room temperature (0.04 atoms/100 e.v. of F, appearing as 0.01 SiF_4). At high temperatures, 218°, the yield of F is larger, about 0.76, which is nearly one atom of F evolved per polymer unit formed. The character of the high-temperature polymer is different - dark and insoluble, in contrast to the clear, light-yellow, soluble glassy product formed at 20°. The structure of the radiation polymer from benzene is known from the literature to be complicated, probably involving cyclohexene and cyclohexadiene rings, and less likely hexatriene open chains, in addition to the original benzene rings.[15,16] The polymer from hexafluorobenzene is likewise complicated. The infrared absorption spectrum, which was done by Dr. John J. Comeford of the National Bureau of Standards, has not yielded any ready interpretation in terms of the spectrum of the parent compound. The polymer is also accompanied by small amounts of slightly volatile crystalline material, perhaps perfluorobiphenyl or perfluoroterphenyl.

Hexafluorobenzene and benzene.- The radiation stability of hexafluorobenzene in mixtures with ordinary benzene depends on the temperature. At high temperature (218°) little departure from additivity is noticed (Table IV and Fig. 8), but at room temperature dilution with benzene steadily decreases the stability of hexafluorobenzene, at least down to 0.114 mole fraction C_6F_6 (Table V and Fig. 8). Qualitatively this increased sensitivity is connected with the possibility of forming the highly stable molecule hydrogen fluoride in the mixture but not in either component singly. Any process able to form this molecule is likely to be highly exothermic. Restricting ourselves to free-radical processes, a few reactions in the mechanism may be:

$$C_6F_6 \longrightarrow C_6F_5\cdot + F\cdot$$

$$F\cdot + C_6H_6 \longrightarrow HF + C_6H_5\cdot$$

$$C_6H_5\cdot + C_6F_6 \longrightarrow C_6H_5\text{-}C_6F_6\cdot$$

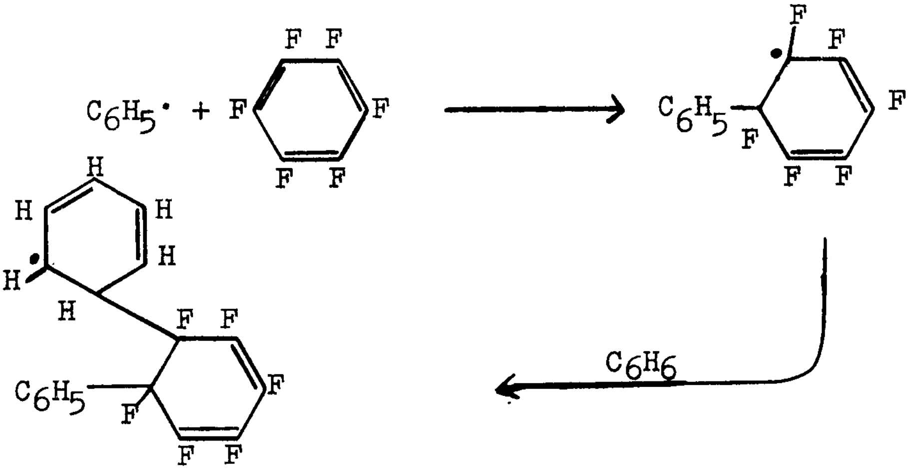
$$C_6H_5\text{-}C_6F_6\cdot + C_6H_6 \longrightarrow C_6H_5\text{-}C_6F_5 + C_6H_5\cdot + HF$$

$$2 \text{ Radicals} \longrightarrow \text{Molecule}$$

It is very curious that the mixed benzenes C_6F_5H and C_6H_5F were not seen at all, although mechanism for their formation is obvious:

$$C_6H_5\cdot + C_6F_6 \longrightarrow C_6H_5F + C_6F_5\cdot$$

Structurally, some of the possibilities are shown below:



Since the HF remains less than the polymer yield, some of the increased rate of polymer formation could be due not to HF elimination but simply to the alternating-polarity effect familiar in vinyl polymerization, a fluorocarbon radical preferentially adding to a hydrocarbon monomer molecule, and vice versa. The occurrence of a maximum in yields at such a low hexafluorobenzene concentration remains to be explained.

Hexafluorobenzene and hydrogen.- Under 34 atmospheres hydrogen at room temperature, hexafluorobenzene yields somewhat larger amounts of corrosive fluorine than it does in the pure state (Table VI).

Perfluoroheptane and mixtures with hexafluorobenzene.- The radiolysis of perfluoroheptane C_7F_{16} produced much higher yields of corrosive fluoride than C_6F_6 at room temperature, 0.67 atom F/100 e.v. (Table VII). The fragment molecules C_6F_{14}, C_5F_{12}, etc. were too numerous in kind to permit any very accurate analysis by the mass spectrometric method used, especially since the perfluoroparaffins occurring here, unlike perfluorobenzene, furnish inordinately few molecule ions and many small fragment ions, which adds to the difficulty of distinguishing individual compounds in a complex mixture. For this type of radiolysis mixture, an extended study by vapor chromatography would be more appropriate. For determining the smaller molecules, e.g. CF_4, the objection is unimportant, as all higher fluorocarbons are frozen out during the analysis.

In mixtures with hexafluorobenzene, the yields of all products are low at high hexafluorobenzene concentration (Table VII, and Fig. 9). There is some doubt about the reality of the maximum near 0.30-0.40 mol fraction C_6F_6, because the points for pure C_7F_{16} are an average of two other discordant analyses.

Other mixtures.- It is likely that some other fluorocarbon-hydrocarbon mixtures produce much more hydrogen fluoride than those reported here. Capsules of perfluoroheptane plus cyclohexane, hexafluorobenzene plus cyclohexane, and perfluoroheptane plus benzene, exposed for the same period as those reported here, were corroded and broken at the glass seal without exception.

CONCLUSION

Present work has shown that both crosslinking and scission occur in the action of radiation upon fluorocarbon polymers. In some cases scission seems to be much reduced in vacuo as compared to irradiations in air. Electron spin resonance offers an opportunity to estimate the number of radicals formed in the irradiation of suitable polymers. The hexafluorobenzene ring was shown to be in a different class from saturated fluorocarbon structures as regards radiation resistance, but sensitive when mixed with hydrocarbons. At present the investigation of perfluoroaromatic structures is being extended to high and low temperatures, and it is intended to investigate related structures when they become available, e.g. triazines, the "Florida Polymer" of H. C. Brown, perfluoropolystyrene, polyphenyl, and others. The extension of electron spin resonance investigations to very low temperatures offers hope of detecting atoms and radicals less stable than those found in polymers thus far.

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Table I. Radiation Yields from Polytetrafluoroethylene

Product	G-values, molecules/100 e.v.		
	A	B	C
SiF_4	0.148	0.211	0.0005
CO_2	.06	.12	.002
CO	.036	.037	Not determined
CF_4	.009	.005	.0006
C_2F_6	$<.001$	.007	0
C_3F_8	Trace	.003	0
$i\text{-}C_4F_8$	0	.005	0
$1\text{-}C_4F_8$	0	.004	0

A: Irradiated 350×10^6 R.

B: Irradiated as in A, then post heated 300° for 30 minutes.

C: Effect of exposure to air. Irradiated as in A, system evacuated, opened, reevacuated, heated 310° 15 minutes.

Table II. Radiation Yields from Polytrifluoroethylene

Exposure dose, megr	22.9	74	126	126,post
$G(SiF_4)$, molecules/100 e.v.	0.668	0.767	0.864	0.94
$G(CHF_3)$	.018	.025	.016	.029
$G(CO_2)$	.092	.098	.113	.123
$G(CO)$	.243	.147	.137	.14
$G(H_2)$	.028	.033	.120	.091
Relative G (mass 82)	57	36	49	61

Table III. Kel-F Molecular Weight Degradation

Dose, e.v./g	0	6.13×10^{20}
ZST, sec, 250° C	347	90.1
Molecular weight	600,000	60,000

Table IV. Radiation Yields, $C_6F_6 + C_6H_6$, 218° C, 350 megr

Mol fraction C_6F_6	1.00	0.256	0
$G(SiF_4)$ molecules/100 ev	0.21	0.0263	0
$G(C_2H_2)$ " "	0	.0048	.017
$G(CO)$ " "	.054	.0063	0
$G(CO_2)$ " "	.022	.0048	0
$G(H_2)$ " "	0	.0075	.0022
G(polymer), C_6X_6 units/100 ev	1.3 ± 0.2	1 ± 0.5	1.3

Table V. Radiation Yields, C_6F_6 + C_6H_6 at 20° C

Dose 275 megr

Mole fraction C_6F_6	1.00	0.667	0.114	0^b
G(SiF_4), molecules/100 ev	0.010		0.326	
G($CH{=}C{=}CH_2$) " "	0		.027	
G(CO) " "	.0012		0	
G(H_2)	.0007		.063	0.044
G(polymer)[a] " "	1.72	2.18	3.55	.93

a. Base molecules converted.

b. Gordon, van Dyken, and Doumani, reference 15.

Table VI. Radiation Yields, $C_6F_6 + H_2$,
34 atm, 20° C, 319 megr

	C_6F_6, pure	$C_6F_6 + H_2$
G(SiF_4), molecules/100 ev	0.010	0.105
G(CO_2)	0	.004
G(CO)	.0012	

Table VII. Radiation Yields, $C_6F_6 + C_7F_{16}$ at 20° C

Dose 330-408 megr

Mole fraction C_6F_6	0	0.38	0.74	1.0
$G(SiF_4)$, molecules/100 ev	0.167	0.308	0.088	0.010
$G(CO_2)$, " "	.028	.025	.003	..0012
$G(CF_4)$, " "	.195	.131	.085	0
$G(C_2F_6)$, " "	.081	.122	.008	0

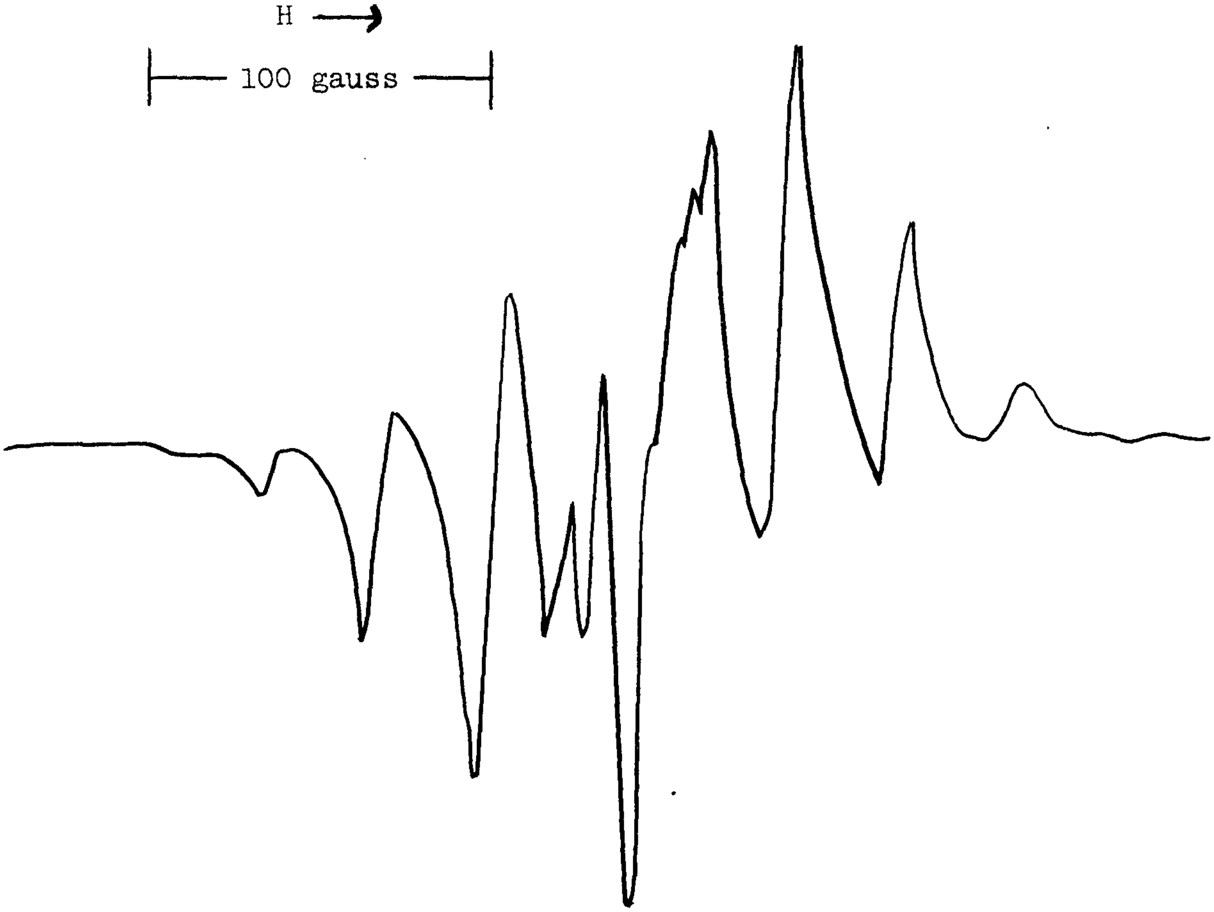

Figure 1. ESR Spectrum of Irradiated Teflon.

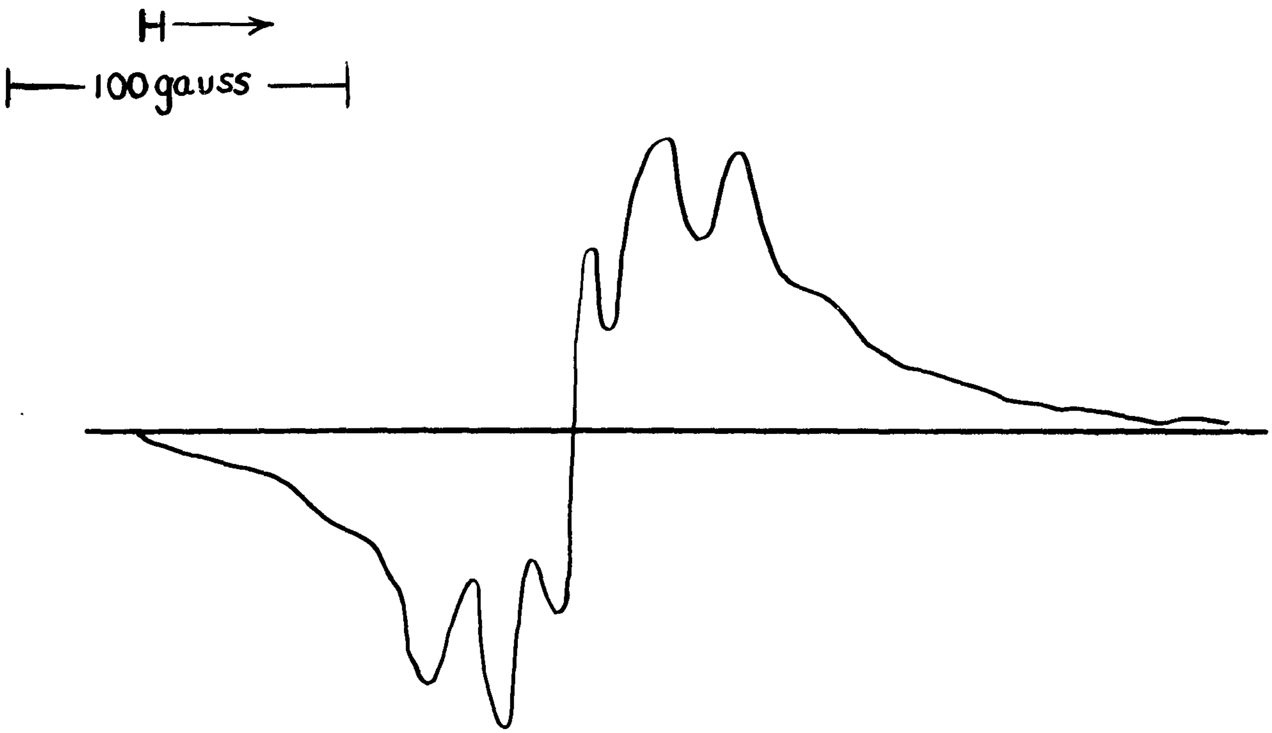

Figure 2. ESR Spectrum of Irradiated Teflon 100X.

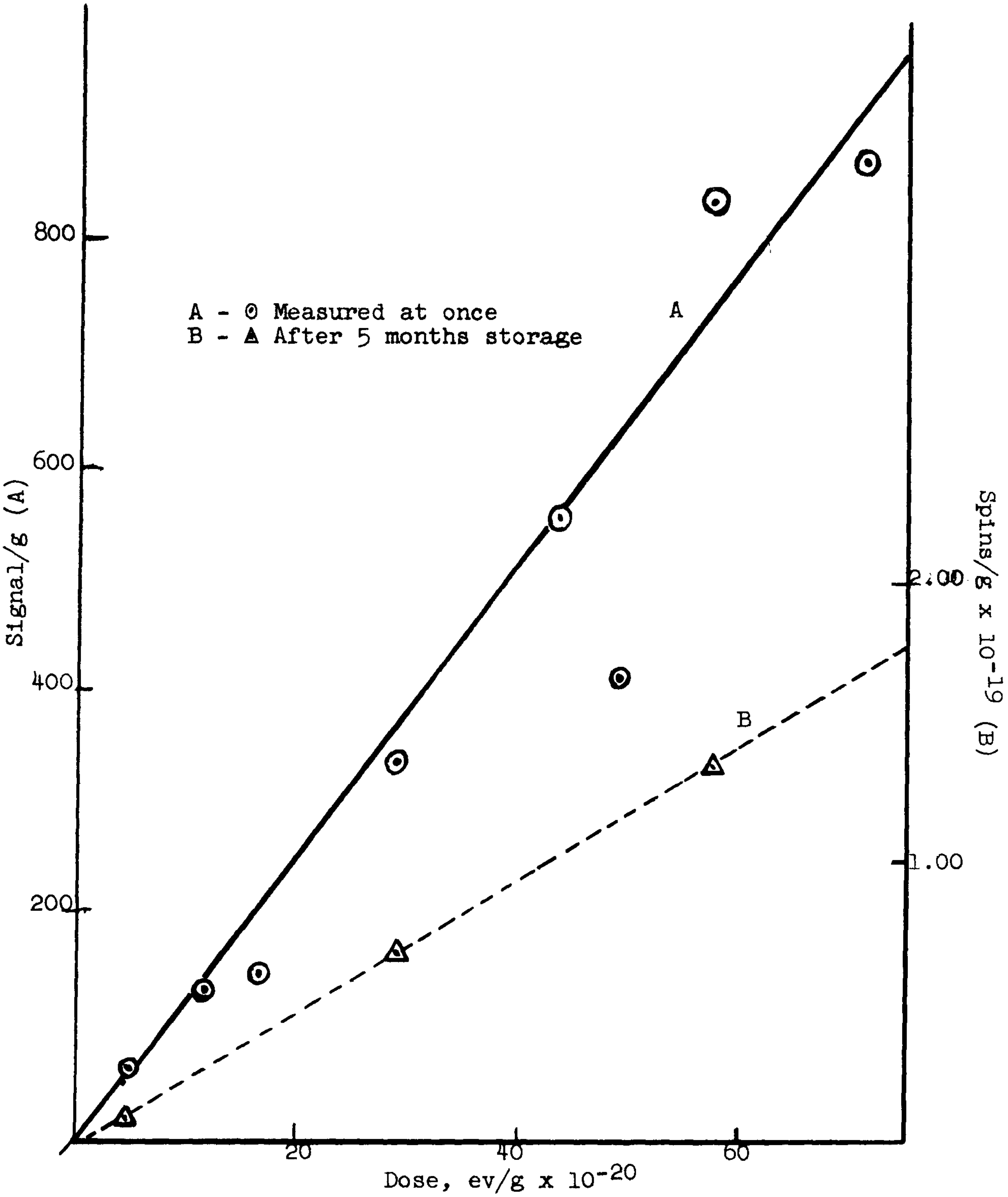

Figure 3. Accumulation of free radicals in irradiated Teflon.

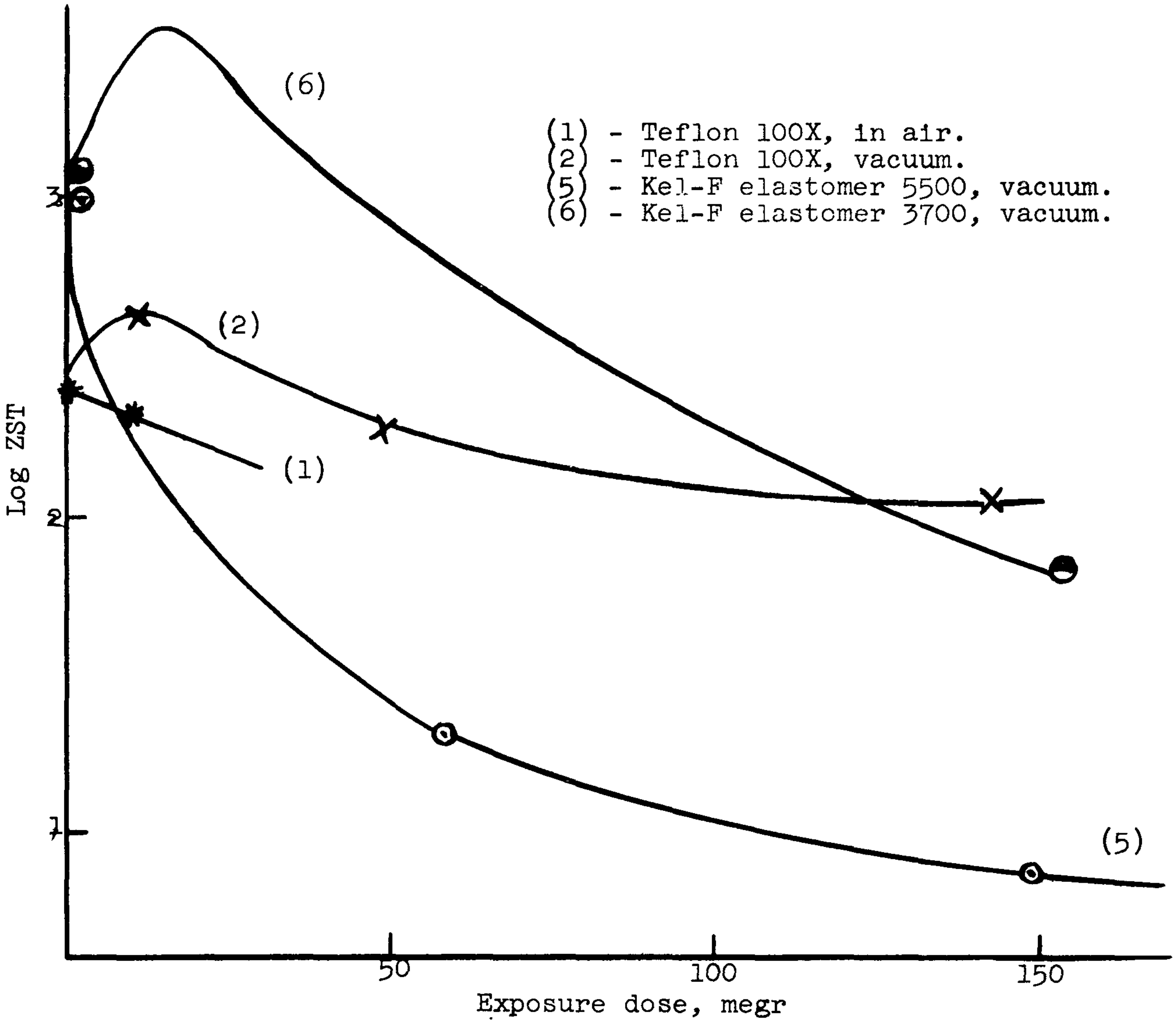

Figure 4. Zero-strength-time of Irradiated Polymers.

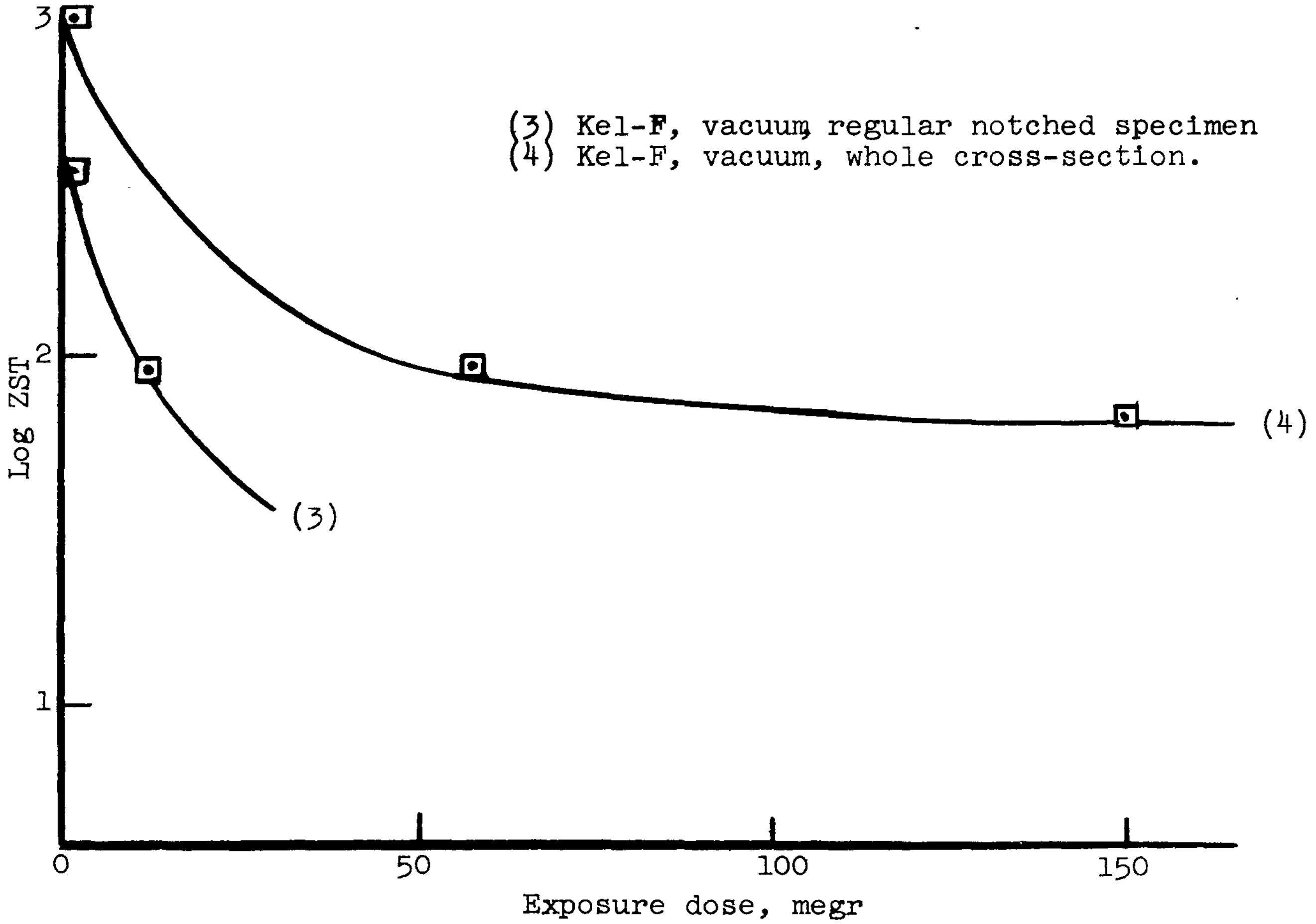

Figure 5. Zero-strength-times of Irradiated Polymers.

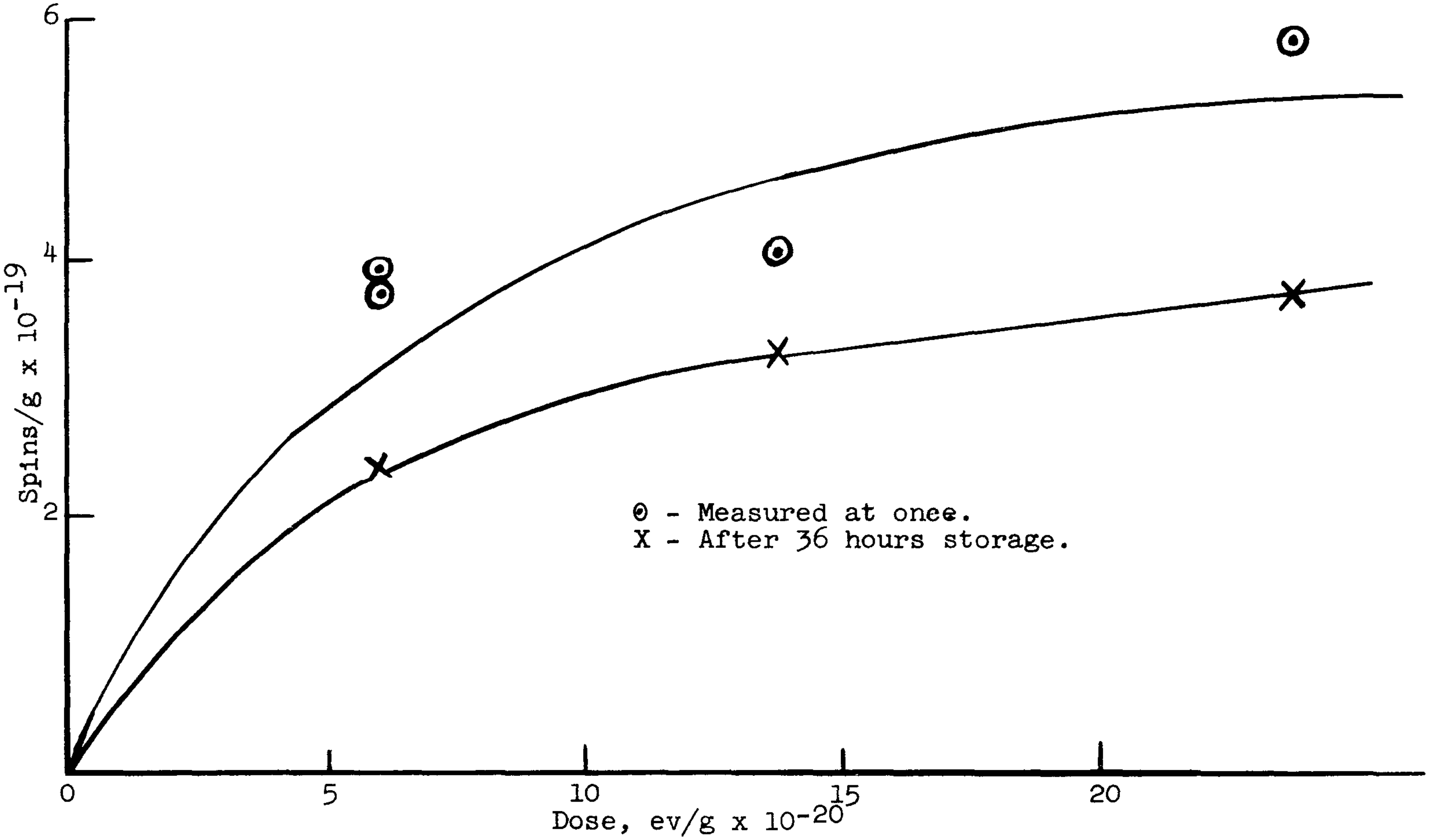

Figure 6. Accumulation of Free Radicals in Irradiated Teflon 100X.

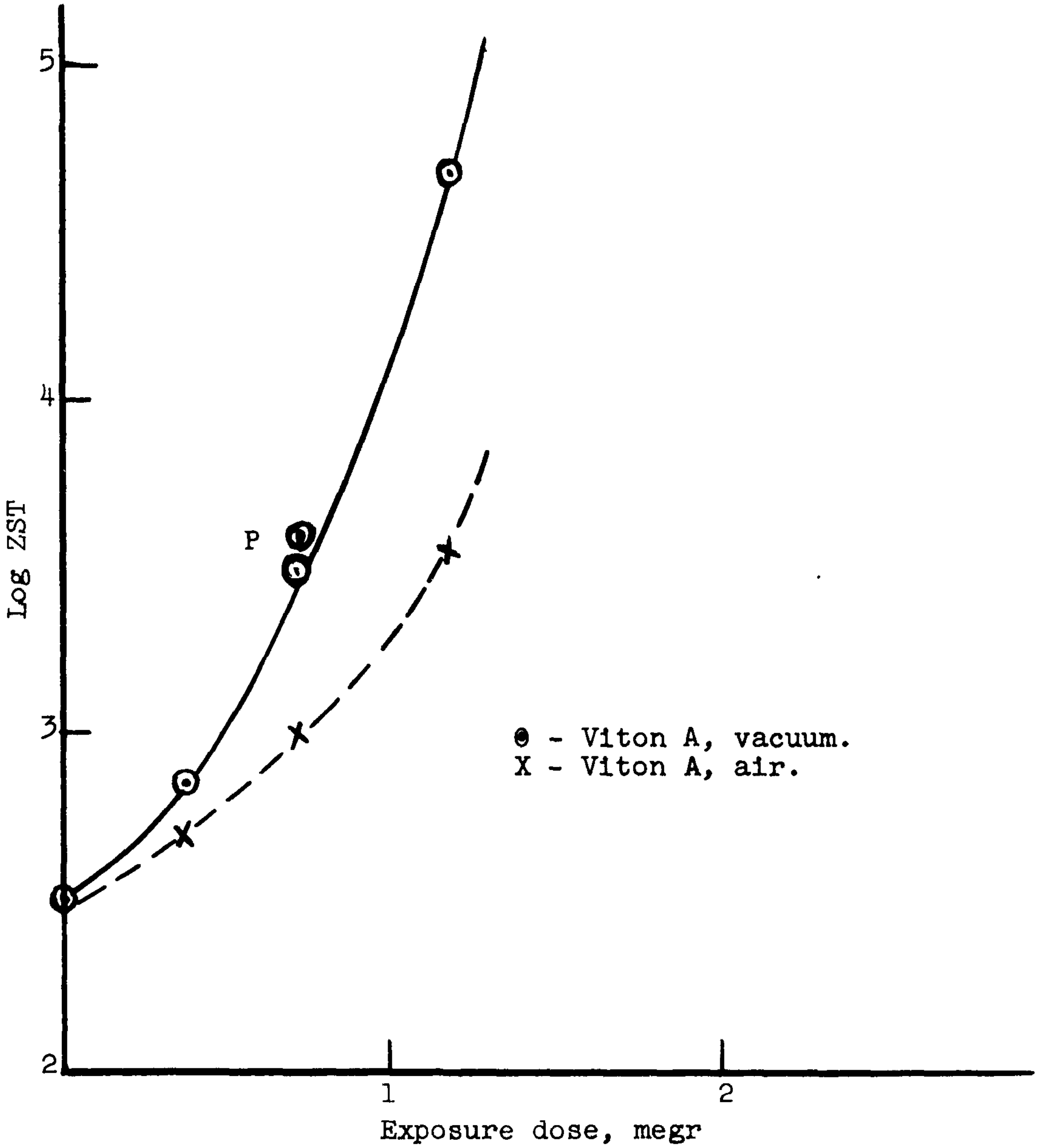

Figure 7. Zero-strength-time of Irradiated Polymers.

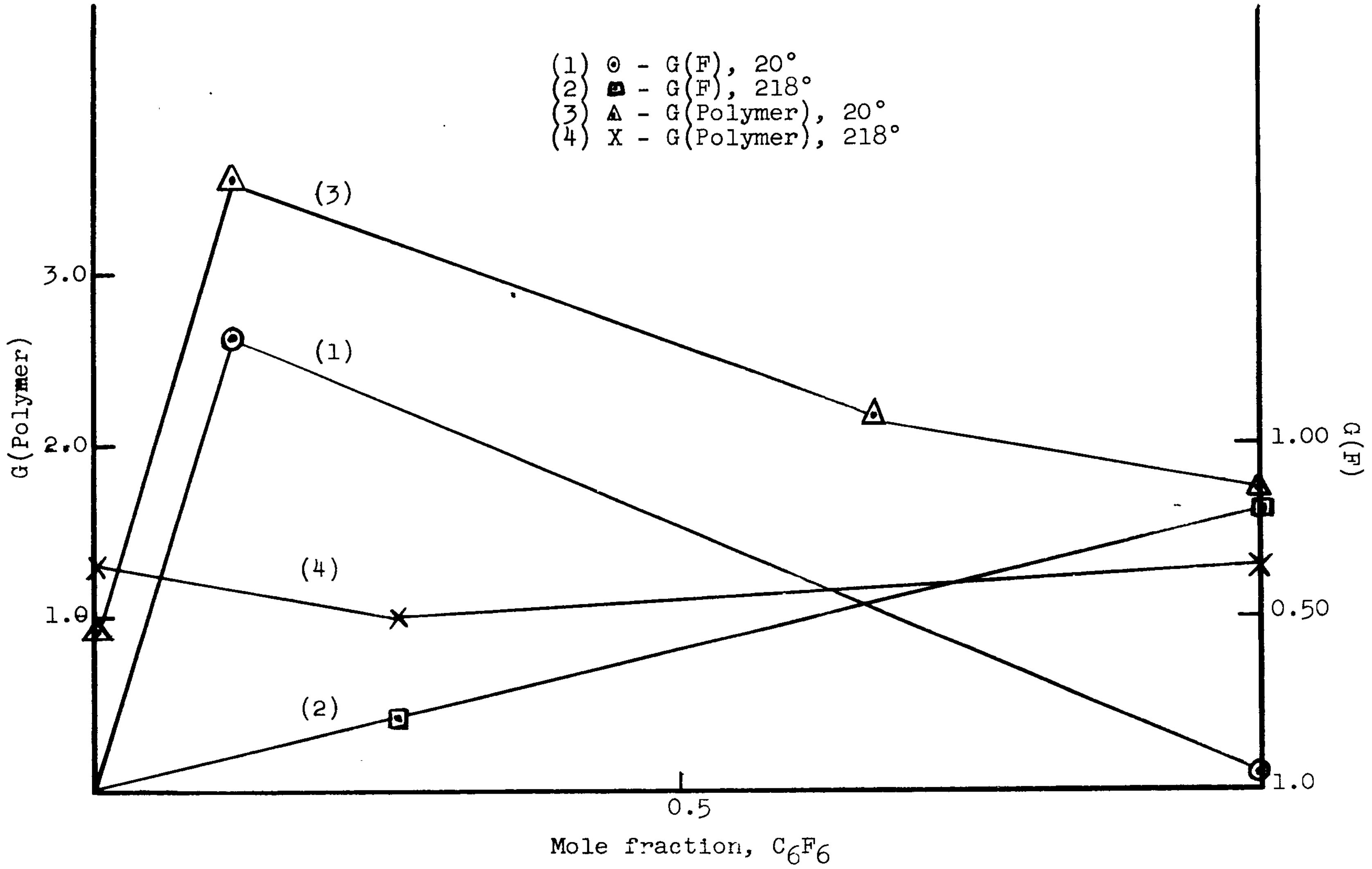

Figure 8. Radiation Yields from C_6F_6-C_6H_6 Mixtures at 20° and 218°.

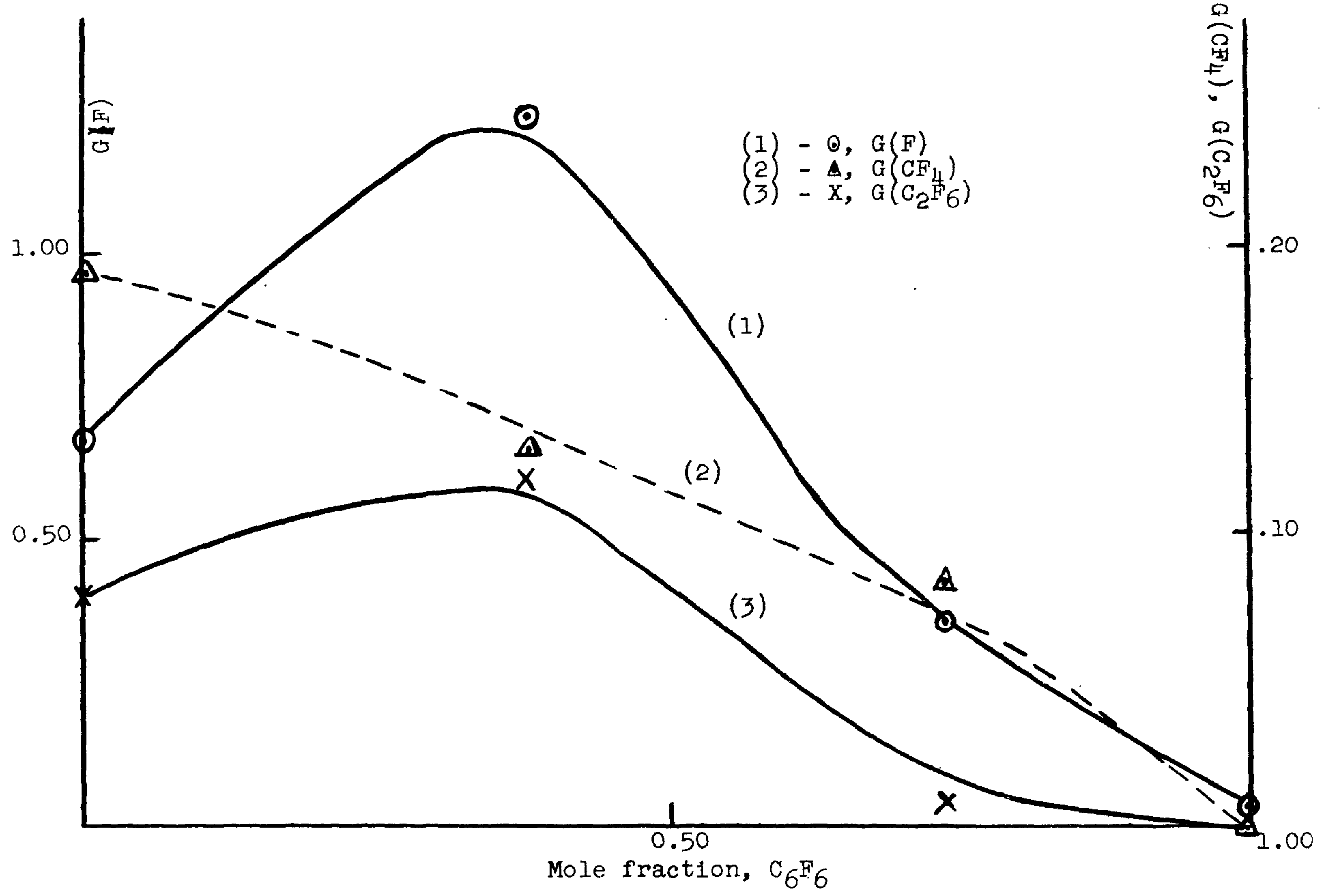

Figure 9. Radiation Yields of C_7F_{16}-C_6F_6 Mixtures. Yields in Molecule/100 ev.

FAST NEUTRON ACTIVATION OF SEAPLANE MATERIALS

by

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Activation of a seaplane hull bottom by the predominantly fast leakage flux from a propulsion reactor is expected. An experimental approach to this activation problem was necessary because of the presence of impurities in commercial materials, and because cross sections are not well known in the fast region. Small specimens of aluminum alloy 2014 sheet coated with a number of substances such as paints, primers, tapes, sealants and seawater residue were irradiated for 2 hours in a fast flux of about 5.53×10^9 with a fast to thermal ratio of 72.5. Specimen activity was measured. Most of the activity was from the aluminum alloy with little originating in the surfacing materials or sea water.

This paper is classified and is bound in Volume Six.

BOEING AIRPLANE COMPANY

SEATTLE 24, WASHINGTON

DOCUMENT NO. D2-1819

UNCLASSIFIED TITLE EFFECTS OF NUCLEAR RADIATION ON CORK, LEATHER, AND ELASTOMERS

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SUMMARY

Samples of cork, leather, and various elastomers were irradiated in the cobalt 60 gamma source of the California Research Corporation at dosages of ca. 10^7 to 10^{10} ergs/gram.

No significant changes were observed for cork. Tensile strength of leather was affected; no hardening was noticed. These materials can be used in certain systems in nuclear environments. Elastomers SE-551 and SE-371 are affected by nuclear radiation. At ca. 10^{10} ergs tensile strength and elongation properties decrease considerably, while hardness increases to the point of crumbling. High temperature Thiokol exhibits good properties after irradiation.

Viton A retains usable tensile strength up to ca. 10^{10} ergs, with some increase in hardness. At ca. 10^{10} ergs the percent of elongation of Viton A drops considerably.

Viton A and high temperature Thiokol appear to be promising materials for use in nuclear environments. Additional work is being planned.

TABLE OF CONTENTS

I. INTRODUCTION

A literature search failed to produce usable data on the effects of nuclear radiation on cork and leather. These items are used in airplane systems as gaskets and back-up rings, and as such are important.

New elastomers have been developed, which show promise for high temperature O-ring use. No data was available on the effects of nuclear radiation on these materials.

II. PURPOSE

The purpose of this investigation was to obtain data usable for design purposes. Such data will be useful in the design of systems for airplanes and missiles using nuclear energy for propulsion or exposed to nuclear radiation.

III. MATERIALS AND TESTS

Facilities

A literature survey failed to reveal usable data on the effects of nuclear radiation cork and leather. Also, new elastomers were developed; no usable data existed on the effects of nuclear radiation on these materials. Tests were necessary to obtain data. Therefore, arrangements were made during the latter part of 1956 with Messrs. J. L. Cooley and R. O. Bolt, California Research Corporation, to irradiate these materials in the CRC gamma facility.

The California Research Corporation's cobalt 60 gamma source produces 2.68×10^5 roentgens per hour. Samples of cork, leather, and elastomers were placed in sealed containers and irradiated to varying exposure dosages. After irradiation physical properties of the materials were measured. The results were tabulated and plotted.

Materials and Specimens

The cork gaskets used in the experiments conform to Military Specification No. HHC-576. These gaskets are located in the near wheel well of the present B-52. Wafers and strips were cut from a sheet of the material. The wafers were 0.688 inches in diameter; the strips were 1" x 3" x 1/8". The cork contains animal glue as a binder.

The leather specimens were hydraulic back-up rings, which meet Military Specification No. AN-R-22. The specimens had an outside diameter of 1.875", a width of o.188", and a thickness of 0.094".

The elastomers used in the experiments were:

1. SE 551 (white), Silicone

2. SE 371 (red-iron oxide compound), Silicone
3. Viton A (hexafluoropropylene, vinylidene fluoride copolymer - supplied by Jerome M. Kelble, Senior Project Engineer, WADC)
4. High temperature Thiokol

The specimens were in the form of O-rings. With the exception of the Viton A specimens, the dimensions were 1.475 ± .010" dia. x 0.210 ± .005" width (AN 6227-28). The Viton O-rings had dimensions of 0.984" ± .006" dia. x 0.139" ± .004" width (AN 6227-19). (Viton A is also known as Compound No. 051-16A.)

<u>Testing</u>

The following tests were made on the <u>cork</u> specimens:

Compression-deflection, conforming to Federal Specification HH-C-576
Compression set " " " " "
Flexibility " " " " "
Tensile Strength " " " " "

Ultimate load tests were made on the <u>leather</u> back-up rings.

The following tests were made on the <u>elastomer</u> O-rings.

Durometer Shore A hardness, ASTM D 412
Compression Relaxation, WADC TR 56-272 (see page 10)
Stress-Strain, Boeing Document D-17416-3 (see page 10)

IV. RESULTS

Cork

Compression Set

Testing conformed to Federal Specification HH-C-576. The specimen, at least 0.125 inches thick, was placed under a 1 psi load for 15 seconds and the thickness of the specimen measured. The pressure was increased to 100 psi. After a period of one minute the amount of compression was measured. The pressure was then reduced to 1 psi and after a period of five minutes the thickness was again measured. The percentage of compression and recovery was calculated according to the formulas below:

$$\text{percentage compression} = \frac{(100)\ (\text{amount of compression})}{\text{Original thickness}}$$

$$\text{percentage recovery} = \frac{(100)\ (\text{recovered thickness})}{\text{Original thickness}}$$

The following results were obtained:

Dosage, Ergs/gram	% Compression	% Recovery
0	27.9	97.2
8.3×10^6	29.9	97.3
8.3×10^7	29.2	97.8
8.3×10^8	27.6	97.3
8.3×10^9	29.0	95.4

Compression - Deflection

Three specimens of cork discs, each having a circular area of one square inch, were assembled on top of each other and a compressive force of 600 pounds was applied after which the pressure was immediately released. This gave a compression-deflection curve. It was difficult to get reproducible results, and so the test was discontinued.

Flexibility

Tests were conducted according to Federal Specification HH-C-576, which states:

> "Samples of sheet cork 0.1875 inches or less in thickness shall not break or separate when rolled over a rod the diameter of which shall be five times the thickness of the sample."

The following results were obtained:

Dosage, Ergs/gram	
0	passed
8.3×10^6	passed
8.3×10^7	passed
8.3×10^8	passed
8.3×10^9	passed

Tensile Strength

Testing was done in accordance with Federal Specification HH-C-576.

The results were:

Dosage, Ergs/gram	Tensile Strength, psi
0	53.2
8.3×10^6	55.2
8.3×10^7	50.0
8.3×10^8	55.2
8.3×10^9	55.2

(See Figures 1 - 3.)

Leather

Tensile strength was the only test performed on the leather back-up rings. Some of the specimens were inadvertently notched, weakening the areas. Therefore, these results are inconclusive.

The results were:

Dosage, Ergs/grams	Ultimate load, lbs
0	110.8 (average of 8)
8.30×10^6	113.8 (average of 3)
8.22×10^8	68.6 (average of 3)
5.48×10^9	10.8 (average of 3)
8.22×10^9	7.1 (average of 3)

(See Figure 4.)

No visual changes were noticed. There was no hardening or discoloration due to irradiation.

Elastomers

Samples of Viton A (Compound 051-16A, supplied by WADC), SE-371 (copolymer of dimethyl siloxane and methylvinylsiloxane) (red) and SE 551 (polymethylvinyl siloxane) (white) were irradiated at varying gamma dosages.

Viton-A O-rings were irradiated at 8.34×10^7 ergs/gram, 1.34×10^9 ergs/gram, and 8.30×10^9 ergs/gram. No visual changes were observed after irradiation.

SE-551 O-rings were irradiated at 8.34×10^7 ergs/gram, 8.30×10^8 ergs/gram, 1.34×10^9 ergs/gram, and 8.30×10^9 ergs/grams. At 8.34×10^7 ergs/gram no visual changes were observed. At 8.30×10^8 ergs/gram stiffening was noticed. At 1.34×10^9 ergs/gram the elastomers were noticed to be harder. At 8.30×10^9 ergs/gram an O-ring broke when handled.

SE-371 O-rings were irradiated at 8.34×10^7 ergs/gram, 1.34×10^9 ergs/gram, 8.30×10^8 ergs/gram, and 8.30×10^9 ergs/gram. No appreciable visual changes were noticed after irradiation.

Flat slabs of high temperature Thiokol were irradiated at 8.34×10^7 ergs/gram, 3.87×10^8 ergs/gram, 8.30×10^8 ergs/gram, and 4.15×10^9 ergs/gram. No significant visual changes were observed after irradiation.

A cupped seal ring made of ceramic filled Teflon (Duroid 5600) was irradiated at 8.30×10^8 ergs/gram. This was completely crumbled after irradiation; no tests were possible.

Tests

The following tests were made on the Silicone O-rings, compounds SE 371 and SE 551 (size AN 6227-28), and Viton A O-rings (size AN 6227-19):

1. Durometer (Shore A)
2. Compression Relaxation according to WADC TR 56-272 page 6, with the exception that the time is extended to five minutes.
3. Stress-strain determination according to January 1957 Boeing Progress Report D-17416-3 Page 10 with the exception that the samples were tested in air at room temperature.

The following physical properties were determined on high temperature thiokol sealant:

1. Ultimate tensile and Elongation, ASTM D 412
2. Durometer (Shore A), ASTM D 676

Data

The data resulting from these tests are summarized in Tables I, II, III, and IV. The data have been plotted on Figures 5, 6, 7, and 8.

V. CONCLUSIONS AND RECOMMENDATIONS

The following conclusions are made;

1. Cork gaskets and leather back-up rings can be used in certain systems in nuclear environments.
2. Elastomers SE-551 and SE-371 have limited use in nuclear environments. These are not ideally suited for o-rings in the presence of high intensity radiation.
3. High temperature Thiokol and Viton A exhibit good properties after high radiation dosages.

Further environmental dynamic tests are planned for the Thiokol and Viton A elastomers.

TABLE I VITON-A IRRADIATED O-RINGS
(Supplied by WADC)

SUMMARY DATA

CODE	DOSAGE ERGS/GRAM	TENSILE STRENGTH, PSI	ELONGATION, PERCENT	HARDNESS, SHORE A	COMPRESSION RELAXATION SLOPE
–	Unirradiated (Average of 3)	1658	307	81	12.8
X-1	8.34×10^7	2240	230	65	10.2
825-8-1, 825-9-3	1.34×10^9 (Average of 2)	1498	165	88	7.3
825-6-1-X-10	8.30×10^9	1170	135	90	13.3

TABLE II SE-551 (WHITE) IRRADIATED O-RINGS
(Prepared by Boeing Airplane Company)

SUMMARY DATA

CODE	DOSAGE, ERGS/GRAM	TENSILE STRENGTH, PSI	ELONGATION, PERCENT	HARDNESS, SHORE A	COMPRESSION RELAXATION SLOPE
Control	Unirradiated	680	85	60	19.2
X-3	8.34×10^7	680	87	60	18.2
X-7	8.30×10^8	370	-	65	34.5
-	1.34×10^9	(Crumbled			)
X-12	8.30×10^9	(Broke when removed, crumbled when handled			)

TABLE III SE-371 (RED) IRRADIATED O-RINGS
(Prepared by Boeing Airplane Company)

SUMMARY DATA

CODE	DOSAGE, ERGS/GRAM	TENSILE STRENGTH, PSI	ELONGATION, PERCENT	HARDNESS, SHORE A	COMPRESSION RELAXATION – SLOPE
Control	Unirradiated	260	170	30	14.7
X-2	8.34×10^7	290	160	35	16.1
X-6	8.30×10^8	280	-	50	21.3
-	1.34×10^9	280	-	52	21.3
X-11	8.30×10^9	(Broke when removed, crumbled			)

TABLE IV HIGH TEMPERATURE THIOKOL, SLABS
(Prepared by Boeing Airplane Company)

SUMMARY DATA

CODE	DOSAGE, ERGS/GRAM	TENSILE STRENGTH, PSI	ELONGATION, PERCENT	HARDNESS, SHORE A	COMPRESSION RELAXATION - SLOPE
Control	Unirradiated	450	400	67	-
X-4	8.34×10^7	430	390	69	-
X-5	3.87×10^8	450	440	68	-
X-8	8.30×10^8	440	380	68	-
X-9	4.15×10^9	400	275	68	-

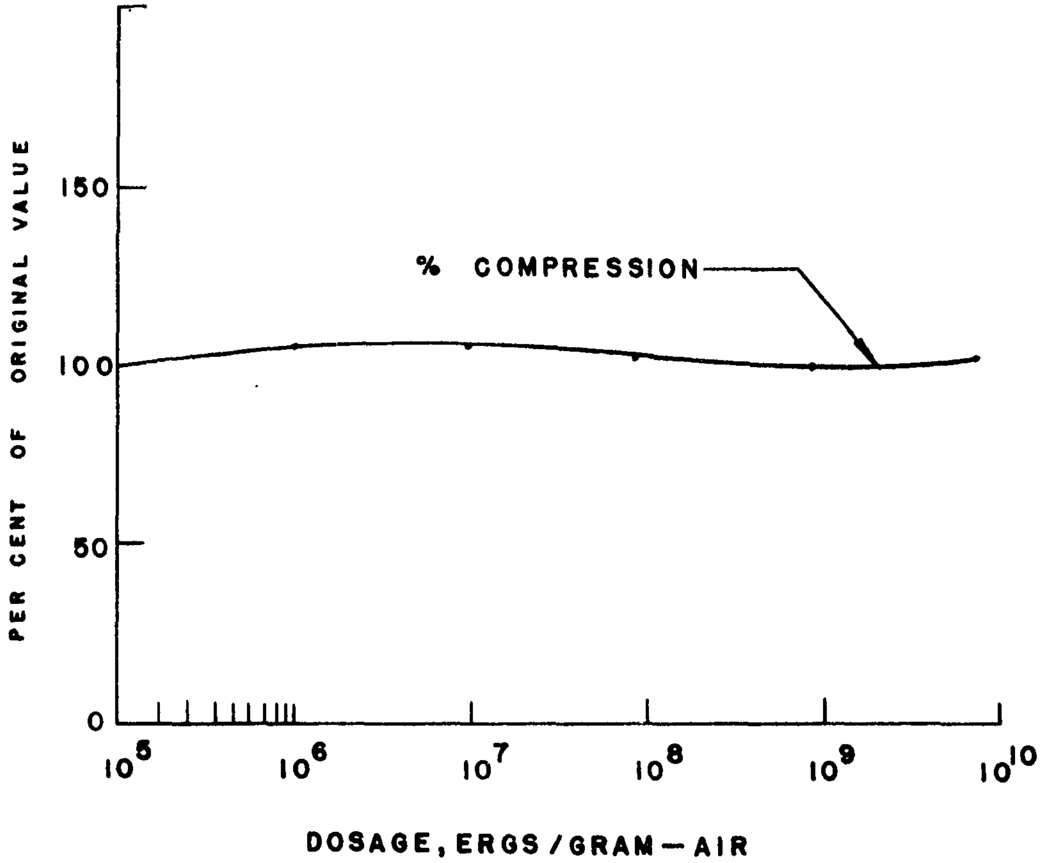

FIG. I EFFECT OF GAMMA RADIATION ON CORK GASKETS PER CENT COMPRESSION

EFFECTS OF NUCLEAR RADIATION ON CORK, LEATHER AND ELASTOMERS

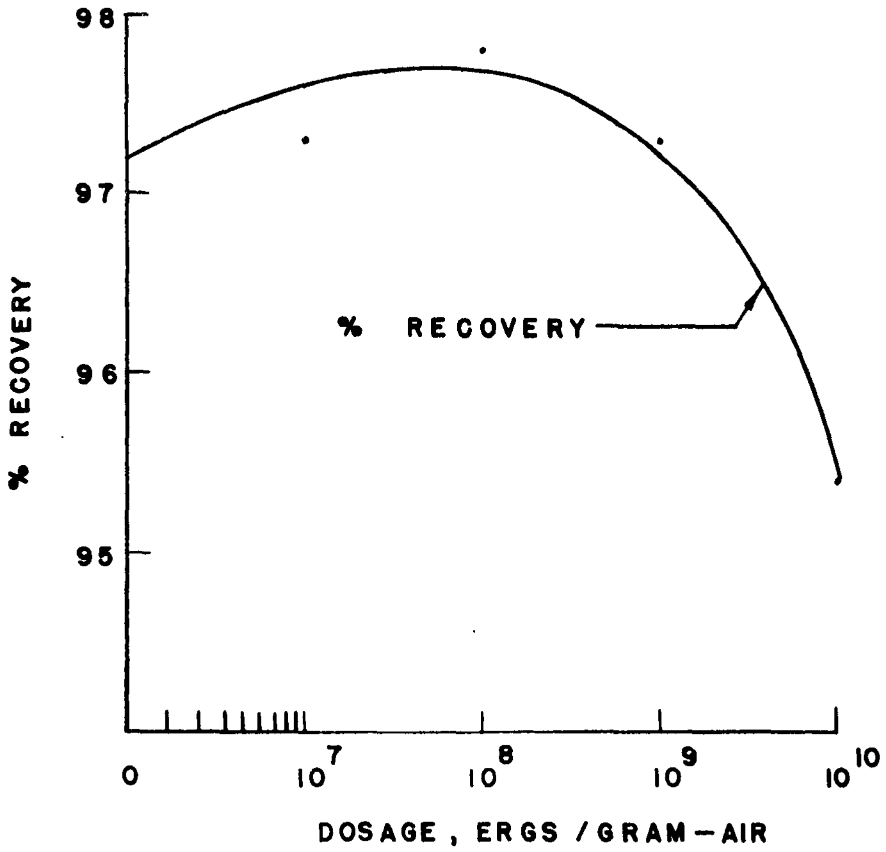

FIG. 2 EFFECT OF GAMMA RADIATION ON CORK. PER CENT RECOVERY

EFFECT OF NUCLEAR RADIATION ON CORK, LEATHER, AND ELASTOMERS

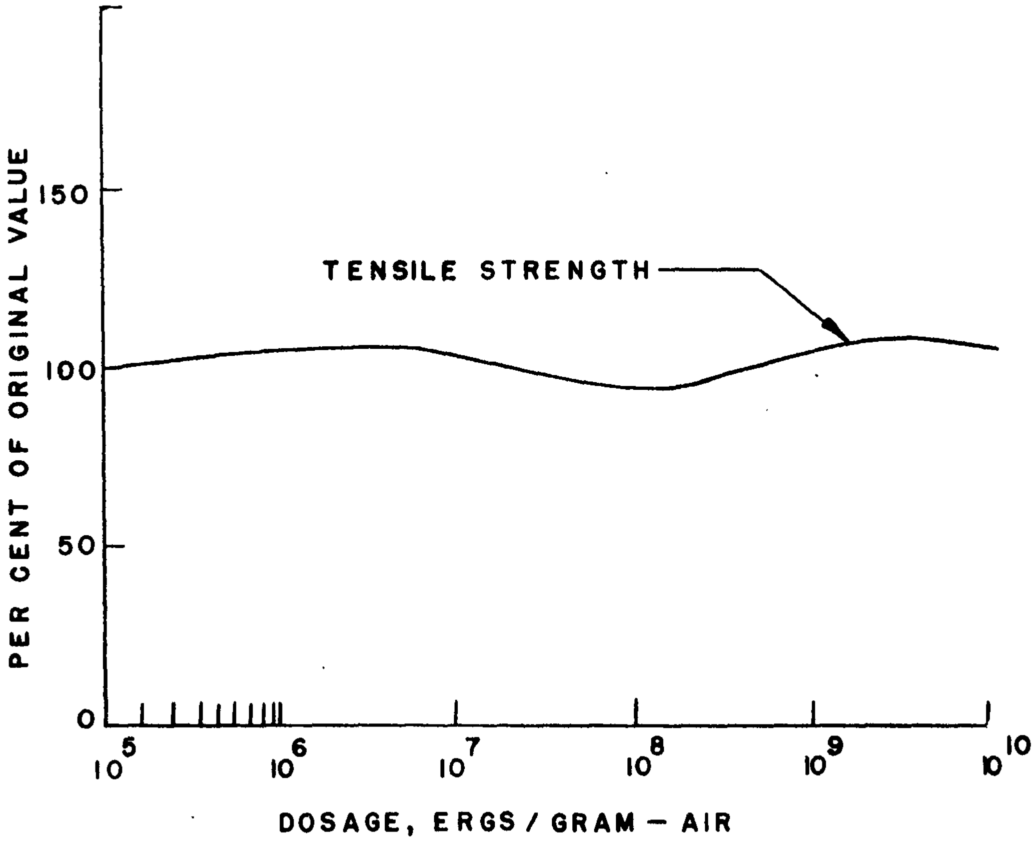

FIG. 3 EFFECT OF GAMMA RADIATION ON CORK GASKETS.

TENSILE STRENGTH

EFFECTS OF NUCLEAR RADIATION ON CORK, LEATHER, AND ELASTOMERS

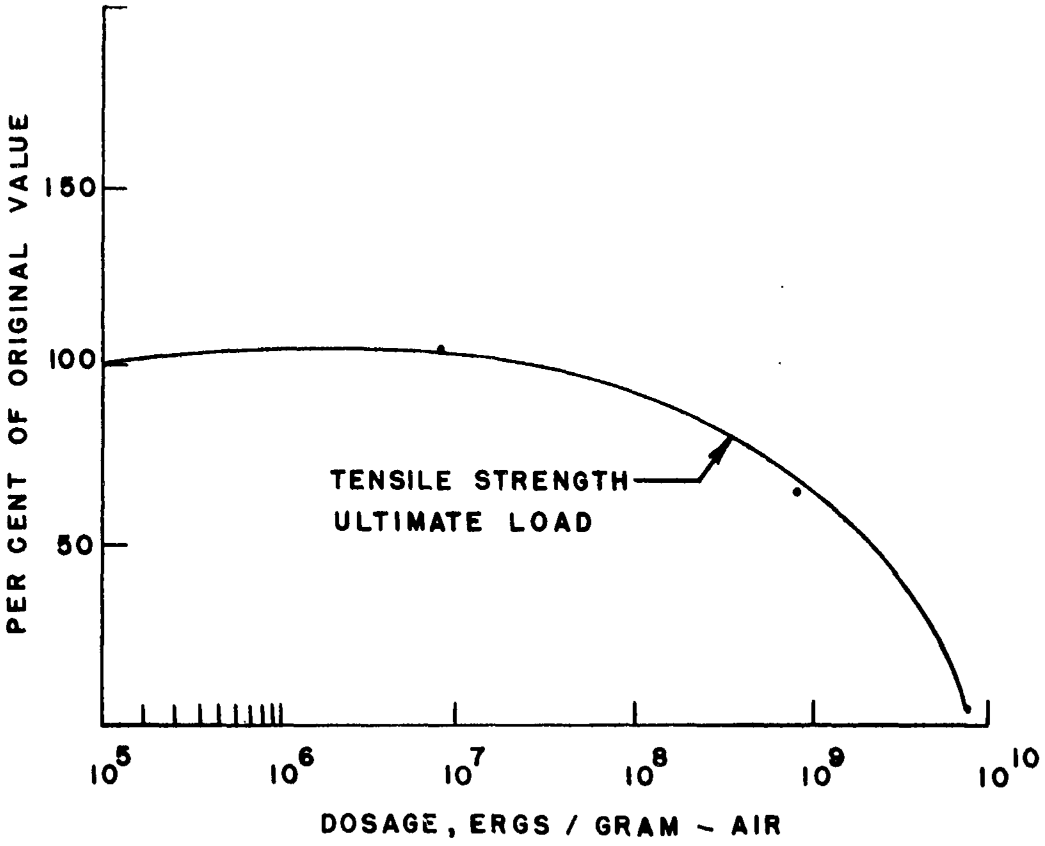

FIG. 4 EFFECT OF GAMMA RADIATION ON LEATHER. HYDRAULIC BACK-UP RINGS

TENSILE STRENGTH, ULTIMATE LOAD

EFFECTS OF NUCLEAR RADIATION ON CORK, LEATHER, AND ELASTOMERS

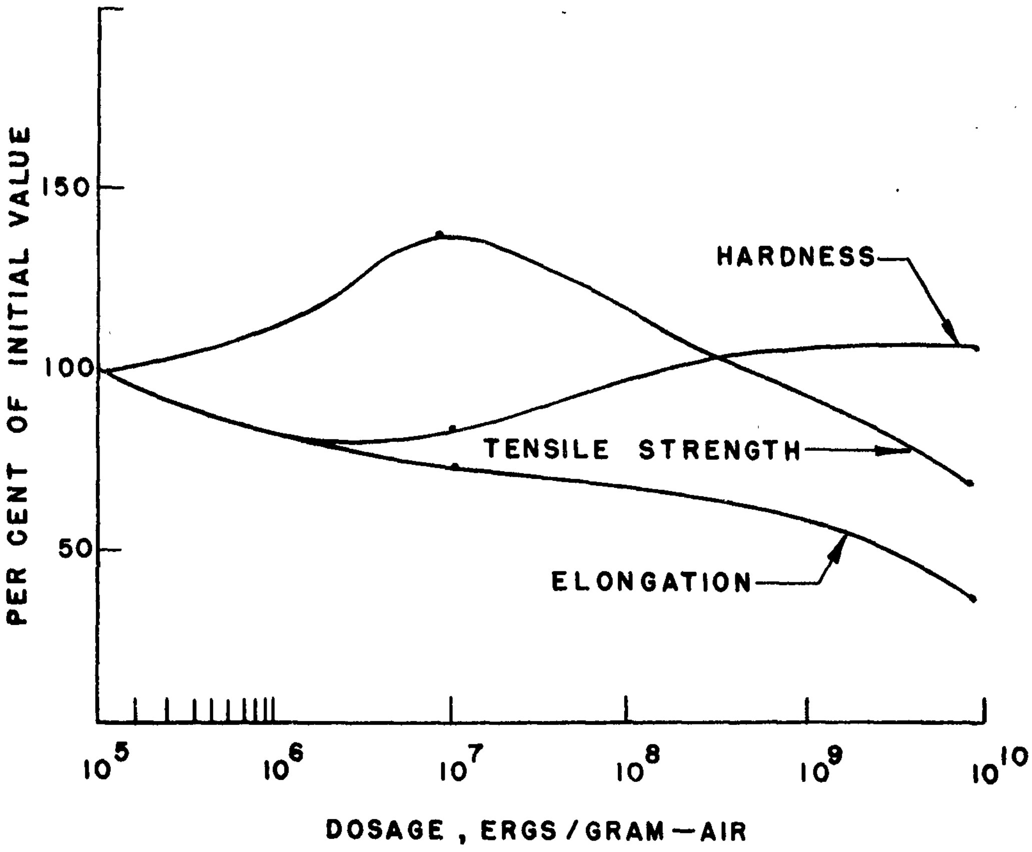

FIG. 5 EFFECT OF GAMMA RADIATION ON VITON—A, ROOM TEMPERATURE TESTS.
HEXAFLUOROPROPYLENEVINYLIDENE FLUORIDE COPOLYMER O-RINGS

EFFECTS OF NUCLEAR RADIATION ON CORK, LEATHER, AND ELASTOMERS

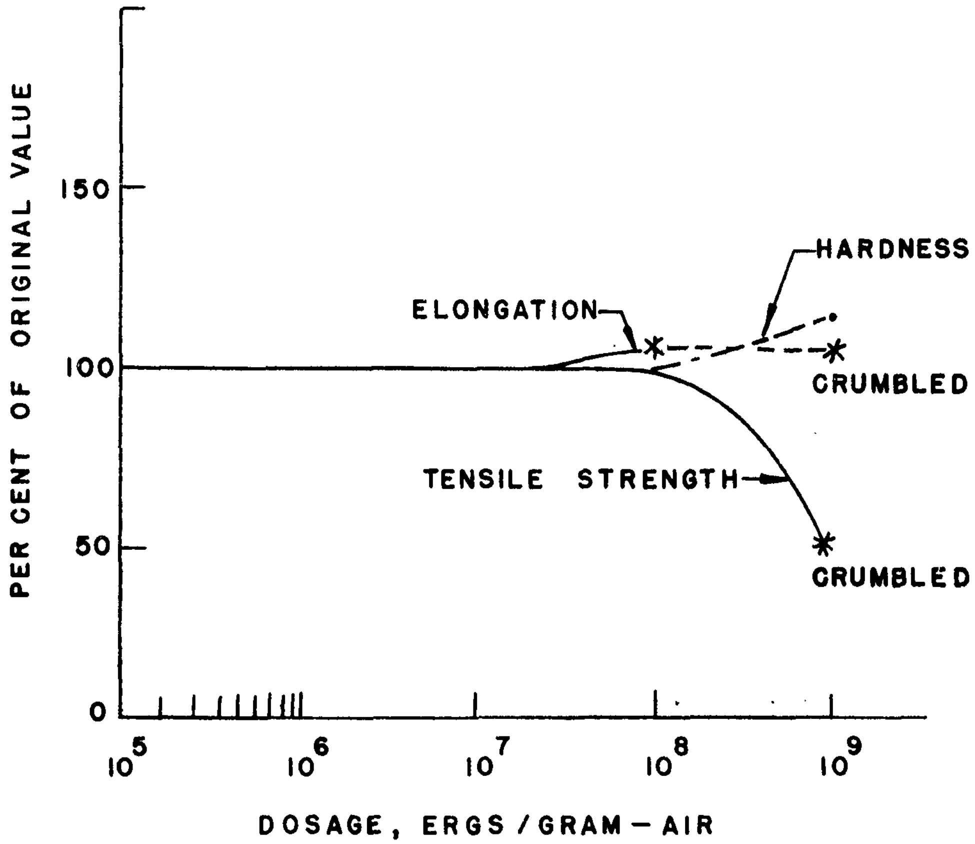

FIG. 6 EFFECT OF GAMMA RADIATION ON SE–551.
ROOM TEMPERATURE TESTS
SILICONE RUBBER O–RINGS.

EFFECTS OF NUCLEAR RADIATION ON CORK,
LEATHER, AND ELASTOMERS

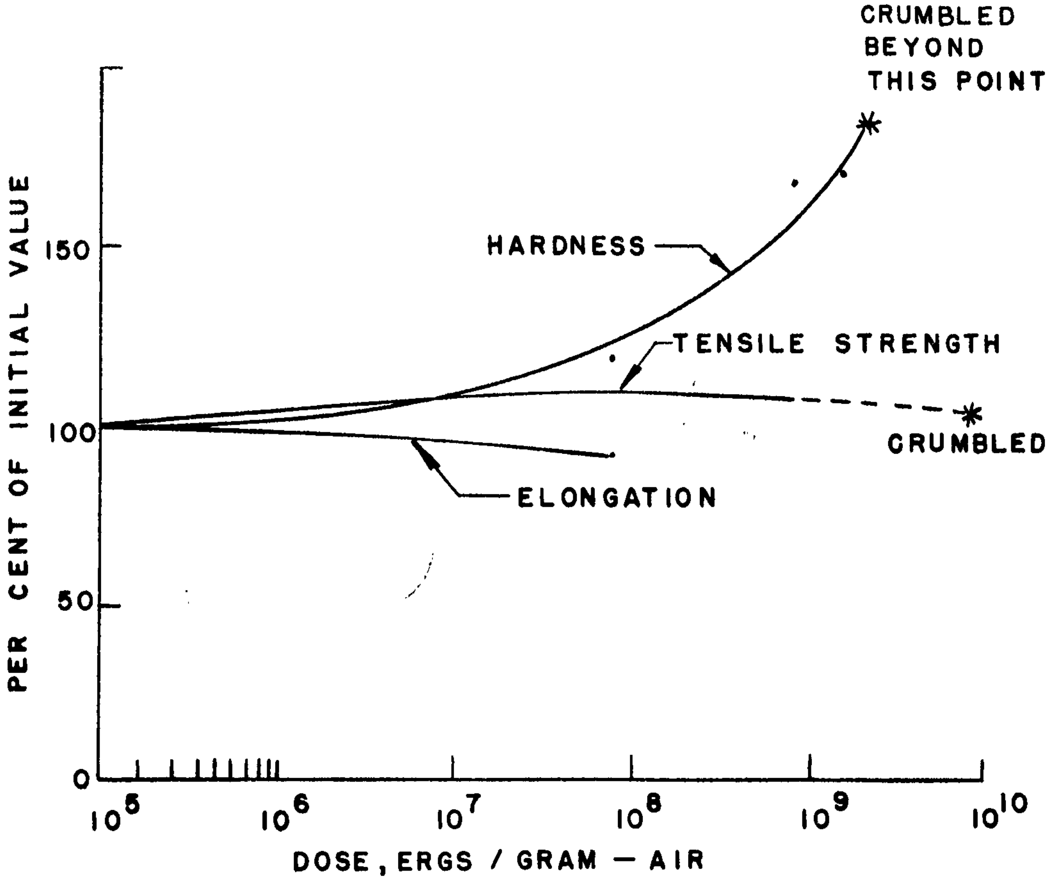

FIG. 7 EFFECT OF GAMMA RADIATION ON SE-371
ROOM TEMPERATURE TESTS.
SILICONE RUBBER O-RINGS

EFFECT OF NUCLEAR RADIATION ON CORK, LEATHER, AND ELASTOMERS

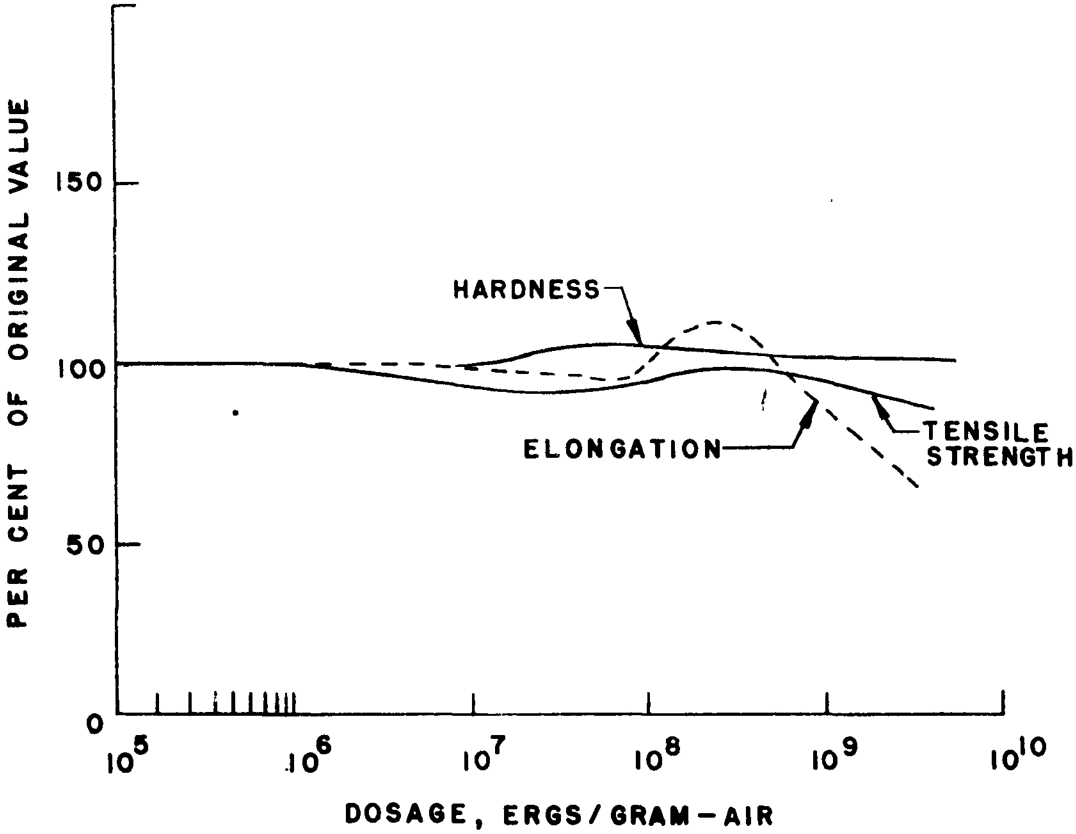

FIG. 8 EFFECT OF GAMMA RADIATION ON HIGH TEMPERATURE THIOKOL

EFFECT OF NUCLEAR RADIATION ON CORK, LEATHER, AND ELASTOMERS

THE PLATE SHEAR METHOD FOR DETERMINING RADIATION EFFECTS ON THE MODULUS OF RIGIDITY OF HONEYCOMB SANDWICH PANELS

by

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A new testing method - the Plate Shear Method - has been developed for obtaining the modulus of rigidity in a mixed radiation field. The Plate Shear Method has proved to be more consistent and more reliable than the Beam Deflection Method. Furthermore, it is adaptable to testing during the irradiation process.

This paper describes the Plate Shear Method, its application, and the remotely controlled equipment required for its application. In particular, it discusses the advantages of the new method in yielding design data on honeycomb sandwich panels being tested for use in a nuclear-powered aircraft.

INTRODUCTION

In the past Convair-Fort Worth has made extensive studies of the effects of radiation on honeycomb core sandwich panels. These studies have been directed toward the effects on both the core material and the various adhesives used for bonding. This discussion will emphasize the techniques of testing these materials rather than the results that have been obtained. Techniques currently in use exhibit large between-specimen variation and physical testing can be carried out only *after* radiation exposure.

Preliminary experiments prove that accurate and consistent micromeasurements for modulus of rigidity data are easily made by the Plate Shear Method. This method lends itself readily to radiation dynamic testing, utilizing simplified remote controls.

DISCUSSION

The most common types of tests used for determining radiation effects on sandwich panels are: compression, tension, flexural strength, and modulus-of-rigidity by the Beam Deflection Method. The control specimens for these tests have consistently had excessive between-specimen variations. These variations exist between specimens cut from the same panel as well or for specimens from different panels.

Preliminary experiments have proven that, with a properly designed test jig, extremely accurate modulus-of-rigidity data can be obtained by the Plate Shear Method. Figure I shows the test jig for applying plate shear load to specimen with a calibrated differential transformer mounted to record total strain versus total shear load. The pulling jaws of the jig have sufficient cross section area, so that elongation of the jaws will be negligible for proposed loads. The roller clamps are needed because the eccentric loading on the test specimen has a tendency to separate the aluminum skin from the Fiberglas core. The differential transformer has a linear variation in output voltage with respect to the position of its movable iron core and is calibrated accordingly. The output of the transformer connects to a digital voltmeter with a printer, thus giving a permanent record of strain for each predetermined shear load. The load is applied to the pulling jaws by a hydraulic jack which may be controlled remotely from a panel in the nuclear reactor control room.

Modulus-of-rigidity data obtained by the Plate Shear Method has proven more consistent and more accurate than by Beam Deflection Method. In the Plate Shear Method the formula is of simpler form, and data measurements are made directly. By definition modulus-of-rigidity may be expressed by

$$G_c = \frac{f_s}{e},$$

where f_s = unit shear force between skin and core in psi (force per unit area of skin in contact with core).

e = unit deformation in inches per inch (total deformation divided by core thickness).

In preliminary testing of Fiberglas honeycomb core impregnated with phenolic resin Hexcel 91LD (3/16-inch cell size and weight of 9.0 lb/ft^3), the variation of G_c was consistently within 500 psi from an average G_c of 35,000 psi. Variation in calculated G_c as great as 10,000 psi are common by the Beam Deflection Method. The accuracy of the Plate Shear Method was not immediately apparent at the beginning of the preliminary testing. For the initial testing of a specimen, the changes in deformation for uniform load intervals were very erratic. If the specimens are subjected to two or three cycles of loading to approximately 30% of their ultimate strength before testing, uniform results are consistently obtained. Pre-stressing the specimens in this manner allows strain relaxation within the bond between the honeycomb core and sandwich skin. Table I indicates typical test data for a test specimen before and after pre-stressing.

The large variations in G_c by the Beam Deflection Method are mostly due as complex formulas which magnify slight errors in data several fold. For example, the difference in reading of the width of a pencil point on stress-strain charts may vary the calculated G_c as much as 5000 psi. Also, these formulas contain experimental constants for the various materials which have a considerable realm of doubt. The general formula is

$$d = \frac{PL^3}{48D} + \frac{PL}{4U},$$

where

d = deflection of panel at mid-point in inches

P = total load in pounds

L = length of span in inches

$$D = \frac{E_f bf(H+c)^2}{8K}$$

and

$$U = \frac{G_c bH(H+c)}{2c},$$

where

E_f = modulus of elasticity of facing material in psi

b = width of panel in inches

f = thickness of facing material in inches

H = panel thickness in inches (including facing)

c = honeycomb core thickness in inches

K = $1 - S^2$ where S is Poisson's ratio of facing material

TABLE I

MODULUS-OF-RIGIDITY DATA - PLATE SHEAR METHOD HEXCEL 91LD FIBERGLAS HONEYCOMB CORE

Loading Cycle	Load in Pounds	Deformation (Mils)	Mils per 500 lb/increment
No. 1	0	0	
	500	0.6	0.6
	1000	2.1	1.5
	1500	2.8	0.7
	2000	4.0	1.2
No. 2	0	0	
	500	0.6	0.6
	1000	1.6	1.0
	1500	2.4	0.8
	2000	3.1	0.7
Nos. 3 thru 5	0	0	
	500	0.6	0.6
	1000	1.2	0.6
	1500	1.7	0.5
	2000	2.3	0.6

and G_c = honeycomb core modulus of rigidity in psi,

The derivation of the general formula is based on the assumption that the loaded test specimen assumes a uniform radius of curvature between its two supports. This is not believed to be strictly true.

The modulus-of-ridigity test jigs developed are readily adaptable to radiation dynamic testing. With the test apparatus set up as described earlier (Fig. 1), complete sets of test data may be taken immediately before, during, and immediately after irradiation of the test specimen. This eliminates the need for post-radiation environmental storage. Also, by taking data at regular intervals during irradiation, damage thresholds may be determined with only one test run. Otherwise, time-consuming test setups are required for each predetermined radiation dose.

CONCLUSION

The Plate Shear Method is much more accurate and reliable than the Beam Deflection Method for determining possible radiation effects on modulus-or-rigidity of sandwich panels. Due to the between-specimen variation and magnification of experimental errors by complex formulas, radiation effects may not be detected by the latter method. The computations and test procedures for the Plate Shear Method are comparatively simple. Also, extremely accurate data is obtainable, provided the test specimens are prestressed to allow strain relaxation. The test jigs with simplified remote controls are readily adaptable to irradiation dynamic testing and the revised test techniques eliminate the requirements for environmental handling and storage. Only one irradiation test run may be required to determine threshold damage with the dynamic testing procedure.

HONEYCOMB TEST GAUGE

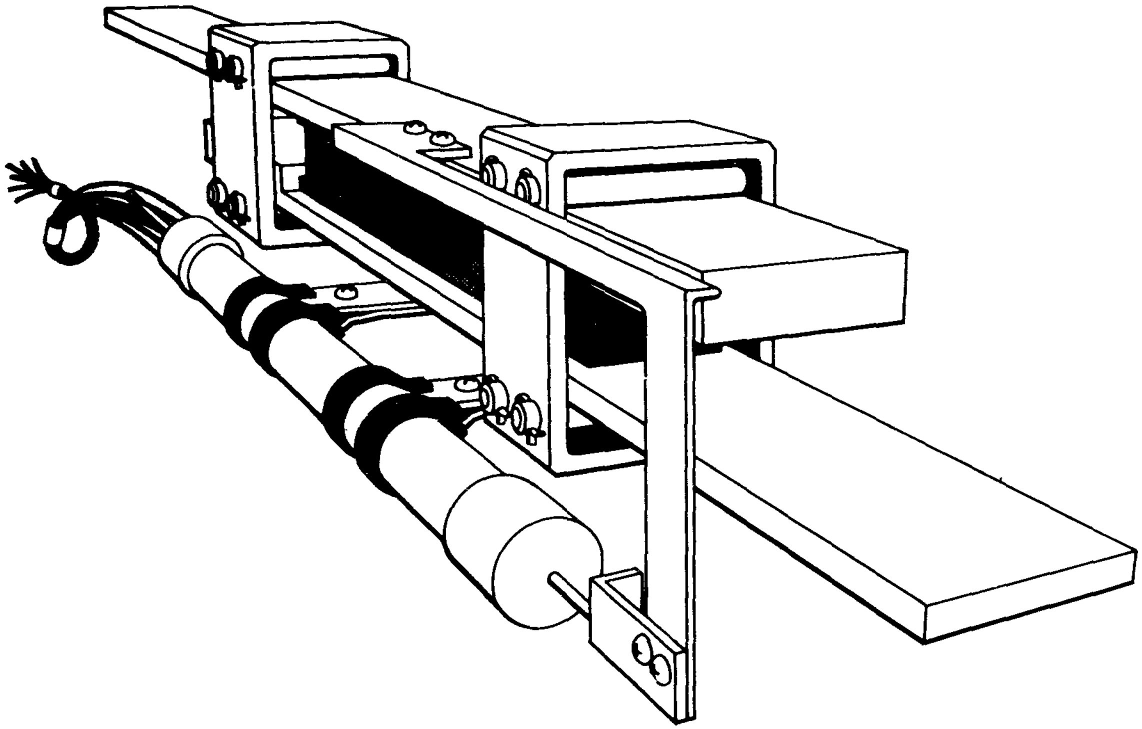

FIGURE 1

"O" RING TESTING IN A MIXED FIELD IRRADIATION

by

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This report describes work directed toward the development of "O" rings that are resistant to the combined effects of radiation, fluid, temperature and pressure. This work is in two parts, screening of existing compounds, and actuator seal tests.

In the screening tests aircraft "O" ring compounds were compared to control samples to determine the percent damage.

For the actuator seal tests, equipment was built to simulate "O" ring seal conditions. This equipment gives information on the sealing ability of "O" rings in actual working conditions.

Compounds that were least effected in the screening test were tested in the actuator seal test. The most promising material tested was Parco 363, a neoprene WT rubber.

Present work on this program is being directed toward development of testing techniques to give a more accurate environment for the screening tests. In addition testing will be done in the development of a more radiation resistant "O" ring.

This paper was not available for publication.

RADIATION EFFECTS ON 23 SILICONE RUBBERS AT AMBIENT TEMPERATURE

by

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Convair-Fort Worth has conducted screening tests on 23 silicone rubbers, irradiated at three temperatures and four fluxes. The Ground Test Reactor was used. The information obtained to date is from tests conducted during February and March 1957 (MCI-4). Standard physical tests were performed.

The materials were obtained from Dow Corning, General Electric, and Union Carbide. The materials found to be the most radiation resistant were: Silastic 7-170, SE 381, Silastics 2048 and 80, and 81641 (GE). There was a definite correlation between the filler content and the damage, with the percent damage varying inversely with the percent filler.

INTRODUCTION

Convair-Fort Worth is conducting tests to determine the effects of radiation on silicone rubbers and other types of elastomers. The radiation tests are performed at various temperatures and environments using the Ground Test Reactor. The information covered in this report is from tests conducted on 23 silicone rubbers during February-March 1957 and concerns ambient temperature irradiations at four exposure levels. These silicone rubbers were submitted to Convair by Dow Corning, General Electric and Union Carbide. The materials are being screened for radiation resistance. Both dynamic-irradiation and post-irradiation tests are being performed.

The material investigations are separated into three phases in support of experimentation toward developing materials resistant to radiation: (1) experimental screening of materials of interest to determine their radiation resistance and to provide design data; (2) environmental tests designed to determine the interdependence of radiation and environmental effects; and (3) theoretical studies to determine the basic mechanisms of radiation damage.

The tests reported in this paper are part of Phase I, as shown above, and include irradiation at ambient temperature and air environment, at four integrated fluxes.

CONCLUSIONS

There was no evidence in the tests performed that any one of the three principle groups of silicone rubbers (dimethyl, methyl phenyl, and methyl vinyl) is more resistant to reactor irradiation than the other two. The fluorinated type is not resistant to radiation, as would be expected.

There is strong correlation between the silica filler content and the extent of radiation damage. In two of the properties this correlation could be expressed mathematically:

Tear Strength: $\delta = 1.73 \quad -35$

Elongation: $\delta = 1.10 \quad -19$

Where: $\delta = \%$ of original property

And $f = \%$ filler

Apparently the strength supplied by the mechanical bonding of the filler particles to siloxane chains is less subject to degradation under radiation than the covalent bonding in the polymer itself. If siloxanes can be made in such a way that satisfactory hardness and other properties can be maintained while using a high filler content, then the material should have an improved radiation resistance.

The materials with the best radiation resistance of the twenty-three screened in this test were SE 381 and DC 7-170. The poorest material was LS-53. There were no standouts among the remaining twenty rubbers, but DC 2048, DC 80, and 81641 were considered the three best in the tests performed.

Standard post-irradiation tests are acceptable for screening a variety of materials. However, these tests do not give complete design data nor do they give much insight as to the mechanisms of the radiation damage. Convair-Fort Worth is testing materials in application tests (Ref. 4) and in other dynamic tests simulating aircraft conditions. As indicated in the two special tests, irradiation under stress gives more sensitive detection of changes than post-irradiation tests. Increased emphasis is being placed on modulus and other measurements made on stressed samples during irradiation.

MATERIALS AND PROCEDURES

Materials

Silicone rubbers manufactured by the three leading companies in this field were irradiated. The material, class, and manufacturer are shown in Table I. [*]The composition and type of gum stock are given in Table II. For the sake of brevity, the prefix "DC" is used throughout this report in place of the trade name "Silastic" for the Dow Corning rubbers.

Physical Testing Procedures

With two exceptions, engineering properties were determined after irradiation by standard physical methods. The tests conducted were as follows:

a.	Tensile Strength and Elongation	ASTM D412-51T, Die C
b.	Tear Strength	ASTM D624-54T, Die B
c.	Low-Temperature Brittleness	ASTM D736-54T, Tensile Die C
d.	Hardness (Shore "A")	ASTM D676-55T Instant Reading

[*] See author's note added in print, page 39.

TABLE I

MATERIALS USED

Materials	Class	Manufacturer
1. DC-50	General Purpose	(Materials No. 1-11, Dow Corning Corp., Midland, Michigan)
2. LS-53	Fuel and Oil Resistant	
3. DC-80	General Purpose	
4. DC-152	General Purpose	
5. DC-250	Extreme Temperature	
6. DC-675	Extreme Temperature, Low Compression Set, Low Shrinkage	
7. DS-2048	General Purpose	
8. DC-6-127	Extreme Temperature	
9. DS-6162C(651)	Low Compression Set	
10. DS-6508	General Purpose	
11. DC-7-170	Low Compression Set	
12. SE-361	Low Compression Set	(Materials No. 12-20, General Electric Co., Silicone Products Dept., Waterford, New York)
13. SE-371	Low Compression Set	
14. SE-381	Low Compression Set	
15. SE-450	General Purpose	
16. SE-551 A	Extreme Low Temperature, Low Shrinkage	
17. SE-750	Extreme High Temperature	
18. SE-751	Extreme High Temperature	
19. 81640(SE452)	Low Compression Set	
20. 81641(SE482)	Low Compression Set	
21. Y-1631	Low Temperature	(Materials No. 21-23, Union Carbide and Carbon Corp., Silicones Div., Tonawanda, New York)
22. Y-1632	Experimental - Low Temperature	
23. Y-1633 (improved version produced as XK1205)	Low Temperature	

TABLE II

COMPOSITION OF MATERIALS USED

Material	Composition	Percent
1. DC-50 (Dimethyl) 24/480 post cure	401 Gum Silica	69.1 27.3
2. DC-80 (Dimethyl) 24/480 post cure	401 Gum Silica	64.8 32.1
3. DC-7-170 (Dimethyl) 24/480 post cure	Gum Silica	52.5 48.0
4. DC-152 (Dimethyl) 24/480 post cure	Gum Silica	67.7 30.6
5. DC-250 (Dimethyl & Phenyl Methyl) 24/480 post cure	Gum Silica	69.5 27.1
6. DC-675 (Dimethyl & Phenyl Methyl) 12/480 post cure	Gum Silica	63.6 35.4
7. DC-2048 (Dimethyl & Phenyl Methyl) 4/480 post cure	Gum Silica	63.5 33.6
8. DC-6-127 (Dimethyl & Phenyl Methyl) 24/480 post cure	Gum Silica	70.2 28.0
9. DC-6162C (Dimethyl & Phenyl Methyl) 12/480 post cure	Gum Silica	70.3 28.5
10. DC-6508 (Dimethyl & Phenyl Methyl) 1/480 post cure	Gum Silica	78.6 21.4
11. LS-53 (Methyl Trislurro propyl 24/300 post cure	Gum Silica	76.9 22.3
12. SE-361 (Methyl Vinyl) 24/480 post cure	SE-33 Gum Silica	56 44
13. SE-371 (Methyl Vinyl) 24/480 post cure	SE-33 Gum Silica	50 50
14. SE-381 (Methyl Vinyl) 24/480 post cure	SE-33 Gum Silica	43 57
15. SE-450 (Dimethyl) 24/480 post cure	SE-76 Gum Silica	67 33
16. SE-551 A (Methyl Phenyl) 24/480 post cure	SE-52 Gum Silica	67 33
17. SE-750 (Dimethyl) 24/480 post cure	SE-30 Gum Silica	67 33
18. SE-751 (Methyl Vinyl) 24/480 post cure	SE-33 Gum Silica	67 33
19. 81640 (Methyl Vinyl) 24/480 post cure	SE-33 Gum Silica	67 33
20. 81641 (Methyl Vinyl) 24/480 post cure	SE-33 Gum Silica	59 41
21. Y-1631 (Methyl Phenyl, 10% Phenyl) 24/480 post cure	Gum Silica	69 31
22. Y-1632 (Methyl Phenyl, 20% Phenyl) 24/480 post cure	Gum Silica	69 31
23. Y-1633 (Methyl Phenyl, 10% Phenyl) 24/480 post cure	Gum Silica	69 31

The exceptions mentioned above are two special tests performed to determine the effect of radiation on samples which were stressed while being irradiated. The first test, constant deflection compression set, was run on two types of silastics: DC 7-170 and DC 250. The method used is a modification of ASTM D395-55, Method B. Samples were compressed 25 percent and 50 percent in a constant deflection compression jig. Both control and irradiated samples were maintained under compression for 30 hours at an elevated temperature. The thicknesses were measured 30 minutes after removal from the test jigs.

The second special test consisted of determining the permanent set of tensile specimens maintained at 50 percent elongation during irradiation. Permanent set was measured 30 minutes after removal from the test jigs. Ultimate strength was determined on the samples after completion of the special tests. This test was performed on one Silastic only, LS-53.

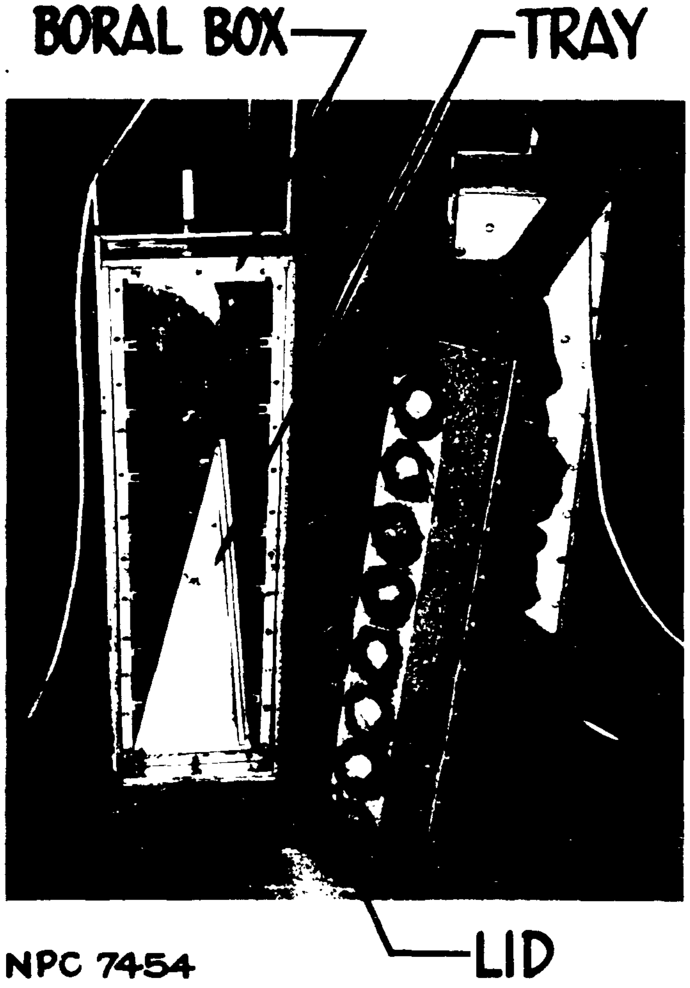
Statistical Analysis Procedures

Standard statistical methods were used in evaluating the data. A maximum of five specimens were tested for each condition of irradiation as well as for the controls. The significance of deviations between the irradiated and non-irradiated sample means was determined at the 95 percent confidence interval. This interval may be defined as the range of the plus and minus deviations from the observed difference which included the true difference 95 percent of the time. If the confidence interval of a specific example included zero, there is no assurance that a true difference exists. Correlations between damage and other variables were made using the method of least squares. Low-temperature brittleness was determined on two specimens. In the event one specimen passed and the other failed, two other specimens were tested.

Irradiation Procedures

The sample mounting procedures and irradiation equipment are shown in Figures 1 and 2. All samples were mounted normal to the reactor flux in such a way that none of the samples were shielded by the other samples. The boral covered irradiation chambers were placed under water beside the reactor. Four inches of water separated the boxes from the reactor core. This irradiation took place during February 1957 at Convair-Fort Worth.

SPECIMEN MOUNTING



NPC 7454

SPECIMEN LAYOUT
(NOTE COLOR CHANGE AT HIGHER FLUX)

FIGURE 1

BORAL SAMPLE BOX IRRADIATION

NPC 1681

FIGURE 2

Four different doses were obtained by adjusting the GTR power level and the radiation time. The exposures covered four decades of integrated power as follows:

Exposure	Power Level (kw)	Time (Hours)	Ambient Temp. of Samples (°F)
1	10	1	75
2	100	1	75
3	100	10	85
4	500	20	150

The last column is the approximate temperature of the samples during radiation. The temperature inside the boxes was not monitored but was estimated from temperature measurements made at a later date.

Dosimetry

The neutron flux values were determined from bare and 20 mil cadmium covered gold foils (2 mil thick) and 3 gm sulfur tables. Gamma dose measurements were made with chemical (tetrachloroethylene) dosimeters.

The Standardization Committees at Convair-Fort Worth and WADC (WADC-TN-57-207) recommend the gamma dose be reported in ergs per gram absorbed in carbon. Neutron flux for sulfur is reported as the number of neutrons/cm^2-sec above the "effective threshold" of the dosimeter. The threshold for sulfur is 2.9 Mev. Gold foil data are reported as the epicadmium flux, the neutrons/cm^2-sec above the cadmium cutoff,which is 0.48 ev.

The gamma chemical dosimeters consist of 0.8 ml tetrachloroethylene containing 3 gm/liter Ionol overlayed with 0.2 ml water containing 16 mg/liter chlorophenol red indicator flame sealed in siliconed neutraglas ampules. These ampules are enclosed in 10 mil of lead. The dosimeters are calibrated with a cobalt 60 source. The gamma dose in R is multiplied by a factor of 87.7 to get ergs/gm (C).

The average integrated neutron fluxes and the incident gamma doses for the four exposures are listed in Table III.

TABLE III

INTEGRATED NEUTRON FLUX

Exposure No.	Epicadmium (>0.48 ev)	Fast (>2.9 Mev.)	Gamma ergs/gm(C)	n/γ Ratio (Rem Basis)
1	3.48(12)	1.01(12)	1.01(7)	1.03
2	3.46(13)	9.73(12)	1.00(8)	1.03
3	3.04(14)	9.00(13)	7.42(8)	1.03
4	3.19(15)	9.14(14)	9.00(9)	1.04

The exact flux received by each sample varied according to the location of the samples. These values were used to establish the curves showing the results of each physical test (Figs. 3-22). The aggregate uncertainties in the dosimetry values are as follows:

gold	± 38%
sulfur	± 41%
gamma	± 42%

The uncertainty is increased in the process of combining neutrons and gammas, as was necessary to plot curves. The addition was based on tissue dose techniques, converting neutron and gamma values to rem. The use of this technique should not be interpreted as meaning 10^8 rems will cause the same damage whether from neutrons or gammas.

RESULTS

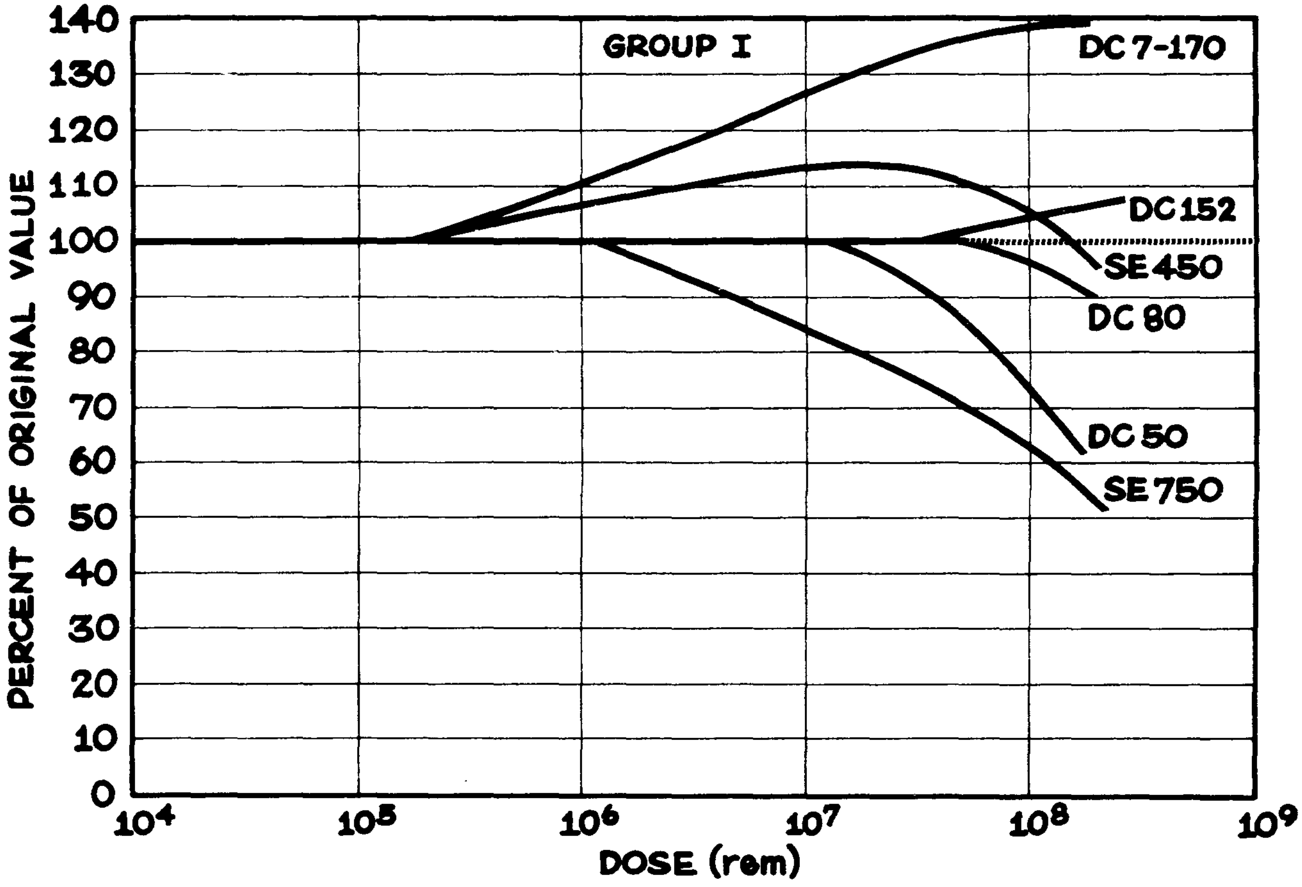
Standard Physical Tests

The results of the physical tests are presented in Figures 3 through 22. Each physical property is plotted for a series of related silicone rubbers. The materials were divided into groups according to the molecular structure of the silicone gum stock. It was felt that the best comparison between materials could be made in this way.

The groups are as follows:

Group 1	Dimethyl siloxanes
Groups 2 and 3	Methyl phenyl siloxanes
Group 4	Methyl vinyl siloxanes
Group 5	Methyl trifluoropropyl siloxanes (one only)

TENSILE STRENGTH DIMETHYL SILOXANE



NPC 7442

FIGURE 3

TENSILE STRENGTH METHYL PHENYL SILOXANE

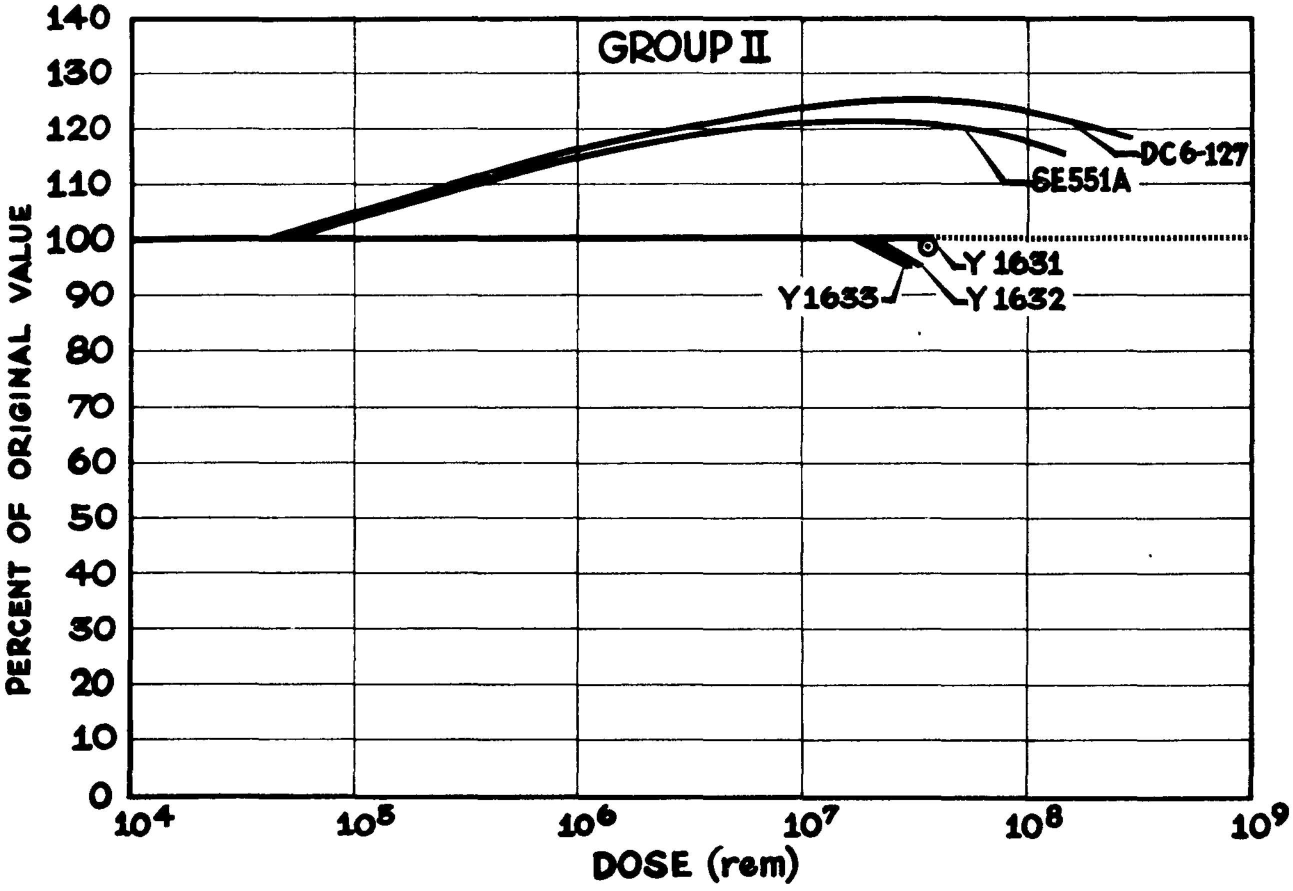


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FIGURE 4

TENSILE STRENGTH METHYL PHENYL SILOXANE

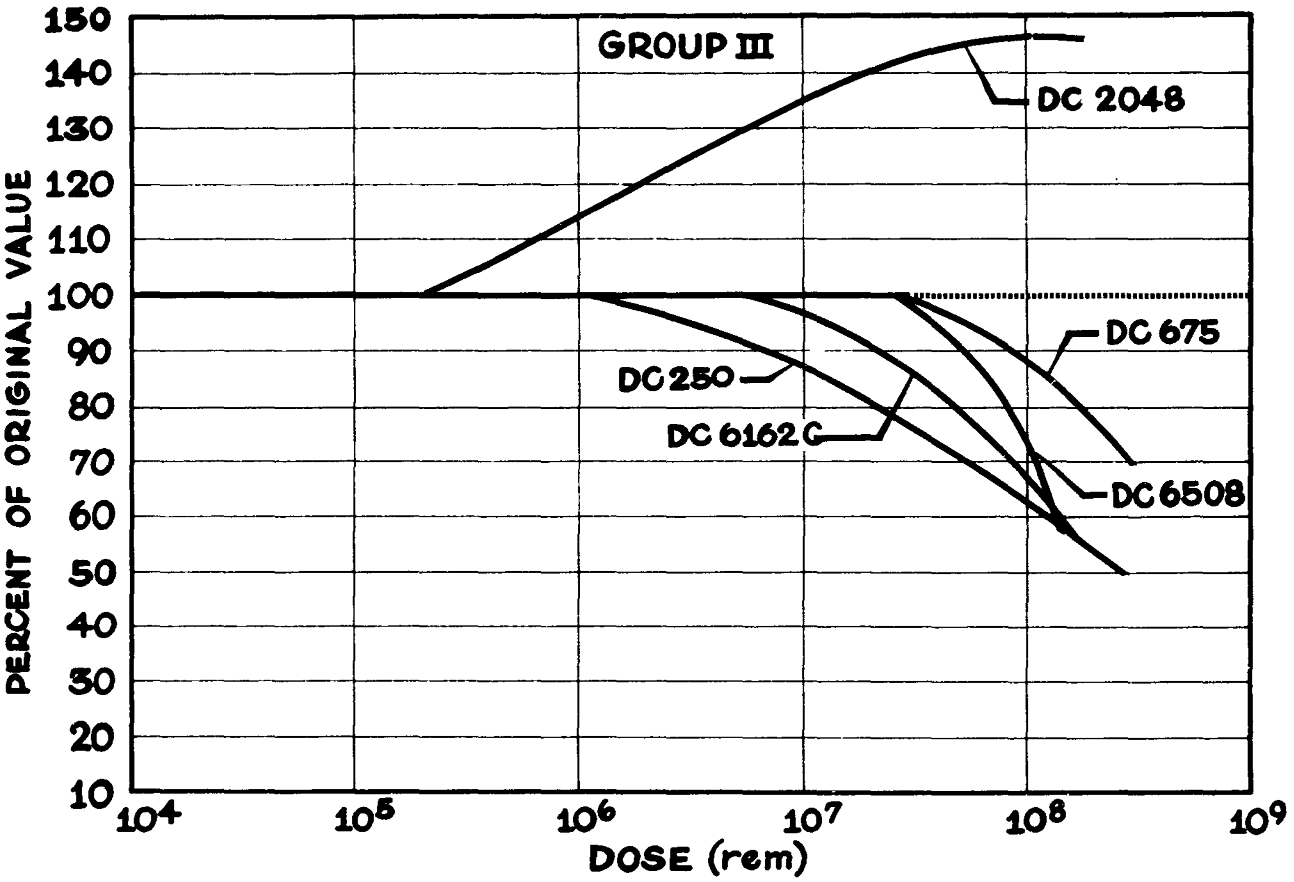

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FIGURE 5

TENSILE STRENGTH METHYL VINYL SILOXANE

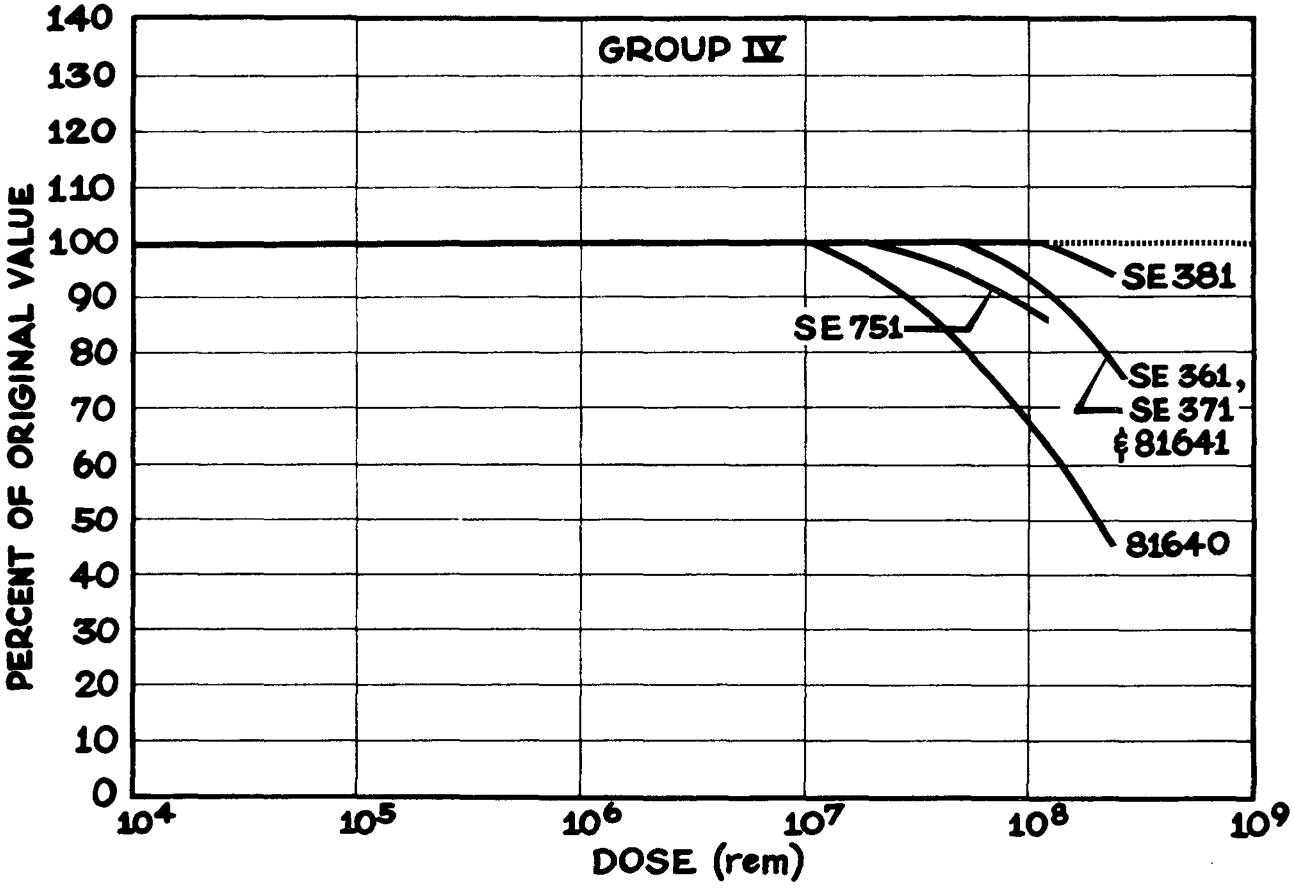

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FIGURE 6

TENSILE STRENGTH METHYL TRIFLUOROPROPYL SILOXANE

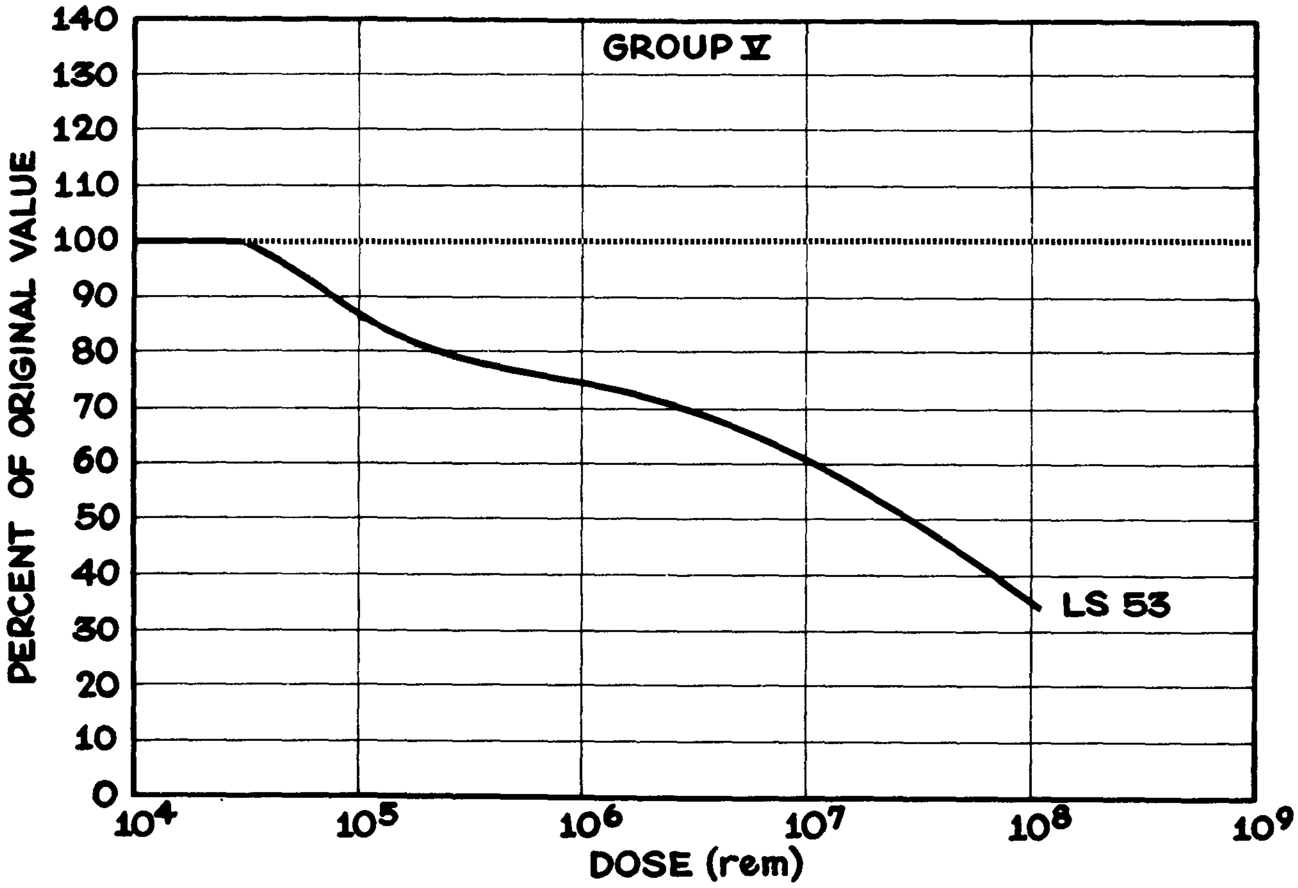

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FIGURE 7

PERCENT ELONGATION DIMETHYL SILOXANE

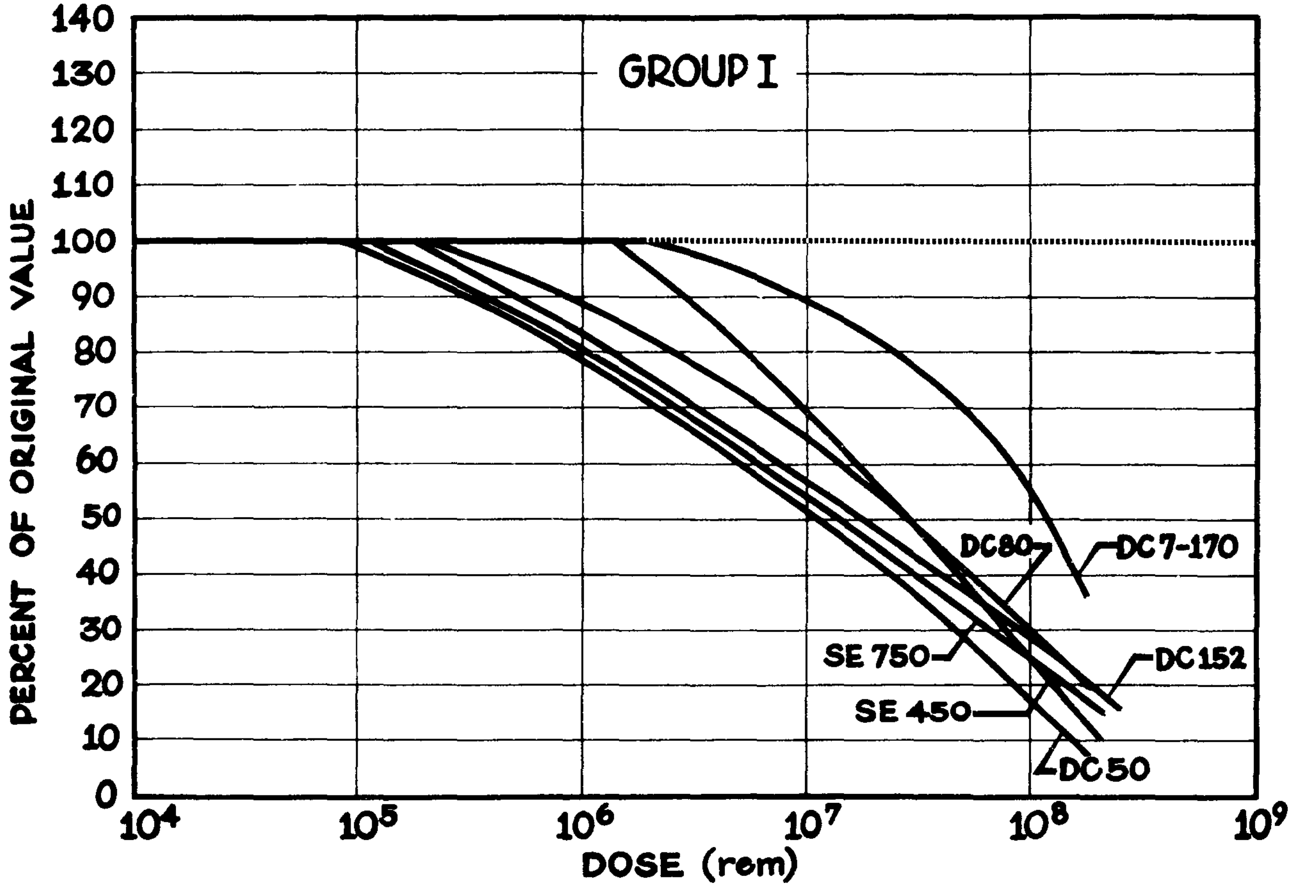

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FIGURE 8

PERCENT ELONGATION METHYL PHENYL SILOXANE

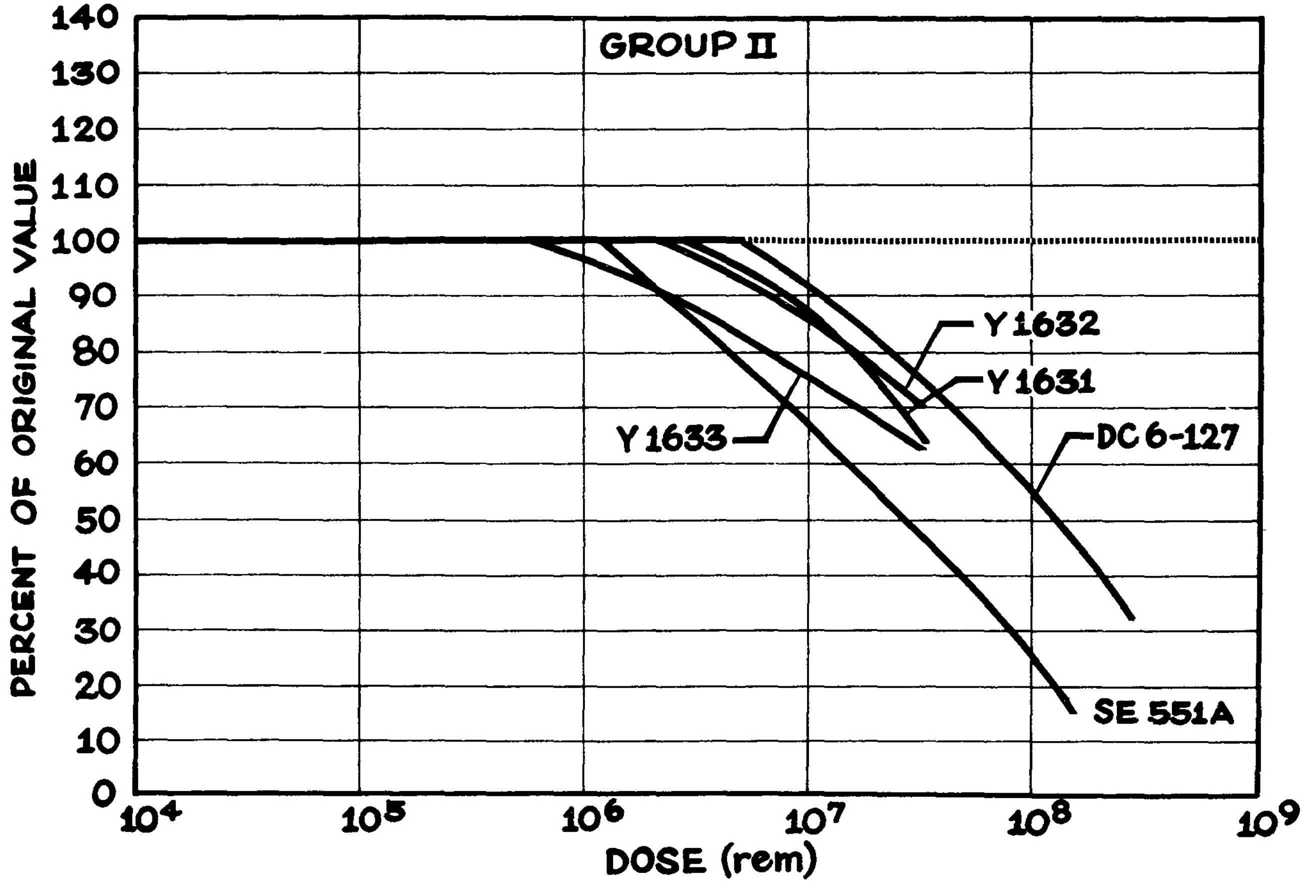

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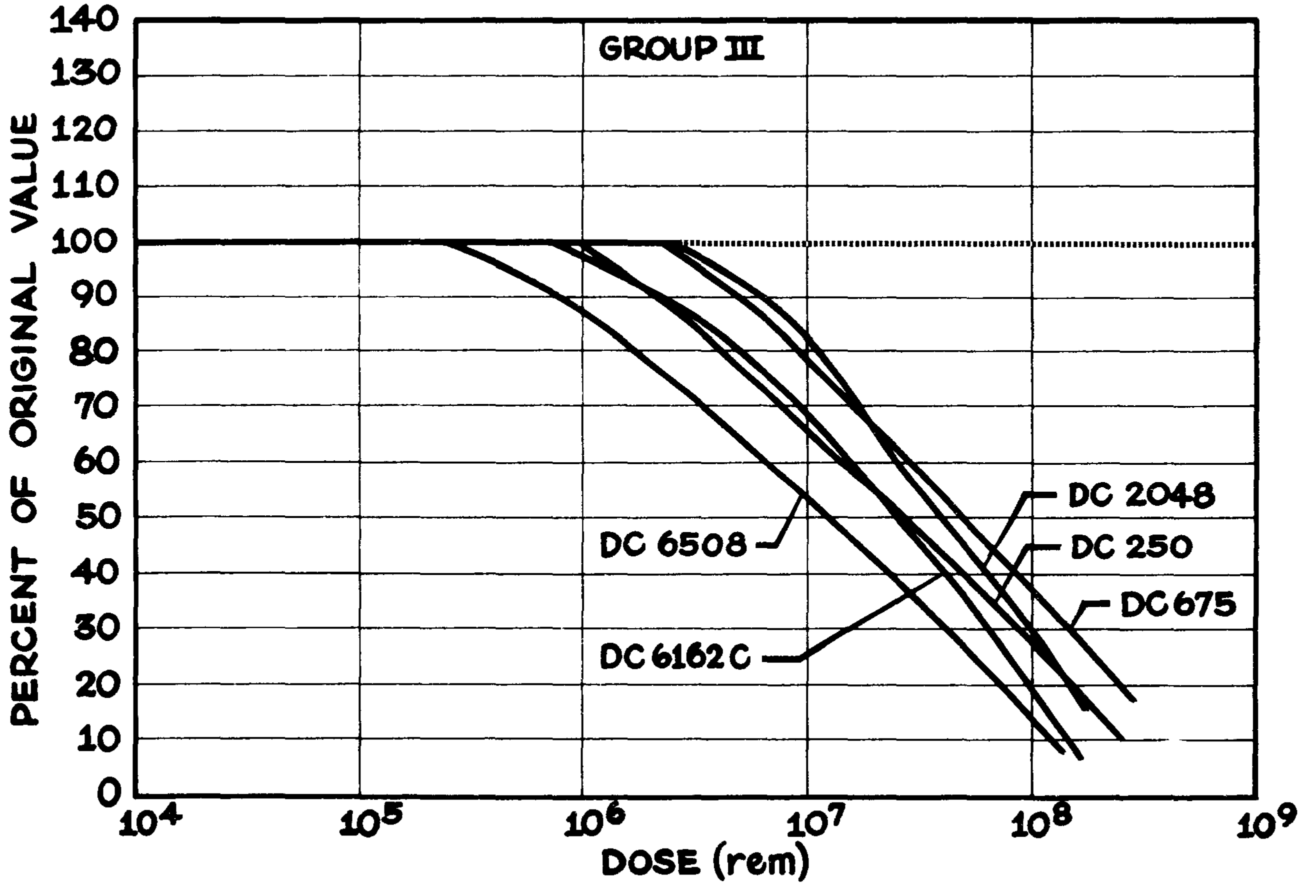
FIGURE 9

PERCENT ELONGATION METHYL PHENYL SILOXANE



NPC 7456

FIGURE 10

PERCENT ELONGATION METHYL VINYL SILOXANE

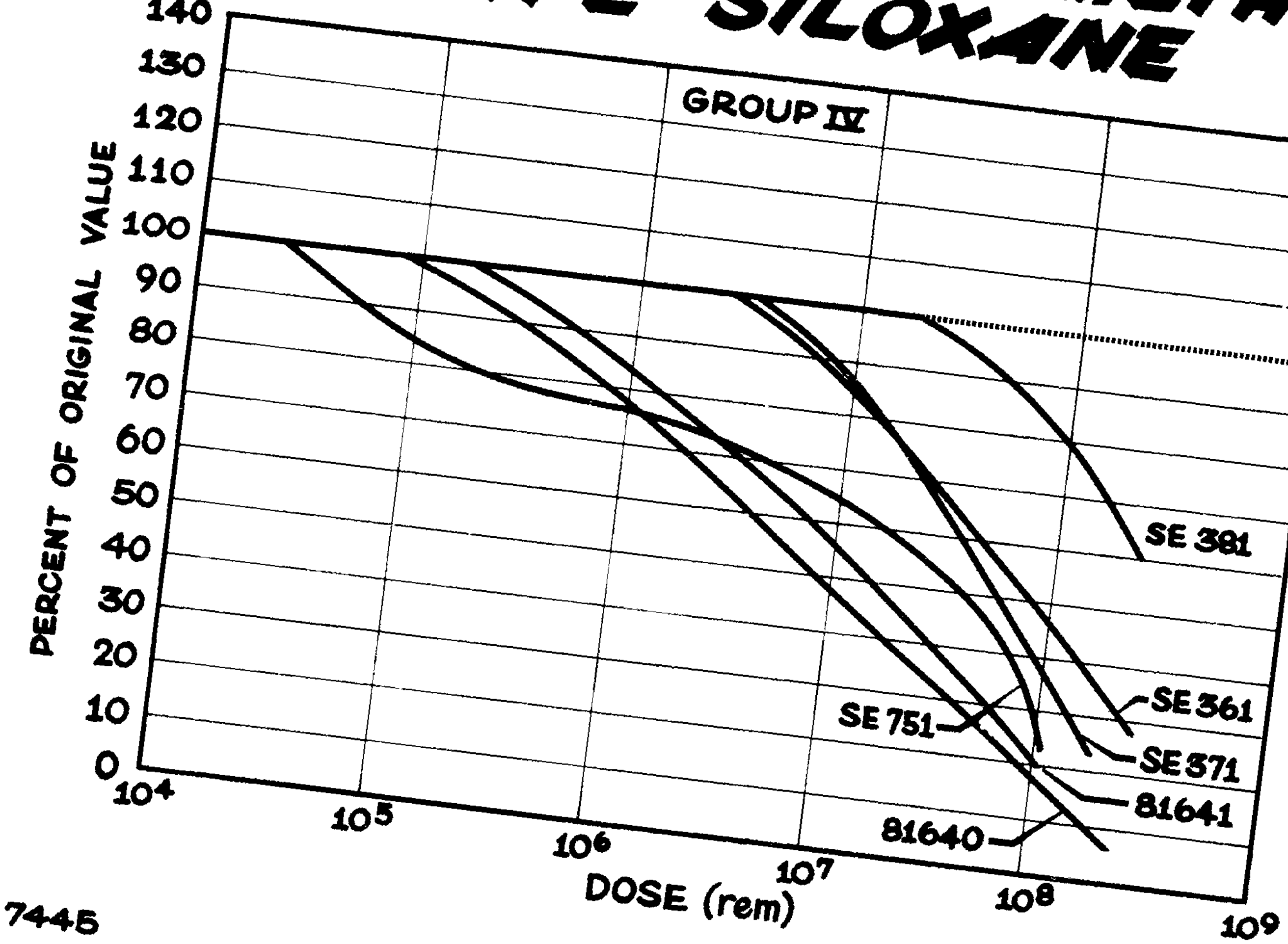


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FIGURE 11

PERCENT ELONGATION METHYL TRIFLUOROPROPYL SILOXANE

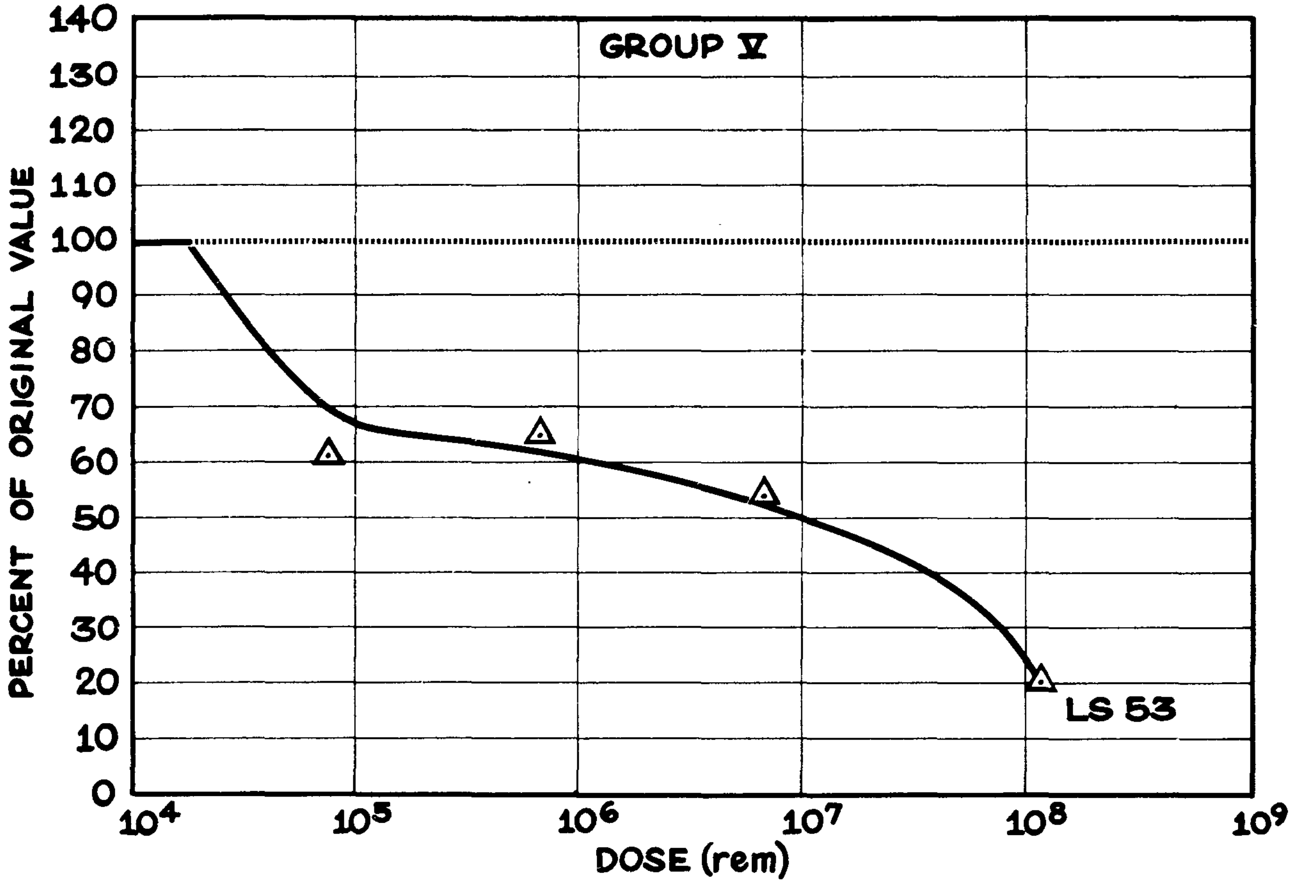

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FIGURE 12

TEAR STRENGTH IN LBS/INCH DIMETHYL SILOXANE

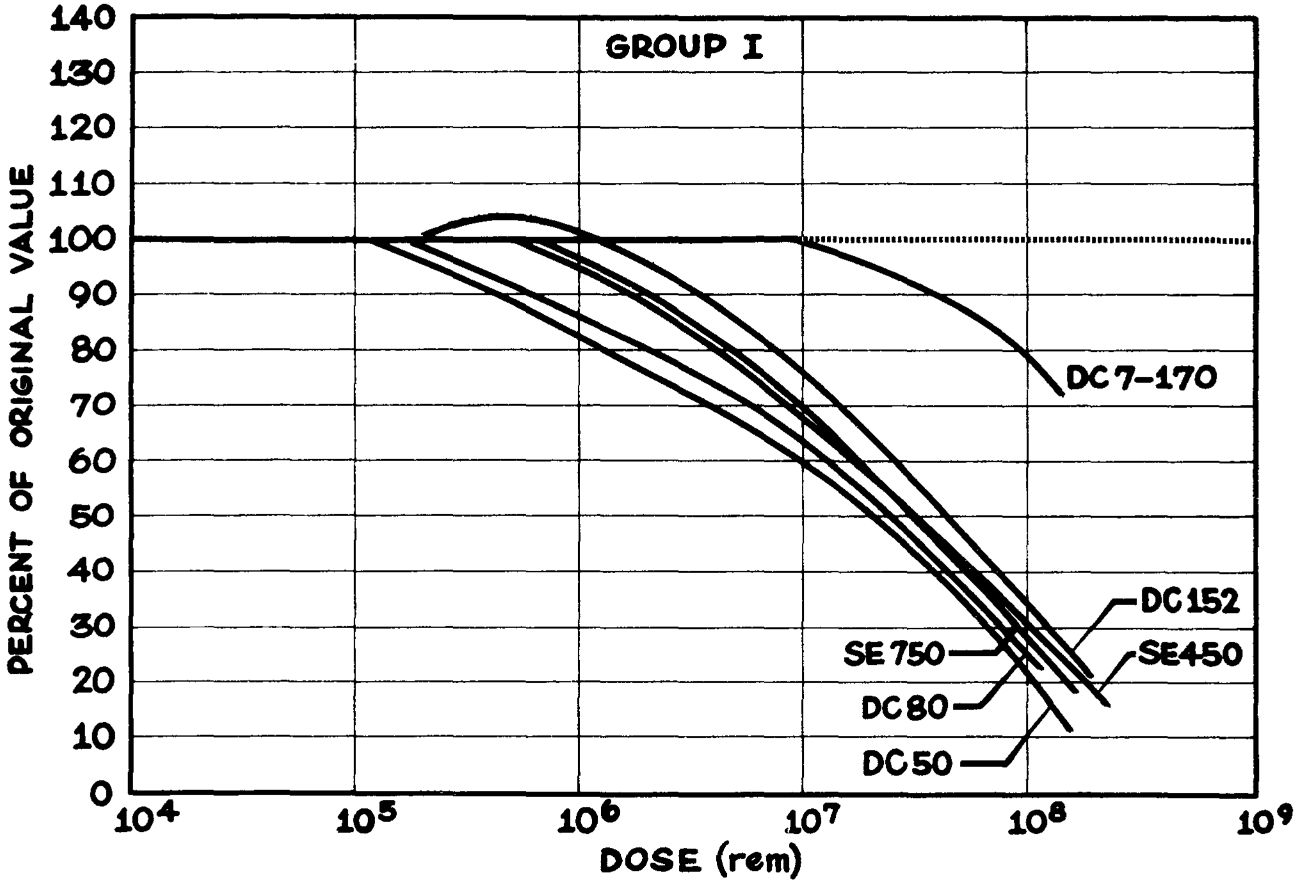

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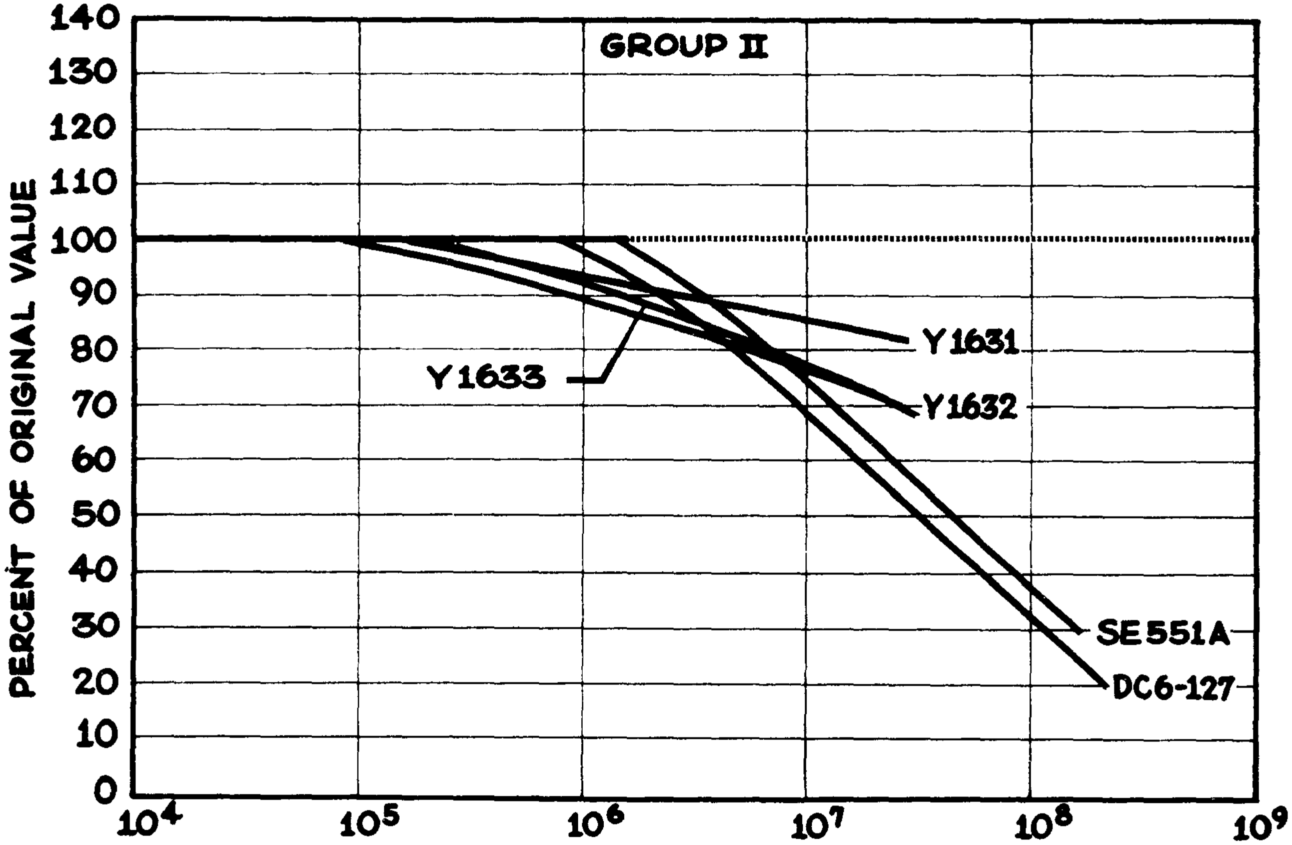
FIGURE 13

TEAR STRENGTH METHYL PHENYL SILOXANE



NPC 7457

FIGURE 14

TEAR STRENGTH METHYL PHENYL SILOXANE

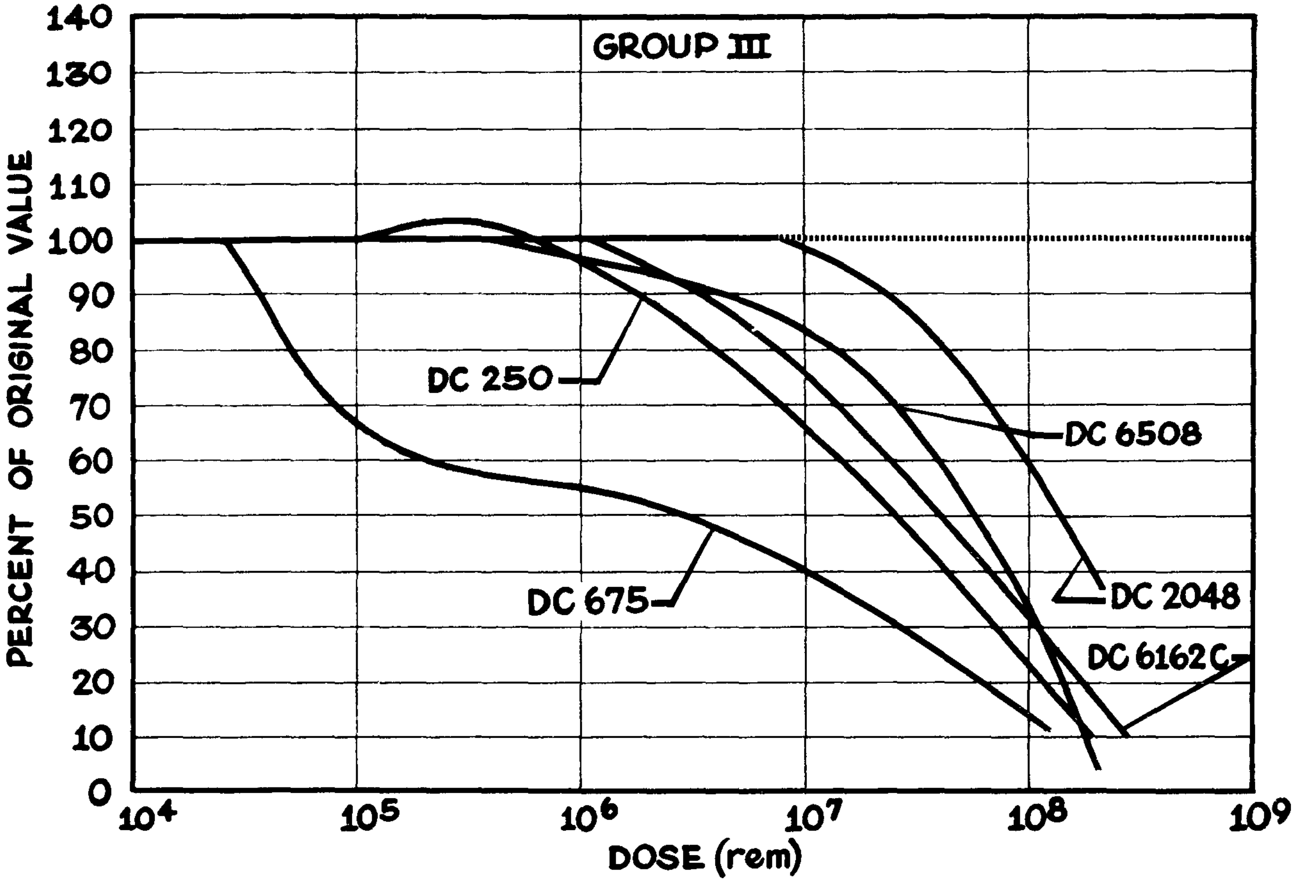


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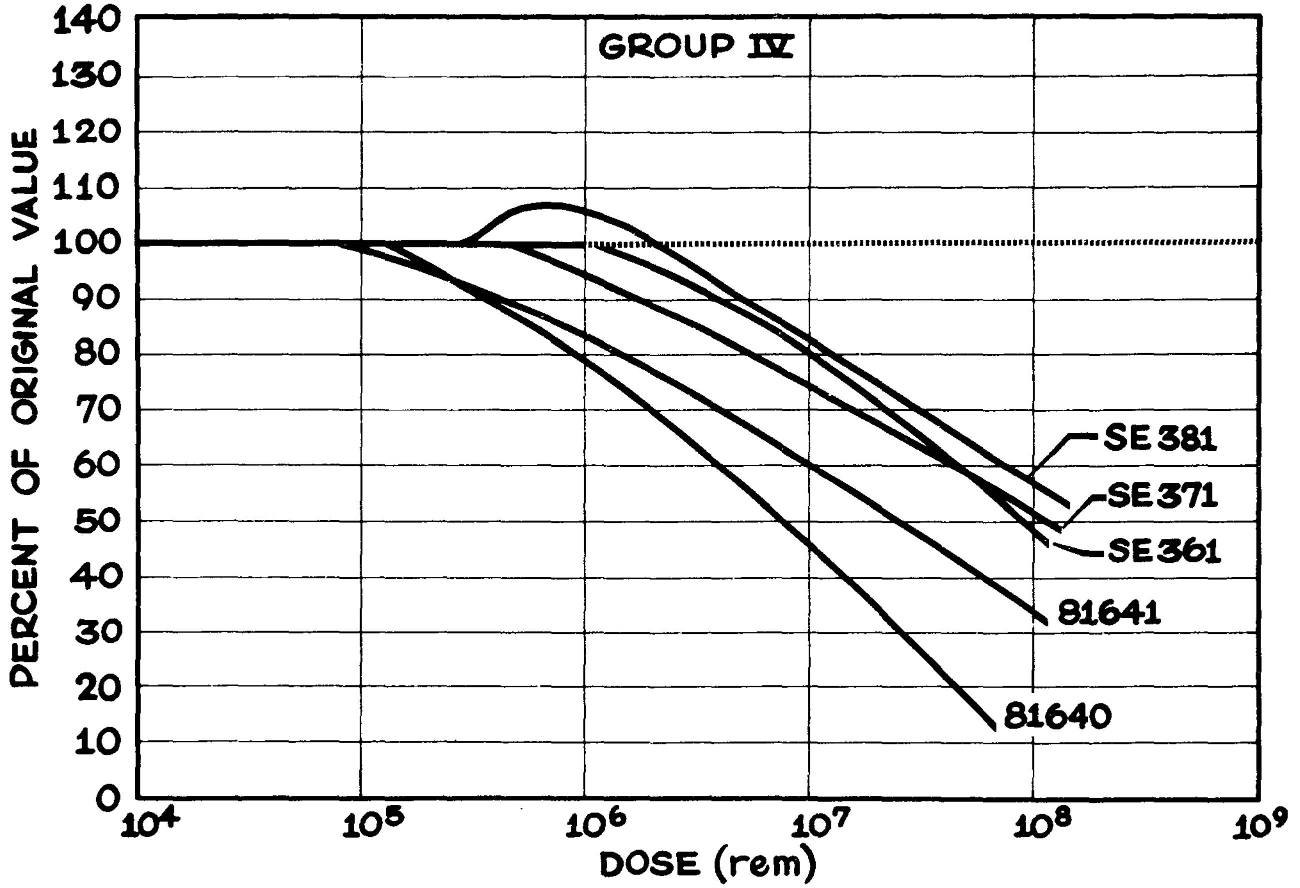
FIGURE 15

TEAR STRENGTH METHYL VINYL SILOXANE



NPC 7459

FIGURE 16

TEAR STRENGTH METHYL TRIFLUOROPROPYL SILOXANE

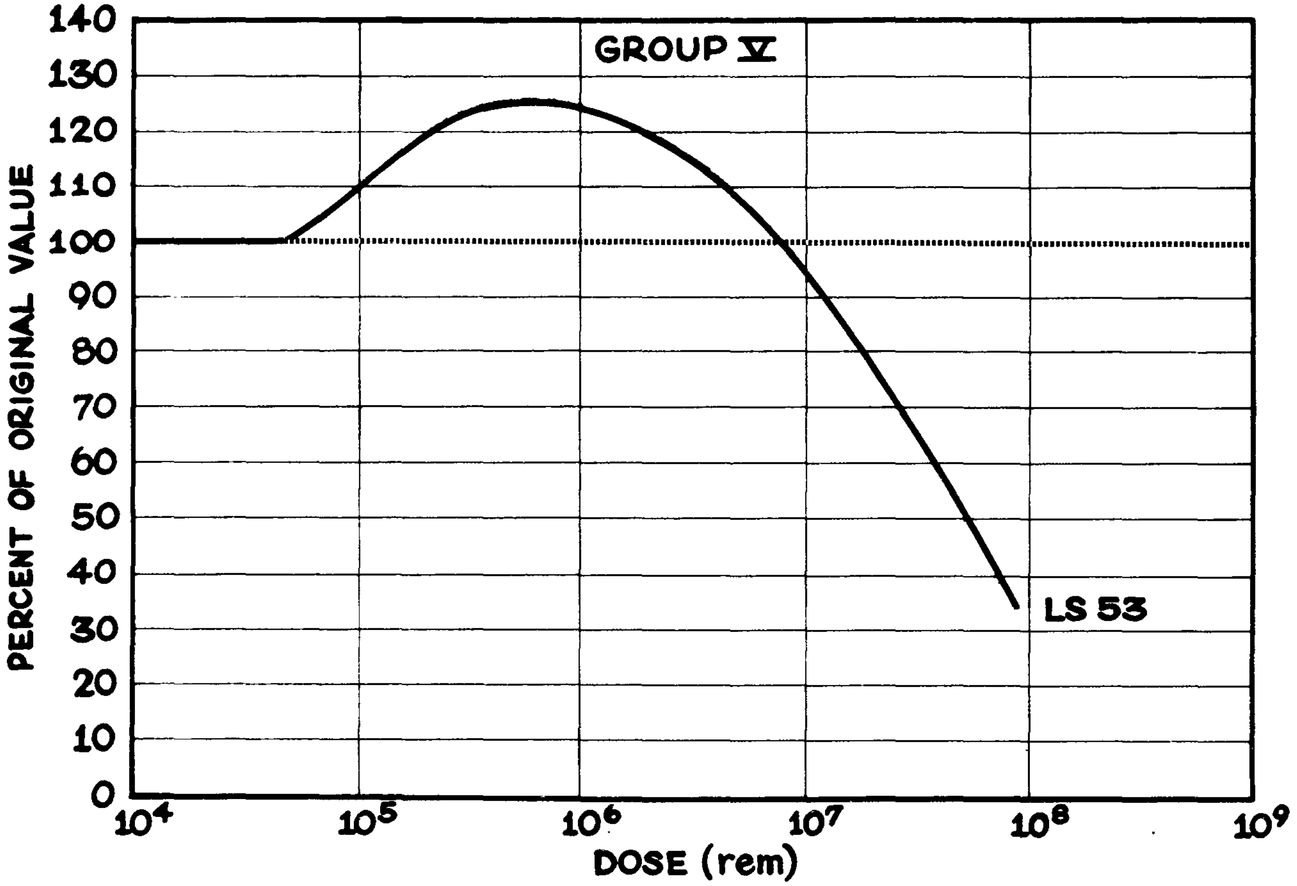
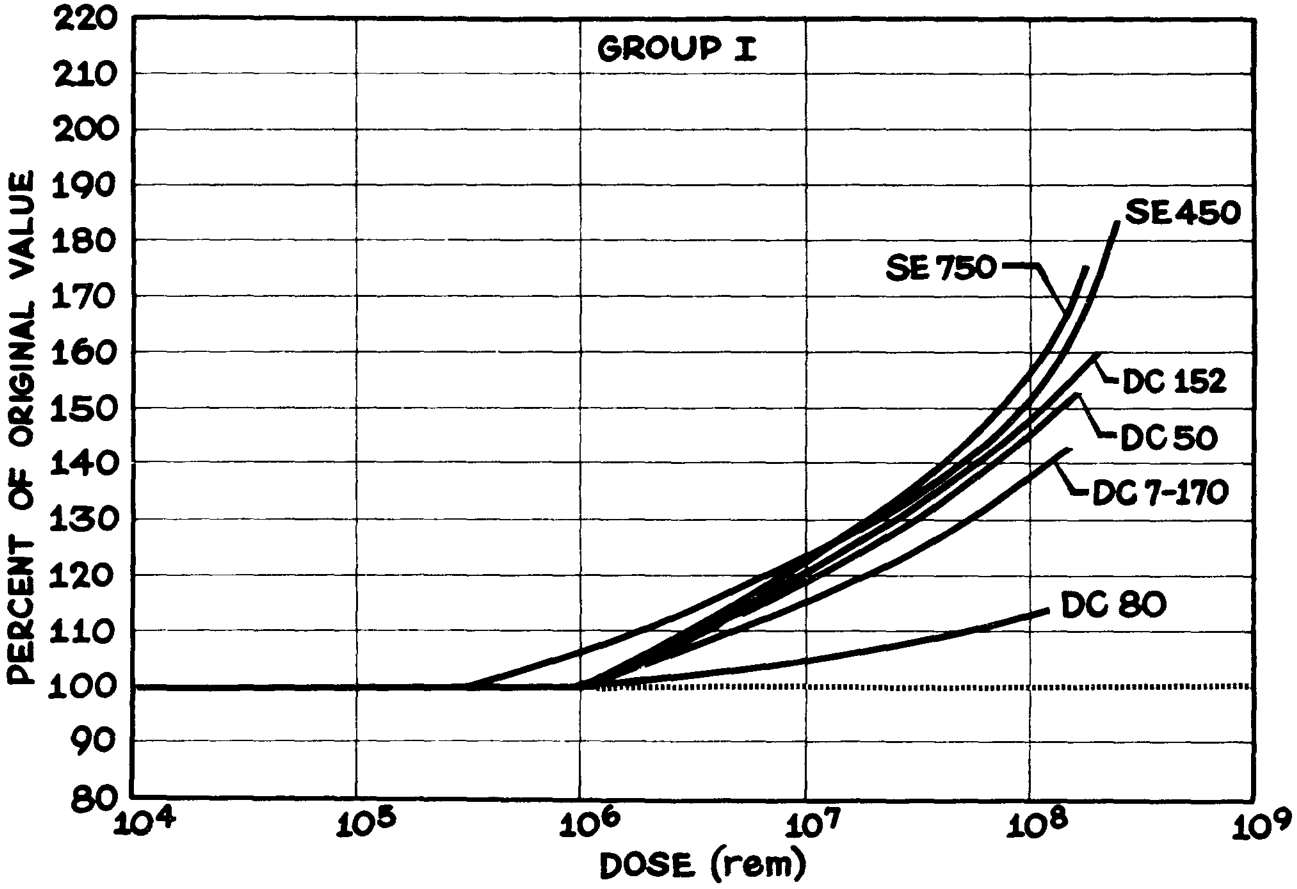


FIGURE 17

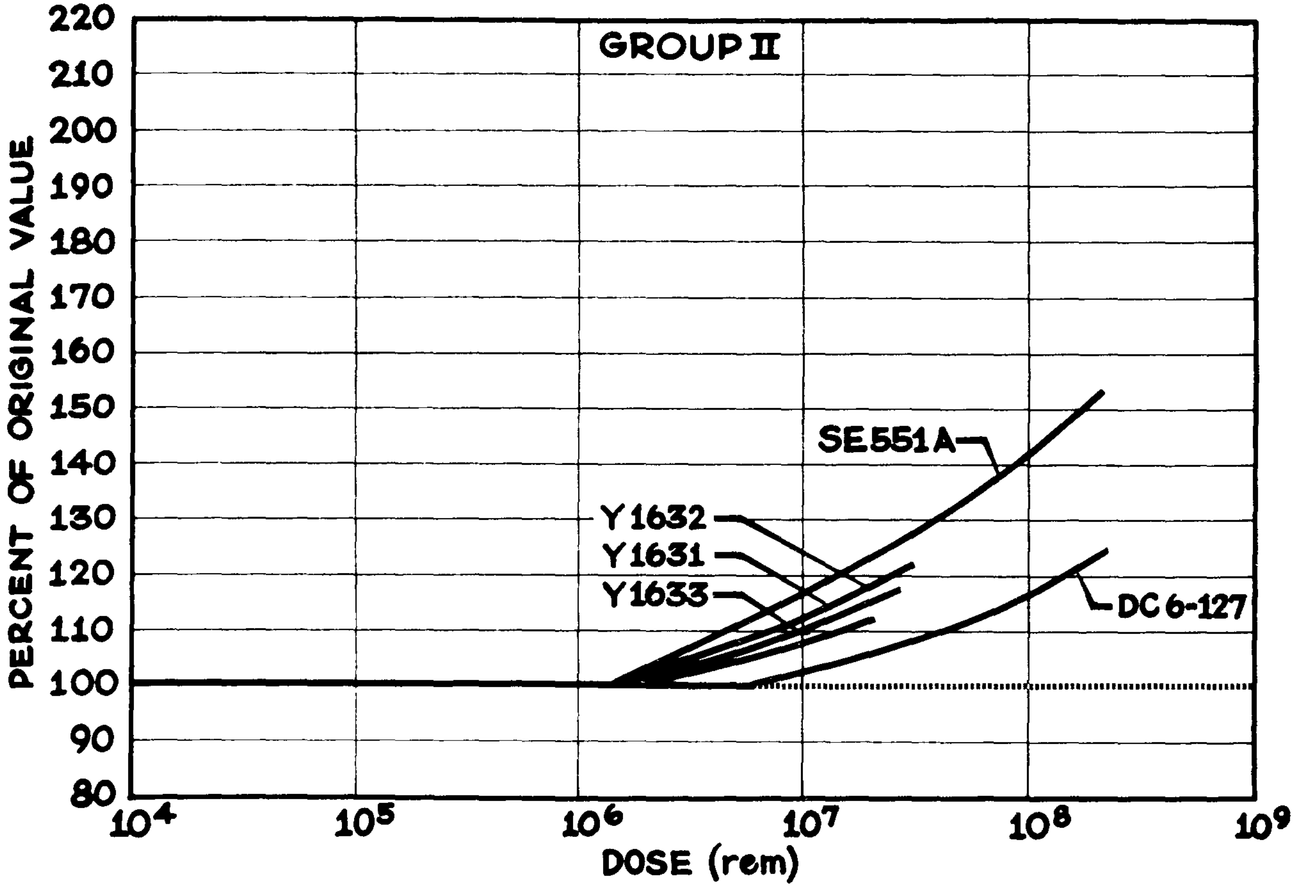
HARDNESS-SHORE "A"
DIMETHYL SILOXANE



NPC 7461

FIGURE 18

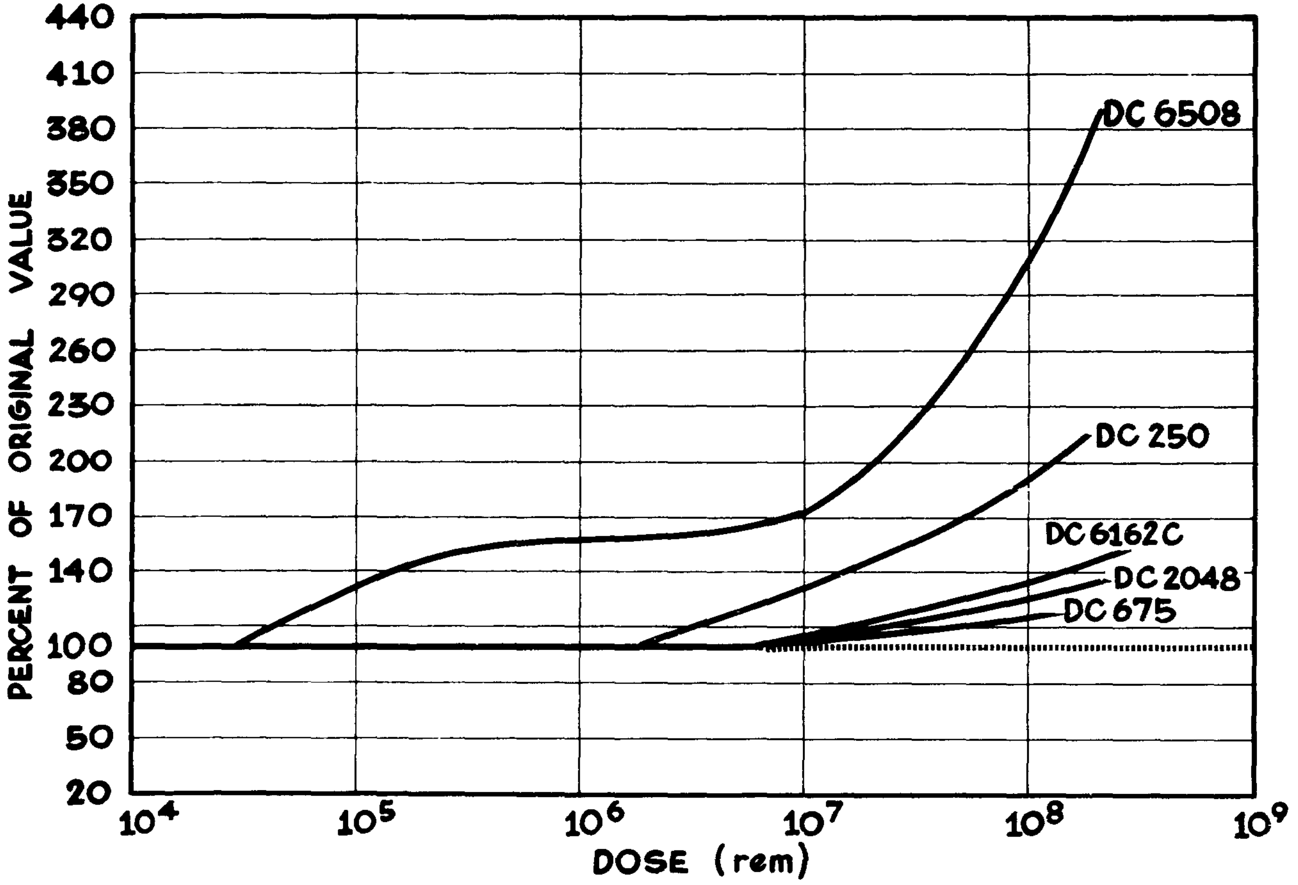
HARDNESS-SHORE "A" METHYL PHENYL SILOXANE



NPC 7462

FIGURE 19

SHORE "A" HARDNESS METHYL PHENYL SILOXANE



NPC 7447

FIGURE 20

HARDNESS - SHORE "A" METHYL VINYL SILOXANE

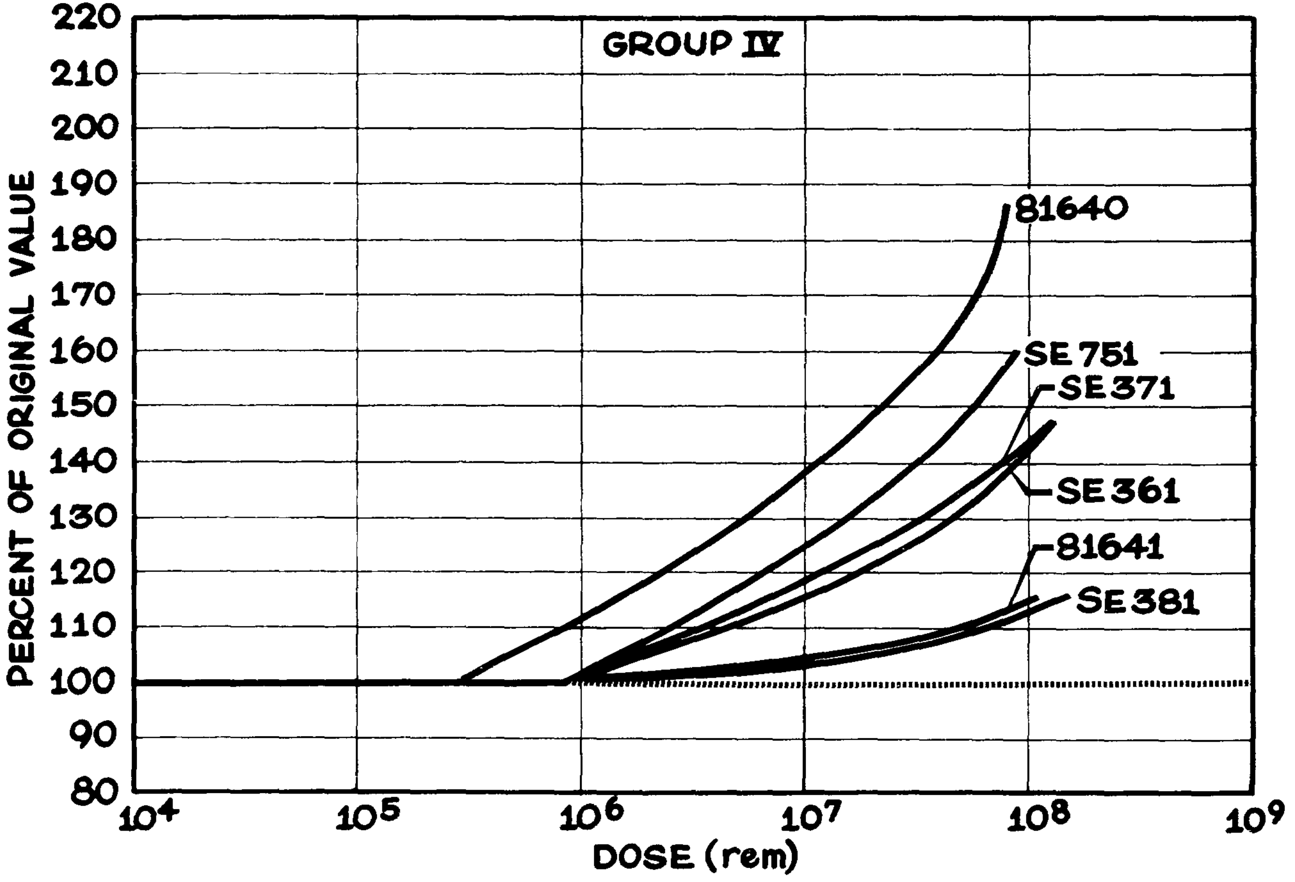
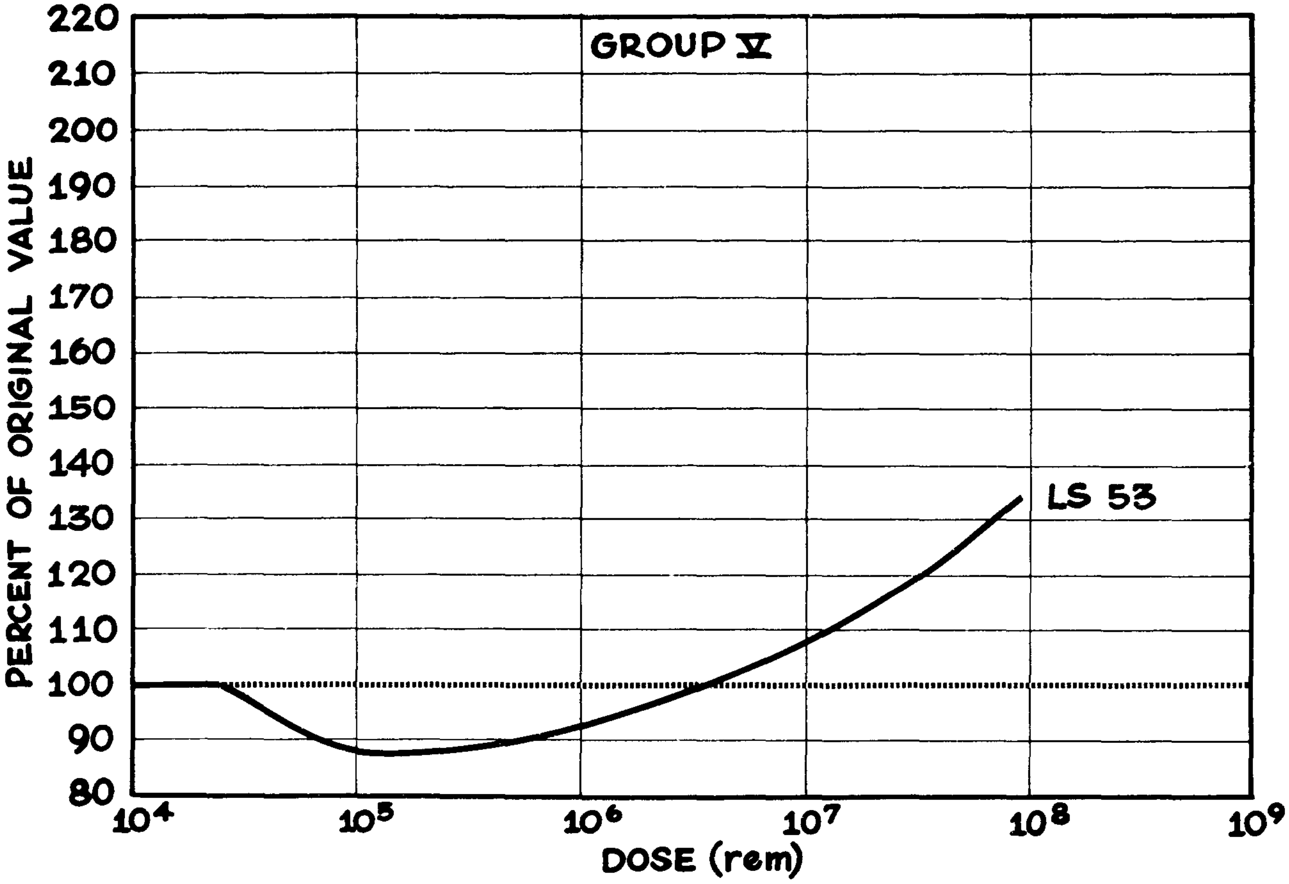


FIGURE 21

HARDNESS-SHORE "A" METHYL TRIFLUOROPROPYL SILOXANE



NPC 7464

FIGURE 22

The only distinction between Groups 2 and 3 is that Group 2 comprises all extreme low temperature stocks, while Group 3 comprises mixed application types including low temperature, general purpose, and low compression set.

For convenience in analyzing the results, all physical property changes were plotted in terms of percent of original. The means of the original control samples (groups of 5 specimens) are listed in Table IV. Satisfactory agreement was found within each group of five. However, it has been found that when an experiment is repeated, a systematic error is found between the means of the two samples. This will occur even with the same batch of material and when all parameters are carefully replicated. To obtain an accurate measure of a damage threshold on a batch of material, one or two replications should be made. However, for screening purposes and to determine the exposure at which severe damage occurs a single experiment such as the one reported here is sufficient.

The temperature could not be controlled in the irradiation chambers used in this test. The ambient temperature of samples was subject to gamma heating of the water surrounding the reactor. The effect was small except at Exposure 4, when the temperature reached about 150°F. This temperature will not normally affect silicones, but the possibility of an interaction between temperature and radiation environments exists. This possibility is under examination at the present time in Convair tests. Another environment known to be a factor in radiation damage is the oxygen content of the atmosphere. Siloxanes will degrade more in air than in an inert atmosphere (Ref. 1). Since silicones in a nuclear-powered aircraft will be in contact with air, this is the best environment for design data studies. Other studies will be made in an inert atmosphere and in an ozone-controlled atmosphere in order to obtain more basic information.

There were few cases of significant damage in any of the properties at the two lower exposure levels. In more cases, particularly in elongation and tear strength, damage was found at the third exposure level. In nearly all cases moderate to severe embrittlement occurred at the highest exposure level. Analysis of the results over the five groups showed no clear evidence of one group being better than the others. The phenyl types were expected to show the best resistance due to their aromatic content, as has been previously reported (Ref. 1 and 2). No data were obtained at Exposure 4 for the three Union Carbide Rubbers. They were about average for the methyl phenyl groups at the three lower exposures. The summary of results below does not include the Union Carbide silicones because of the lack of Exposure 4 data.

TABLE IV

CONTROL MEANS FOR PHYSICAL TESTS

Material	Tensile Psi	Elongation %	Tear Psi	Hardness Shore A
Group 1				
DC 50	1030	320	79	52
DC 80	780	160	79	80
DC 152	840	270	85	50
DC 7-170	690	85	32	61
SE 450	800	260	74	44
SE 750	1000	230	43	45
Group 2				
DC 6-127	600	90	54	71
Y 1631	740	190	85	56
Y 1632	800	230	96	45
Y 1633	740	220	95	62
SE 551A	660	190	61	56
Group 3				
DC 250	980	280	58	33
DC 675	790	120	103	76
DC S-2048	690	290	76	58
DC 6-508	690	570	96	17
DC 6162C	1210	440	136	53
Group 4				
SE 361	840	90	37	62
SE 371	1060	85	37	60
SE 381	830	50	31	80
SE 751	840	260	*	50
81640	1190	460	90	47
81641	920	200	98	80
Group 5				
LS 53	1150	270	67	57

* No data were obtained.

Tensile Strength

The tensile strength variations for the five groups of materials are presented in Figures 3 through 7. The LS 53 was damaged to 35 percent of the original at Exposure 4, and was damaged significantly even at Exposure 1. The methyl vinyl group showed decreases in all cases at Exposure 4, 81640 being the worst example at 46 percent of the original. The dimethyl and methyl phenyl groups underwent the least damage in tensile strength. DC 7170, DC 152, DC 6-127, and SE 551 actually increased in tensile strength. At Exposure 4, DC 7170 was the best material with an increase of 40 percent.

The original tensile strength of the materials appears to have a direct bearing on the direction and degree of changes due to irradiation. Of the eight materials with an original tensile strength greater than 900 psi, seven decreased significantly in tensile strength. Of the nine materials having an original tensile strength between 700 psi and 900 psi, eight underwent no significant damage. Of the four materials having an original tensile strength of less than 700 psi, two increased significantly. These were DC 6-127 and SE 551, as noted above.

Elongation

LS-53 was the material most affected in elongation as well as in ultimate strength (Figs. 8-12). The damage evident in LS-53 is typical of fluorinated polymers. The extremely high electronegativity of the flouride in the carbon-flourine bond (F-C = 1.5) causes an electron shift toward the flourine, (Ref. 3). This fact along with the related bond energy of 107 kilocalories/mole tends to weaken the adjacent C-C bonds and the nearby Si-O bonds. This results in side chain and main chain cleavage, causing a decrease in tensile strength and especially in elongation.

All methyl and substituted methyl types of siloxanes underwent moderate to severe decreases in elongation. The material least damaged at Exposure 4 was SE 381 which was 60 percent of the original (Fig. 11). Most of the other materials were reduced to less than 30 percent of the original at Exposure 4.

Tear Strength

Most of the materials were damaged quite severely in tear strength (Figs. 12-17). The least affected percentagewise was DC 7-170 which was 72 percent of the original at

Exposure 4. A previous batch of DC 7-170 was irradiated to a dose near Exposure 3 and was damaged quite severely (a reduction from 46 lb/in. to 9 lb/in.). This is one example of the problem in obtaining agreement between different irradiations of the same basic materials. The balance of the dimethyl stocks and the methyl phenyls were damaged to less than 38 percent of the original at Exposure 4. However, the methyl phenyl types were not damaged quite as much as the dimethyls at Exposures 2 and 3. The 300 series of methyl vinyl rubbers by GE held up best in tear strength of the Group 4 materials.

Hardness

All materials increased in hardness as a result of the crosslinking due to irradiation (Figs. 18-22). The dimethyl group changed the most in hardness, averaging 16 percent of original at Exposure 4. DC 80, however, was very good. The methyl phenyl rubbers did not harden nearly as much. With two exceptions all members of this group hardened less than 52 percent. The principle exception was DCS-6508, which increased 388 percent (Fig. 20). This was not surprising since this stock had only a one-hour post cure at 480°F. Also, the filler content of this recipe was the lowest of all rubbers tested, 21.4 percent. This resulted in a very low original hardness, 17 percent, and allowed for a greater degree of hardening due to radiation crosslinking. LS-53 (Fig. 22) was the only rubber which softened before it hardened.

Low Temperature Brittleness

All materials passed the low temperature brittleness test at -100°F except those listed in Table V. There was no correlation between the test results and dose, since failures occurred at all four doses. The methyl vinyl group had the most cases of low temperature embrittlement (four out of a total of six). Generally the phenyl substitution is used for low temperature resistance.

Relationship of Filler Content to Damage

There was a definite correlation between filler content and damage. It was possible to obtain equations by the method of least squares, expressing the damage as a function of filler content. A good fit was found for two of the properties tested. They are as follows, for Exposure 4:

TABLE V

LOW TEMPERATURE BRITTLENESS

Note: Y 1631, Y 1632 and Y 1633 were not tested for Low Temperature Brittleness at Exposure 4. They passed the test at the three lower exposures.

All Materials passed at -100°F except the following:

FAILURES

Material	Group	Exposure	Temperature
SE 450	1	1	-95°F
		2	-95°F
SE 381	4	1	-90°F
		2	-90°F
		3	-95°F
81640	4	2	-95°F
81641	4	4	-100°F
SE 751	4	1	-100°F
LS-53	5	4	-95°F

Tear strength: $\delta = 1.73f - 35$
where: δ = % of original tear strength
f = % filler

Elongation: $\delta = 1.10 \quad - 19$
where: δ = % of original elongation
f = % filler

The above expressions will predict the values to within ± 20 percent with 95 percent confidence for any of the elastomers tested. Within a single group, such as dimethyl, an expression with slightly different factors can be obtained with somewhat better precision.

Special Tests

The purpose of the constant-deflection compression set test was to establish how high a dose was necessary to obtain a significant permanent set. It is felt at Convair-Fort Worth, that standard compression set data obtained after irradiation gives misleading information. The ASTM standard method for testing calls for 70 hours at 212°F.

Compression set is commonly used to test the cure of a rubber. For a given material the set is high if it was undercured and low if overcured. Since radiation cures the rubber, a post-irradiatio compression set test will normally reflect the amount of additional cure obtained. However, if the sample is placed under compression during irradiation, the amount of curing shows up as a sharp increase rather than a decrease in compression set. The elastomer chains are crosslinked while in the stressed position and consequently the percent set is very sensitive to irradiation.

Dow Corning 7-170 and 250 were tested in triplicate according to the special test described in the "Physical Test Procedures" Section. The controls were run in duplicate. There was no permanent set in the controls and all irradiated samples underwent 100 percent permanent set. The controls were maintained at 200°F for 30 hours while the irradiated samples reached a maximum of approximately 150°F.

The fluorinated silastic LS-53 was tested for permanent tensile set under irradiation according to the method described in the "Physical Test Procedures" Section. Standard tensile specimens were used. The permanent tensile set of three specimens maintained at 50 percent elongations for a period of 30 hours, including irradiation time, was as follows; (Table VI).

TABLE VI
TENSILE-IRRADIATION TEST LS-53

Specimen No.	Thickness (in.)	Area (in.^{2})	l_1	l_2	l_3	Tensile Set %	Tensile Strength Psi
1	0.061	0.0153	1.0	1.5	1.329	34	660
2	0.059	0.0147	1.0	1.5	1.329	34	640
3	-	-	1.0	1.5	1.312	38	Reject
Control mean, unstressed specimens							1150

% Tensile set $\frac{l_2 - l_3}{l_2 - l_1}$ X 100

Where l_1 = Original length

l_2 = Length when stressed

l_3 = Length 30 minutes after removal from test jig

The ultimate tensile strength of two of the above specimens was performed at the completion of the special test. The third specimen could not be tested due to distortion of the ends of the specimen during the special test. No controls were run on tensile set at the comparable temperature in the absence of radiation.

The materials in the two above tests were irradiated for 20 hours, receiving doses equivalent to Exposure 4, Table III.

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4. Kerlin, E. E., The Effects of Mixed-Field Radiation on Aircraft O-Rings, Convair-Fort Worth Report FZM-1162 (Oct. 1958).

Author's note added in print:

In the list of Dow Corning rubbers (Table II), the use of vinyl in some stocks was omitted. While the vulcanized stock no longer contains the vinyl groups (they are cured to ethyl crosslinks), the presence of vinyl should have been included in Table II, as follows:

1. DC-50 -- dimethyl and vinyl
2. DC-80 -- dimethyl and vinyl
6. DC-675 -- dimethyl, phenyl, and vinyl
9. DC-6162C -- dimethyl, phenyl, and vinyl
10. DC-6508 -- dimethyl, phenyl, and vinyl

THE RADIATION ENVIRONMENT DUE TO ACTIVATION AND SCATTERING EFFECTS NEAR BASED SEAPLANES

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This paper is classified and is bound in Volume Six.