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EFFECTS OF RADIATION ON AIRCRAFT LUBRICANTS AND FUELS

R. O. BOLT
J. G. CARROLL
CALIFORNIA RESEARCH CORPORATION
RICHMOND, CALIFORNIA

DECEMBER 1957

WRIGHT AIR DEVELOPMENT CENTER

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EFFECTS OF RADIATION ON AIRCRAFT LUBRICANTS AND FUELS

R. O. Bolt
J. G. Carroll
California Research Corporation
Richmond, California

December 1957

Materials Laboratory
Contract No. AF 33(616)-3184
Project No. 2133

Wright Air Development Center
Air Research and Development Command
United States Air Force
Wright-Patterson Air Force Base, Ohio

57WCLT-1841

FOREWORD

This report was prepared by California Research Corporation on Air Force Contract AF 33(616)-3184. The contract was initiated under Project No. 2133, "ANPP Support," Task No. 73071, "Radiation Effects." The work was administered under the direction of the Materials Laboratory, Directorate of Laboratories, Wright Air Development Center, with Lt. W. L. R. Rice (WCRTR-1) acting as Project Engineer. This report covers research conducted from September 1, 1955, to December 1, 1956. Technical service and consultation work with ANP contractors on organic fluids is not included. This is reported separately on a monthly basis only to WCRTR-1 and amounted to about 10% of the contract effort.

Major contributions to the project were made by Messrs. J. A. Bert, R. O. Bolt, S. R. Calish, J. G. Carroll, J. L. Dreher, A. C. Ettling, N. W. Furby, R. C. Gray, J. T. Guerin, K. L. Hall, B. W. Hotten, R. L. Peeler, N. P. Shiells, M. J. Schlatter, and J. M. Stokely.

The over-all classification of this report is CONFIDENTIAL due to the references to target properties in the Abstract, Summary, Introduction, and Lubricant sections and to parts of the Fuels section. The section on Base Materials is unclassified, as are the Appendixes.

ABSTRACT

The objectives of the work reported included the development of radiation resistant lubricants and a survey of the radiation stability of jet fuel types.

The lubricant work was guided by target specifications for a grease, gas turbine fluid, gear oil, and hydraulic fluid. The targets included radiation stability requirements which were sufficiently stringent that stable aromatic fluids were needed. As these are generally not available commercially, most were synthesized. Methods adaptable to barrel-scale work were used. Emphasis was placed on alkylbiphenyls and alkyl diphenyl ethers, but aryl diesters and other alkyl aromatic compounds were also made. Pour points of -60°F and viscosity indexes of 110 were found for aromatic ethers. For alkylbiphenyls, respective values were about -20°F and 90°F.

The grease goal was a MIL-G-25013A usable for 50 x 10^8 r. Greases from alkylbiphenyl or alkylnaphthalene fluids gelled with sodium terephthalamate approached the desired properties. Some were useful from -10°F to 350°F and for dosages up to about 25 x 10^8 r. The mechanism of radiation damage to greases was studied. Gelling agents, particularly sodium stearate, were found more sensitive to radiation than oil components. Bearing tests were conducted in a gamma source at 80°F for about 20 x 10^8 r on two different greases; neither failed, and both indicated that static tests are reliable in predicting grease performance.

For the gas turbine lubricant, the goal was a MIL-L-7808C fluid whose properties remain unchanged at 10 x 10^8 r. Present fluids were found usable below about 5 x 10^7 r. At this dosage, oxidation stability and coking properties were appreciably impaired. A selenide-inhibited polyglycol yielded a very low 700°F coking value of 26 mg after 14 x 10^8 r. Unirradiated alkylbiphenyls and alkyl diphenyl ethers exhibited 700°F coking properties comparable to mineral oils and diesters. Dialkyl selenide was more effective than other inhibitors in oxidation-type tests. From these preliminary tests, the favored fluid for this application is an alkyl diphenyl ether or an alkylbiphenyl compounded with a selenide.

The hydraulic fluid goal is patterned after Specification MIL-H-8446. Use for up to 50 x 10^8 r was also specified. MLO-8200 fluid was found useful up to about 10^8 r, although thermal stability was impaired, and gassing was about 5 volumes per volume of liquid. Gassing, primarily hydrogen, at about 4 x 10^8 r and 250°F ranged from 1 volume to about 15 volumes per volume of octylbiphenyl and of MLO-8200, respectively. After about 8 x 10^8 r, most of the desirable physical properties of 8200 fluid were lost. However, lubrication qualities were not impaired, as shown by satisfactory operation in an aircraft-type piston pump at 3000 psig and 275°F. For higher dosages, an alkyl aromatic fluid will be necessary, possibly an alkylbenzene type thickened with a radiation stable polymer.

The gear lubricant requirement was a low temperature version of MIL-L-6086 for use up to 50 x 10^8 r. Film strength specifications were sufficiently high that extreme pressure additives were required. The radiation stability requirement dictated the use of aromatic base oils. Additive-base oil mixtures were examined for radiation stability, and suitable formulations were selected. Irradiated mixtures of these are under test for film strength performance. The currently favored formulation is an aryl ester or an alkyl aromatic base fluid compounded with a selenide and a sulfurized olefin. However, it is likely that many of the gear oil requirements will be met by the gas turbine lubricant. This may obviate the need for a special gear lubricant.

In the fuel survey, eight production-type jet fuels were irradiated for three gamma dosages. All conformed to MIL-F-5624C, and samples were tested before and after irradiation against the requirements of this specification. After 10^8 r, only minor changes occurred. Thermal stability may be an exception to this; the materials have not yet been examined in the CFR Fuel Coker. After 10 x 10^8 r, distillation ranges and end points, densities, hydrogen-carbon atomic ratios, and viscosities were altered appreciably. JP-5 type fuels were more susceptible to radiation damage than were JP-4 type fuels.

Ethyldecaborane (HEF-3) was irradiated in sealed containers to a maximum of 12 x 10^8 r. A complete analysis was not accomplished, but a lower limit of 16% was established for the HEF-3 altered by this dosage. Gas evolution was about 44 volumes per volume of fluid. These effects were about the same as those observed with hydrocarbon jet fuels.

PUBLICATION REVIEW

This report has been reviewed and approved.

FOR THE COMMANDER:

R. T. Schwartz
R. T. SCHWARTZ
Chief, Organic Materials Branch
Materials Laboratory

SUMMARY OF BEST LUBRICANT PRODUCTS

The lubricant development work was guided by target specifications. The radiation resistance need in these generally required the use of aromatic base stocks rather than conventional fluids. Aromatic stocks have never been employed extensively in lubricants. Thus, a program including synthesis, formulation, and testing was called for. In initial screening work, the philosophy was to eliminate, on the basis of critical properties, undesirable materials and to retain the remainder. The full test program was reserved only for the most promising of the latter.

The synthesis and resultant screening work comprised most of the effort within this report period. Thus, selection of products to meet the target specifications is premature. However, preliminary selections were made to indicate the status of the development program and to show the types of products of promise as radiation resistant lubricants. The selections are summarized in the following paragraphs together with pertinent test results.

Greases

The preferred grease at this time is CALRESEARCH 159. This is made from a C_{16-18} biphenyl inhibited with didodecyl selenide and gelled with a sodium terephthalamate. This grease is probably usable from about -10°F to 350°F as the data in Table I show. Similar formulations[1], also in Table I, have retained usability (even though considerably reduced) after about 30×10^8 r. The full complement of the specification tests is scheduled for the future on irradiated samples of CALRESEARCH 159.

Chevron OHT Grease[2] is a commercial product which meets Specification MIL-L-3545. It is sufficiently stable for lower radiation dosages to be included in Table I. This grease is of interest for possible use as an interim lubricant.

Gas Turbine Lubricants

The currently favored base stock is a C_{16-18} biphenyl. As shown in Table II, physical properties indicate this fluid to be useful to as low as about -30°F. Thermal and oxidation stability were good, and radiation stability may be adequate to about 10×10^8 r. Coking was high at 700°F. Selenide inhibitors produced formulations with improved oxidation stability and lower coking tendencies. Such formulations are preferred at this writing even though the selenide is corrosive to copper and to silver.

---

[1] California Research-AEC Report No. 8 (AECU 3149), "Radiation Resistant Greases," June 30, 1956.

[2] Formerly Calol OHT Grease.

TABLE I

PHYSICAL AND CHEMICAL PROPERTIES FOR RADIATION RESISTANT GREASES

Property or Test	Requirements[a]		2579-21B[b]			Chevron OHT Grease			CALRESEARCH 159
			Octadecyl-alpha-Methylnaphthalene Didodecyl Selenide Sodium Terephthalamate			Mineral Oil Proprietary Additive Sodium Soap			C_{16-18} Biphenyl Didodecyl Selenide Sodium Terephthalamate
1. **Irradiation**, 10^8 r	0	50	0	14	32.5	0	4.3	18.3	0
2. **Dropping Point**, °F	500 (350)	400 (300)				457	428	346	500+
3. **ASTM Worked Penetration**	260-310	200-375	260	336	370	289	452	382	261
4. **Norma Hoffman Bomb**									
a. Copper corrosion, 100 hr at 212°F	No pitting	-							Not Pass
b. Oxidation, 100 hr at 250°F, psi	5 (7.5)	-							3
5. **Dirt Content**, part./cc, max									
>25 microns	2500	-							
>75 microns	1000	-							
6. **Water Resistance**									
% Loss - MIL-L-3545	50 (60)	-				0	17.5		0
7. **Bearing Performance**									
10,000 rpm, Hours at 450°F	500		-	-	-	-	-	-	-
400°F	(500)	100 (50)	-	-	-	-	-	-	279, 188
300°F	-	-	576, 2021, 1899	607, 437	141, 263	1500+	717, 692	69, 51	-
8. **Work Stability**, penetration after 100,000 strokes	375	-							375
9. **Evaporation**, %									
22 hours at 400°F	4 (6)	-				-	-	-	21
18 hours at 300°F	-	-				4.7	8.1	9.3	-
10. **Apparent Viscosity**, poises									
-40°F at 12 sec^{-1}	15,000	-							-
0°F at 12 sec^{-1}	-	15,000							3000
11. **Low Temperature Torque**									
Sec/rev at 0°F	-	-	1	5	-	1	2	200	
12. **Navy Gear Wear Test**									
5-lb load, mg/1000 cycles	Report		2.7	2.4	1.4	1.6	1.5	-	
10-lb load, mg/1000 cycles			6.5	5.8	6.2	5.9	4.7	-	

a. ( ) alternate minima.
b. Developed on Contract AT (11-1)-174.

TABLE II

PHYSICAL AND CHEMICAL PROPERTIES FOR RADIATION RESISTANT GAS TURBINE LUBRICANTS

Property or Test	Requirement[g]	C_{16-18} Biphenyl (Distilled)					C_{14} Diphenyl Ether
		No Additive	5% Didodecyl Selenide				
1. Irradiation, 10^8 r	10	0	0		0.95[a]	7.65[a]	0
2. Viscosity, cs, °F							
400	-	-	-		-	-	-
210	3.0	5.27	5.38		5.63	7.26	4.14
100	11.0	36.4	34.98		36.10	54.05	22.26
-40	-	61,664	-		-	-	13,656
-65	13,000	-	-		-	-	-
3. Pour Point, °F	-75	-55	-				-70
4. Flash Point, °F	400	430	-				445
5. Spontaneous Ignition Temp., °F	700	780	-				820
6. Foaming	Controlled	-	-				
7. Evaporation, 6-1/2 hr at 400°F, %	25	9	-				24.2
8. 300 Lead Corrosion, mg/in²	5.0	-	1.2[c]				-
9. Shell Four-Ball Wear	Report						
4 kg load, mm	-	0.43[d]	-				-
10 kg load, mm	-	0.50	-				-
40 kg load, mm	-	0.84	-				-
10. Ryder Gear Loading, ppi	2000 min	2050, 1700[b]	-				-
11. Panel Coking, 8-hr test							
mg at 600°F	50	-	-				-
mg at 700°F	-	1092	218, 191				368[e,f]
12. Oxidation-Corrosion, 5.0 liters of air/hr							
Hours	72		72	72			72[f]
Temperature, °F	347		347	347			347
Wt. Change, mg/cm²							
Al	± 0.2		+0.04	+0.01			+0.01
Cu	± 0.4		-	-12.6			-0.25
Ag	± 0.2		-	-22.2			+0.06
Fe	± 0.2		+0.06	0			+0.01
Mg	-		-0.02	0			+0.29
Appearance	No Pitting		-				-
Viscosity Change, %							
100°F	-5 to +10		+17.0	+19.4			+6.3
210°F	-		+7.4	+23.4			-
Neut. Number Change	2.0 max		1.1	2.1			0.4
Insolubles, % Wt. or Vol.	1.0 max		-	-			-

a. MTR Canal Source; samples open to air.
b. Tests made at Southwest Research Institute.
c. 2% didodecyl selenide.
d. WADC data.
e. 4-hour test.
f. 2% Parabar 441
g. Before and after 10 x 10^8 r.

Compared to the C_{16-18} biphenyl, the tetradecyl diphenyl ether, also shown in Table II, gives promise of somewhat better low temperature properties with little or no sacrifice in thermal, oxidation, and radiation stability.

Hydraulic Fluids

The preferred lubricant is MLO-8200 fluid[1] as shown in Table III. It is probably of use to about 10^8 r although gassing may be somewhat high at this dosage. Physical properties were drastically altered after 7.8×10^8 r exposure although pump performance at 275°F was not impaired appreciably. The fluid would probably be usable from -65°F to 400°F after this dosage. Its radiation resistance is definitely submarginal in comparison to the target requirements. The diphenyl ether, also noted in Table III, gives promise of considerably better radiation stability. Complete specification tests are scheduled in future work for original and irradiated versions of this fluid with and without inhibitors.

Gear Lubricant

Table IV notes two formulations, either of which would suffice as an interim gear lubricant. The C_{16-18} biphenyl version would probably have better high temperature properties than the diester. The sulfurized olefin is an EP additive which has been shown in other work[2] to produce the desired film strength. The alkylbiphenyl fluid should be usable to about 10×10^8 r. Both formulations in Table IV were included in the group of lubricants forwarded to WADC in August 1956 for Mean Hertz Load tests.

---

[1] Also Oronite High Temperature Hydraulic Fluid 8200.

[2] Carroll and Calish, "Effects of Gamma Radiation on Some Commercial Lubricants," scheduled for presentation before the ASLE National Meeting, Detroit, April 1957.

TABLE III

PHYSICAL AND CHEMICAL PROPERTIES FOR RADIATION RESISTANT HYDRAULIC FLUIDS

Property or Test	Requirement[a]		MLO 8200				C_{12} Diphenyl Ether
1. **Irradiation**, 10^8 r	0	50	0		7.8		0
2. **Viscosity**, cs, °F							
400	2.5	1.0	3.82		-		1.00
210	-	-	11.59		37.15		3.57
100	-	-	33.29		131.6		18.47
0	(2500)	-	-		-		4800
-65	2500	Report	2234		47,363		-
3. **Pour Point**, °F	-75 (-40)	-65 (-10)	<-100		<-80		-75
4. **Spontaneous Ignition Temperature**, °F	700 (500)	500	720		840		830
5. **Irradiation Stability**							
Acid No.		5					
Weight Change							
Cu, mg/cm²		± 0.4 (± 0.6)					
Ag, mg/cm²							
St, mg/cm²							
Al, mg/cm²							
Sludge, %		None (0.5)					
6. **Vapor Pressure**							
at 400°F, mm Hg, max		100	1		1 mm at 150°F		25
7. **Oxidation Corrosion**, 0.5 liters of air per hour							
Hours	48		72	72	72	72	72
Temperature, °F	400		347	400	347	400	400
Wt. Change, mg/cm²							
Cu	± 0.2 (± 0.4)		+0.5	+0.04	2.05	-0.88	-4.54
Ag			0	-0.04	+0.06	-0.14	+0.15
Al			0	-0.02	+0.10	-0.08	+0.09
Fe			0	-0.05	+0.06	+0.04	+0.12
Viscosity at 400°F, cs	0.5		+1.[illegible]% at 210°F		-		-
Pour Point, °F	-20		-		-		-
8. **Hydrolytic Stability**							
24 hours at 400°F (0.5% water)	No Sludge	-	O.K. at 200°F		Not pass at 200°F		
9. **Wear Test**							
Piston pump, 160°F, 100 hr	MIL-F-8446	-	Satisfactory; 150 hours at 160°F, 100 hours at 275°F		Satisfactory; 150 hours at 160°F, 100 hours at 275°F		

a. ( ) alternate minima.

TABLE IV

PHYSICAL AND CHEMICAL PROPERTIES FOR RADIATION RESISTANT GEAR OILS

Property or Test	Requirements[c]		Diisooctyl Terephthalate			C_{16-18} Biphenyl		
			No Additive	5% Sulfurized Olefin 2% Dibenzyl Selenide		No Additive	5% Sulfurized Olefin 2% Dibenzyl Selenide	
1. Irradiation, 10^8 r	0	10	0	0	7.8[a]	0	0	7.5[a]
2. Viscosity, cs. °F								
210	5.5	3.0	4.85	4.85	5.04	5.27	6.59	8.49
100		-	29.43	29.43	42.28	36.54	49.45	71.89
-40	3500 (7000)	-	49,624	-	-	61,604	-	-
3. Evaporation, 6-1/2 hr at 400°F, %	20 (40)	-	11.7			ca. 8		
4. Pour Point, °F	-75 (-30)	-65 (-10)	-65			-55		
5. Mean Hertz Load, psi	40 min	40 (30)		b	b		b	b
6. Irradiation Stability								
Acid No.	-	2						
Weight Change, mg/cm²	-	± 0.4 (± 0.6)						
St	-							
Al	-							
Mg	-							
Sludge	-	No sludge on container walls						

a. 500 cc in aluminum containers open to air; MTR Canal Source.
b. Samples forwarded to WADC for test in August 1956.
c. ( ) alternate minima.

TABLE OF CONTENTS

Page

1. Introduction

2. Base Materials

3. Lubricating Greases

4. Gas Turbine Lubricants

TABLE OF CONTENTS (Cont'd)

LIST OF TABLES

LIST OF TABLES (Cont'd)

LIST OF TABLES (Cont'd)

LIST OF ILLUSTRATIONS

LIST OF ILLUSTRATIONS (Cont'd)

LIST OF APPENDIXES

1. INTRODUCTION

1.1 Objectives

The objectives of the research and development work on this contract were three, as follows:

a. To develop radiation resistant gas turbine lubricants, greases, gear oils, and hydraulic fluids for use in nuclear powered aircraft at radiation dosages of 10×10^8 roentgens (r) to 50×10^8 r.

b. To study the effects of nuclear radiation on the properties of jet fuel types.

c. To assist personnel in the Air Nuclear Power program with special problems pertaining to the present and projected use of organic fluids.

1.2 Scope

For the four lubricants, performance requirements were established by Wright Air Development Center (WADC) at the level of an advanced state of lubricant development. To these were added stringent radiation requirements. The resulting specifications were then regarded as targets, something to be approached; full conformance might not be possible. Actually, materials which meet or approach the performance requirements of the target specifications; such as aliphatic diesters, disiloxanes and silicones, and heat resistant greases; are at the low end of the radiation stability scale. Changes in properties of fluids of these types become appreciable after about 0.1×10^8 r[1]. The best resistance to nuclear radiation is shown by polyphenyl types. These will withstand radiation dosages above 100×10^8 r[2] but are not suitable as bases for aircraft lubricants. Thus, the target specifications set forth were unattainable with existing knowledge. Compromises were necessary between performance on the one hand and radiation stability on the other.

For the jet fuels, a survey was desired on the effect of radiation on fuel properties. Initially, production fuels meeting Specification MIL-F-5624C were of most interest. Results of tests on gamma irradiated fuels were to be compared with original properties in accordance with specification tests.

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[1] "Radiation Resistant Lubricants - Their Development and Status," (California Research-AEC Report No. 7) TID 5186, June 30, 1954 (CONFIDENTIAL)

[2] "Research on the Radiation Stability of Organic Fluids," (California Research-AEC Report No. 6) TID 5148, October 30, 1953 (CONFIDENTIAL)

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Manuscript released by authors April 20, 1957, for publication as a WADC Technical Report.

California Research personnel also served as consultants during the contract period on special problems of application of organic fluids in the ANP program. This function was deemed desirable because of the experience of these people in this and allied fields since 1948. In many instances, samples of special lubricants were also supplied for test work. This activity was reported only to WADC and is not covered in this Summary Report.

1.3 Approach

Basically, there were two approaches in the lubricant development work to give effect to the compromises already noted.

a. The use of conventional base fluids in combination with carefully selected additives. In the finished lubricant, additives may assert a greater limiting effect on radiation resistance than the bulk fluid itself. This approach tended to emphasize lubricant performance over radiation resistance as it sought to retain the well known performance properties of fluids, such as diesters, polyglycols, mineral oils, etc.

b. The use of new base materials, such as alkyl aromatic compounds. This emphasized radiation stability over lubricant performance. Aromatic compounds have been comparatively unexplored for lubricant use due to certain inherent disadvantages. However, this class is high on the radiation stability scale.

1.4 Radiation Sources

Almost all sample irradiations were made in the Materials Testing Reactor (MTR) canal gamma source. The prevailing flux varied from about 2×10^6 r/hr to 20×10^6 r/hr. A small number of irradiations were also conducted in the California Research-AEC cobalt-60 source in which the flux was about 0.3×10^6 r/hr.

Throughout this report the roentgen unit has been retained as the measure of gamma radiation. The values cited are considered accurate to about ± 10%. Other units may be used to express gamma radiation, such as the roentgen equivalent physical (rep)[1] or the rad[2]. Although the concepts of these three units are different, for rough comparisons, they may be considered numerically equivalent.

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[1] Richard Stephenson, "Introduction to Nuclear Engineering," McGraw-Hill, New York, p. 166, 1954.

[2] Nucleonics, 12, No. 1, p. 11 (1954).

1.5 Irradiation Containers Used

Several types of vessels were used, depending primarily on the quantity of organic fluid to be exposed and also whether the container was to be sealed. The horizontal dimensions of the MTR gamma grid were 3 inches by 12 inches and the usable depth about 24 inches. Sample containers were placed in outer canisters which were within these dimensions. It was convenient, for example, to use a 3-inch O. D. pipe as an outer canister. Four-dram glass vials were a convenient type of inner container. A vent hole was bored in the plastic top in each case, and the outer canister was then vented to the canal surface. In exposures in which it was desired to exclude air, capsules[1] of 410 stainless steel were substituted for the glass vials. In some cases the outer canister was heated. This heated canister is shown in Figure 1.

In several instances, larger quantities of irradiated fluid were desired. A convenient container was made by using 1-1/2 inch square aluminum tubing. Four 24-inch sections were welded together to form a four-element container; each element could hold about 625 ml of fluid. Vents were again provided to the canal surface. The largest practical quantity of fluid for a single exposure was about 3-1/2 gallons. This was contained in an aluminum tank, which conformed to the full gamma grid dimensions. A sketch of this tank is shown in Figure 2.

1.6 Methods Used to Test Lubricants and Fuels

The physical property and bench tests were performed, in the majority of cases, by standard methods[2, 3]. In the few instances where special tests were used, the procedures are noted in the text.

---

[1] N. P. Shiells, R. O. Bolt, and J. G. Carroll, "Safe Containers Hold Organics for Irradiations," Nucleonics, 14, No. 8, p. 54-57, August 1956.

[2] Federal Test Method Standard No. 791, December 15, 1955.

[3] ASTM Standards on Petroleum Products and Lubricants; ASTM Committee D-2, November 1955.

CONSTRUCTION NOTES

1. TOP HEATER. 40 WINDINGS NO. 23 N/C 35 Ω.

   TOP 2" - 16 WINDINGS
   NEXT 2" - 11 WINDINGS
   NEXT 2" - 8 WINDINGS
   NEXT 2" - 5 WINDINGS

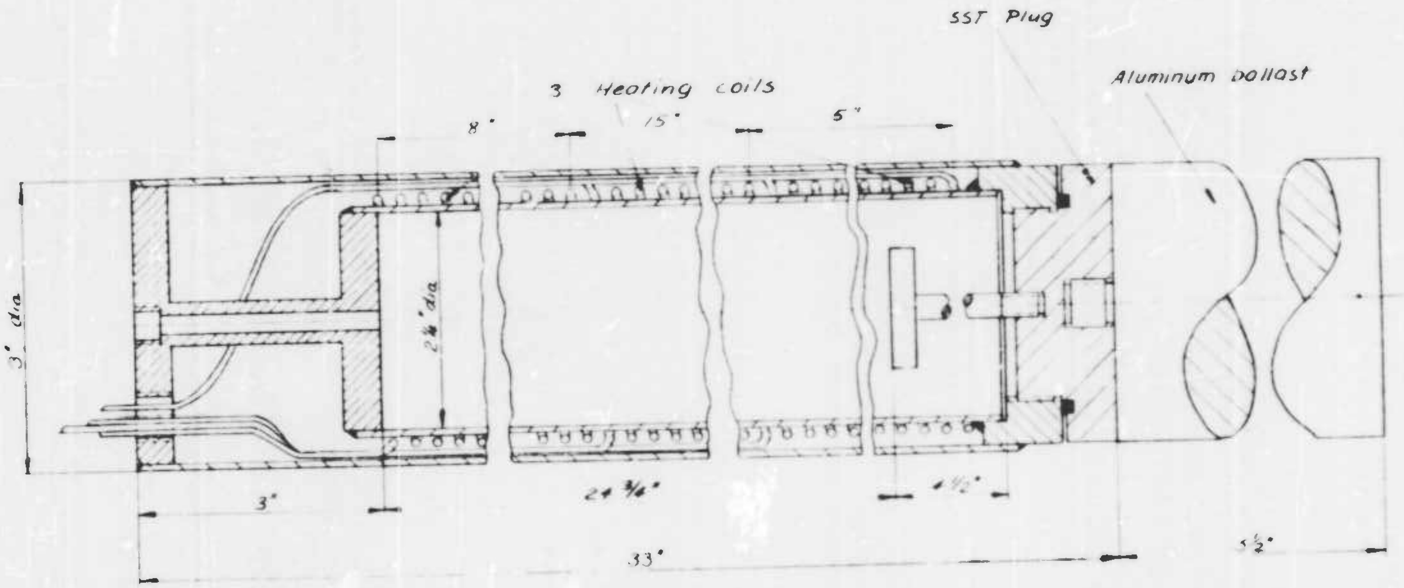
2. CENTER HEATER. 40 WINDINGS NO. 23 N/C 35 Ω.

   UPPER 12" - 32 WINDINGS
   NEXT 2" - 8 WINDINGS

3. BOTTOM HEATER. 40 WINDINGS NO. 23 N/C 40 Ω.

   WINDINGS EVENLY SPACED OVER 5".

HEATERS HAVE COMMON NEUTRAL LEAD. INSTALLATION BETWEEN HEATERS AND INNER TUBE IN ASBESTOS PAPER WRAPPED WITH GLASS TAPE. NO. 15 N/C COMMON LEAD AND NO. 23 N/C HOT LEADS INSULATED WITH CERAMIC BEADS OVER FIRST THREE FEET. THERE SILVERSOLDERED TO FOUR LEAD COPPER CABLE.



None
Fit.

2-16-56

HEATED CANNISTER

FIG. 1 - HEATED CANISTER

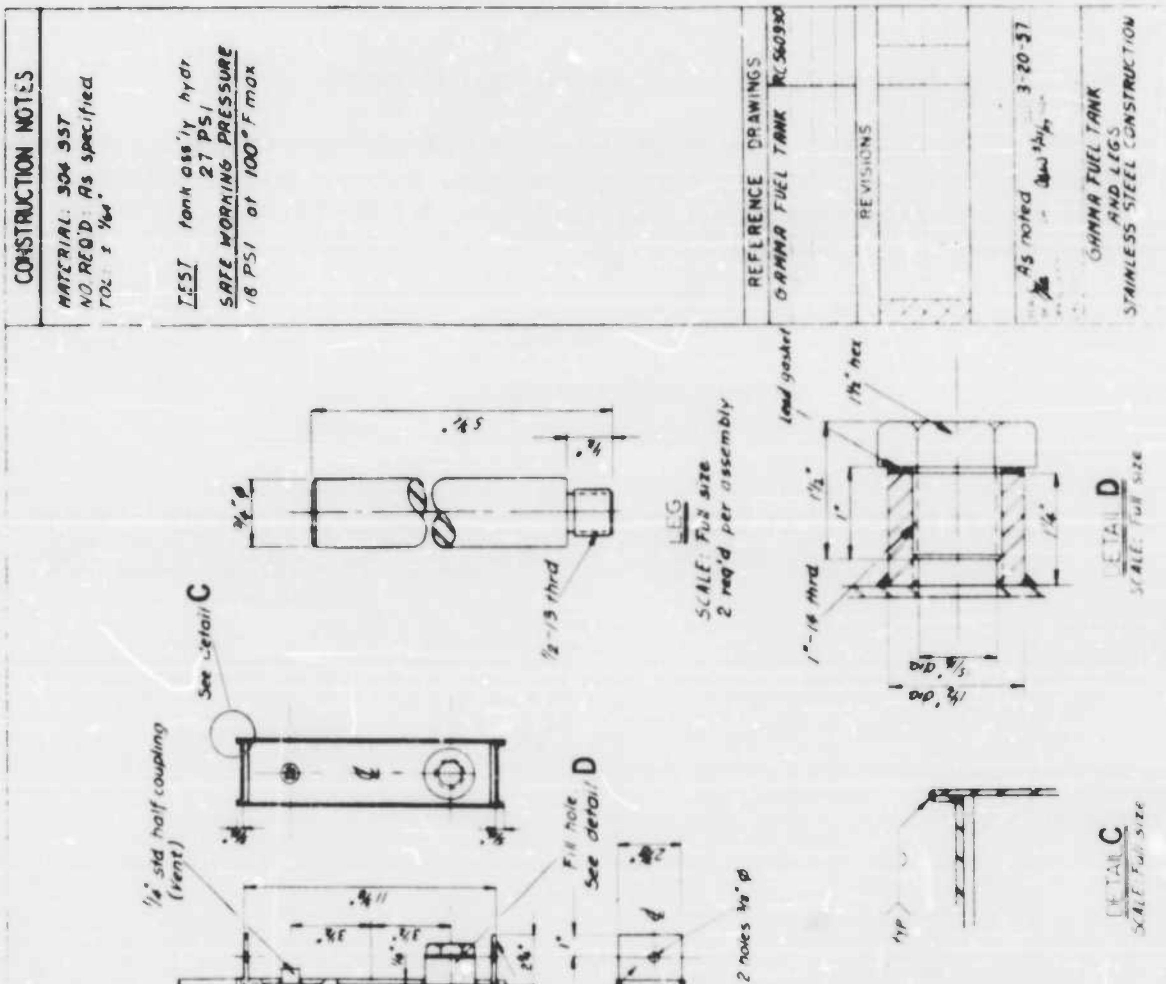


FIG. 2 - GAMMA FUEL TANK

2. BASE MATERIALS

2.1 Available Fluids (R. O. Bolt and R. L. Peeler)

A first step in the consideration of base materials for the new lubricant applications was to survey available products for usefulness. Table V summarizes the general advantages and disadvantages of the various classes of commercial fluids.

Table V

Summary of Properties of Commercial Base Fluid Classes[a, b]

	Radiation Stability[c]	Vis.-Temp. Properties	Volatility	Thermal Stability	Oxidation Stability[d]	Hydrolytic Stability	Lubricity
Naphthenic Mineral Oil	-	-	+	+	+	+	+
Alkyl Aromatic Compounds	+	-	+	+	+	+	+
Aliphatic Diesters	-	+	+	-	+	-	+
Polyglycols	+	+	-	-	-	+	+
Aromatic Phosphate Esters	-	-	+	+	+	-	+
Silicate Esters	-	+	+	+	-	-	-
Silicones	-	+	+	+	+	-	-
Halohydrocarbons	-	-	-	-	-	-	-
Fluorocarbons	-	-	-	+	+	+	-

a. + = advantageous; - = disadvantageous.

b. Staff Article, Chem. Eng. News, 34, No. 36, 4247 (1956), amended.

c. "Effects of Fission Radiations on Lubricants and Lubrication," Final Report, California Research-NEPA Project (Report NEPA 1844), April 30, 1951 (SECRET)

d. At 400°F.

The discussion of this subsection on each of these classes will serve as background for the lubricant development work because whenever possible the base materials used were obtained from commercial sources. Table VI lists many of these fluids and some of their physical properties.

As Table V indicates, the mineral oils may be of some use. Those of interest are highly refined naphthenic oils which may have enough thermal and oxidation stability to find application in the 400-500°F region. However, mineral oils show poor radiation stability and would also involve sacrifice in low temperature performance.

Both the aliphatic diesters and the polyglycols have excellent physical properties as can be noted from Table VI. The principal drawback with the esters is lack of radiation resistance. This disadvantage is overcome somewhat with the polyglycols. These undergo radiolysis to give products of both lower and higher molecular weight than the original[1]. In certain dosage regions the lower molecular weight compounds predominate and a viscosity decrease (or only a small increase in viscosity) takes place. However, the volatility of such radiolysis products is high and their thermal and oxidation stabilities are lower than those of the original.

Inorganic esters show fewer advantages as noted in Table V. The good lubrication qualities of aromatic phosphate esters are offset by poorer viscosity-temperature and hydrolytic stability properties. Likewise, the good viscosity-temperature characteristic of the silicate esters are offset by poorer lubricity and hydrolytic stability.

Silicones show many advantages but are beset by two serious difficulties in the lack of lubricity and radiation resistance. These materials are the most susceptible to radiolysis of any of the classes listed in Table V. The outstanding thermal and oxidation stabilities of the fluorocarbons must be weighed against poor viscosity-temperature, lubricity, and radiation resistance properties. These materials tend to break down on radiolysis into reactive fluorides which promote extensive corrosion[1].

The alkyl aromatics exhibit many advantages. They are the most radiation resistant of all the classes listed in Table V by virtue of their aromatic ring content[2]. However, aromatic materials suitable for lubricant use are quite limited in availability. Most of the alkylbenzenes, alkylnaphthalenes, and alkylbiphenyls of Table VI not only have extremely poor physical properties, but are available only in small quantities. The disadvantage of poor viscosity-temperature properties, listed for the alkyl aromatics in Table V, can be overcome by proper synthesis. The octadecylbenzene of Table VI, an experimental product, shows improved physical characteristics. The aromatic esters, e.g., the terephthalates, also have good physical properties as the data of Table VI show.

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[1] "Effects of Fission Radiations on Lubricants and Lubrication," Final Report, California Research-NEPA Project (Report NEPA 1844), April 30, 1951 (SECRET)

[2] C. S. Schoepfle and C. H. Fellows, "Gaseous Products From Action of Cathode Rays on Hydrocarbons," Industrial and Engineering Chemistry, 23, 1396 (1931)

TABLE VI

PHYSICAL PROPERTIES OF AVAILABLE FLUIDS

	Viscosity, Centistokes, at						Viscosity Index	Pour Point, °F	Evaporation[a] % (6 1/2 hr at 400°F)	Vapor Pressure at 400°F mm	Spontaneous Ignition Temperature °F	Flash, COC, °F	Fire, COC, °F	Gravity, °API
	-65°F	-40°F	-20°F	0°F	100°F	210°F								
Petroleum Fractions														
[illegible] Insulating Oil	-	-	856	-	8.205	2.166	66	-80	-	51	720	-	-	-
Spray H	-	-	-	-	21.44	3.792	54	-40	75	-	-	355	375	29.0
Naphthenic Pale Oil	-	-	-	-	35.2	4.85	39	-40	57	-	-	360	385	25.5
Naphthenic White Oil	-	-	-	14,519	74.51	7.651	63	-30	19	-	735	435	470	-
Extract from Spray H	-	-	-	-	57.85	4.829	-164	-10	-	-	-	355	385	10.9
Naphthenic Spray Oil	-	-	9,282	-	17.15	3.35	55	-55	-	22.8	700	330	370	29.0
Polyglycols														
Polyglycol Ether Ester	-	9,266	3,819	-	17.48	4.16	165	-70	72	-	-	410	440	14.4
Polyglycol Diether (71)	7,940	-	-	-	9.557	2.458	135	<-80	-	-	-	355	395	16.0
Polyglycol Diether (144)	5,512	794	-	103.0	8.88	2.75	168	<-80	35	-	-	370	400	-
Polyglycol Diether (65)	-	-	-	-	57.31	10.41	147	-45	4.6	-	-	430	480	-
Ucon LB 65	-	-	-	-	12.94	3.017	97	-70	-	-	-	295	320	15.0
Ucon LB 135	-	28,200	-	-	29.49	5.603	148	-60	14	-	-	410	450	12.7
Ucon DLB 50E	-	-	-	-	7.272	2.307	145	-80	-	55	-	295	335	19.0
Ucon DLB 62E	-	-	-	-	10.86	3.162	177	-80	39	-	-	340	375	17.7
Ucon DLB 144E	-	-	-	-	32.37	7.156	162	-65	10.1	-	-	455	545	13.4
Ucon DLB 234E	-	-	-	-	50.88	10.47	155	-50	-	-	-	455	530	12.8
Phenyl Carbitol	-	-	-	-	14.19	2.246	-190	-	-	-	-	-	-	-
Esters														
Tridecyl Azelate	-	18,404	-	-	34.75	6.509	139	-80	3.1	-	-	480	565	24.2
Di-2-ethylhexyl Sebacate	8,224	-	-	-	12.66	3.339	150	<-80	14	-	770	430	500	22.6
Diisooctyl Azelate	6,986	-	-	-	12.36	3.39	-	<-80	17.8	-	770	405	485	-
Diisodecyl Adipate	-	-	-	-	14.95	3.559	144	-75	17.4	-	-	435	485	22.5
Diisobutyl Phthalate	-	-	-	-	15.0	2.75	-54	-60	-	22.7	-	355	380	-
Di(4-methyl-2-pentyl) Phthalate	-	-	-	-	20.9	3.24	-54	-30	-	-	-	370	400	10.3
Dibutyl Phthalate	-	2,028	-	-	9.039	2.292	36	-75	-	18.1	790	300	385	1.05[c]
Di-2-ethylhexyl Phthalate	-	59,120	-	-	29.07	4.274	11	-60	27.8	2	-	415	450	11.7
Diisooctyl Phthalate	-	54,930	-	-	27.15	4.254	42	-55	23	-	830	410	465	11.9
Dicapryl Phthalate	-	-	-	-	26.22	4.038	18	-55	-	-	-	380	435	14.0
Diisodecyl Phthalate	-	139,000	-	-	42.00	5.405	59	-45	-	-	770	430	470	14.3
Butyl Octyl Phthalate	-	-	-	-	22.81	3.827	30	-55	-	-	-	415	445	10.7
Butyl Decyl Phthalate	-	-	-	-	20.19	3.598	41	-55	-	-	-	370	410	9.9
Isooctyl Isodecyl Phthalate	-	-	-	-	32.81	4.718	45	-55	-	-	-	400	480	13.7
n-Octyl n-Decyl Phthalate	-	-	-	-	19.88	3.809	93	-45	-	-	-	420	475	13.6
Butyl Benzyl Phthalate	-	-	-	-	20.41	3.408	12	-40	32	-	-	385	455	1.12[c]
Diisooctyl Terephthalate[b]	-	-	-	-	29.09	4.85	90	-65	11.7	-	-	-	-	-
Dipropylene Glycol Dibenzoate	-	-	-	-	44.50	4.415	-140	-10	-	-	-	410	450	1.12[c]
Diisodecyl Terephthalate[b]	-	-	-	-	56.38	7.017	87	-45	-	-	-	490	-	-
Hercoflex 600	-	7,791	-	-	24.35	4.708	132	<-80	7.2	-	775	470	530	-
Silicon Compounds														
DC 702 Fluid	-	-	-	-	21.08	4.375	136	-35	-	3.2	-	410	440	1.09[c]
DC 703 Fluid	-	-	4,720	-	21.71	5.523	180	-40	-	0.85	840	440	480	1.09[c]
Hexa(2-ethylbutoxy)disiloxane	719	-	-	-	11.17	4.00	250	<-80	-	1.0	730	410	400	-
Phosphates														
Cresyl Diphenyl Phosphate	-	-	-	-	18.17	3.254	15	-35	15.4	-	-	475	500	1.20[c]
Tricresyl Phosphate	-	-	-	-	29.96	4.085	-30	-20	9.7	-	-	-	-	-
Ethers														
Alpha-Methyl Benzyl Ether	-	-	-	-	7.264	1.635	-	-30	-	-	-	265	295	9.5
Bis(dimethyl benzyl) Ether	-	-	9,304	-	9.361	2.164	8	-55	-	11.4	995	340	380	13.0
Bis(1,1,3,3-tetramethylbutyl phenyl) Ether	-	-	-	-	1014.0	14.51	-413	+40	-	-	-	-	-	-
Alkylbenzenes														
Alkylbenzene (M.W ~ 250)	-	-	1,015	-	5.212	1.727	-	<-80	-	88	800	270	300	30.6
Alkylbenzene (M.W.~ 350)	-	-	-	-	32.65	4.169	-52	-40	82	15.7	-	340	320	29.3
C_{18} Benzene[b]	-	-	1,793	-	11.45	2.789	95	-40	-	4.0	720	-	-	-
Alkylnaphthalenes														
Nonylnaphthalene (Neolene 210)	-	-	-	-	16.61	2.669	-107	-35	-	26.6	-	-	-	-
Dinonylnaphthalene (Neolene 220)	-	-	-	-	69.5	5.79	-155	-5	-	-	-	-	-	-
Pentalene 90	-	-	-	-	29.30	3.584	-139	-45	-	16.8	-	-	-	-
Pentalene 92	-	-	-	-	153.6	9.064	-27	-15	-	-	-	-	-	-
Pentalene 103	-	-	1,992	-	5.578	1.493	-	-75	-	76	875	-	-	-
Pentalene 195	-	-	-	-	25.76	3.474	-98	-45	-	27.1	-	-	-	-
Alkylbiphenyl														
Amyl Biphenyl (Pentaryl A)	-	-	-	-	10.93	2.193	-59	-45	-	36.0	960	-	-	-
Diamyl Biphenyl (Pentaryl B)	-	-	-	-	90.5	6.31	-85	-20	-	-	-	-	-	-
Poly Sec-amyl Biphenyl	-	-	-	-	116.6	7.814	-27	-20	-	-	-	-	-	-
Mixed Sec-amyl Biphenyls	-	-	-	-	92.02	6.981	-26	-20	-	-	-	-	-	-
Plasticizer HB 20	-	-	-	-	9.178	2.121	2	-55	32	41	-	315	345	14.3
Polybutene														
Polybutene 8	-	-	-	-	137.4	12.44	86	-35	-	75	-	260	285	-
Indopol L-50	-	-	-	-	109.9	11.85	104	-30	-	-	-	270	285	34.8

a. With oxidation inhibitor.
b. Experimental products prepared prior to this contract.
c. Specific gravity.

This brief survey indicated that additional aromatic materials suitable for lubricant use should be synthesized. Of particular interest were the alkylbiphenyls, alkyl diphenyl ethers and aryl esters. The remaining parts of Section 2 deal with the products made in this effort.

2.2 Synthesis of a Diester of An Aromatic Dibasic Acid (M. J. Schlatter)

The properties shown in Table VI (page 8) for diisooctyl terephthalate made this compound of interest for a gas turbine lubricant base material. As it was not available commercially, the compound was prepared on a barrel scale for test work.

The first batch was made by transesterification of dimethyl terephthalate with Enjay "isooctyl" alcohol using sodium methylate as catalyst. This gave good results in the laboratory, but in the large scale preparation, partial hydrolysis occurred during removal of the catalyst. The product contained a considerable quantity of monoisooctyl terephthalate.

Additional laboratory work showed that litharge in small amounts was as effective as sodium methylate as an ester interchange catalyst. Furthermore, the litharge could be completely removed by treatment with "Norite A" decolorizing carbon. This method eliminated the danger of hydrolysis during catalyst removal and was used in a second barrel-size preparation. A total of 175 pounds of diisooctyl terephthalate was recovered from both batches. A detail of the procedures used in these preparations is attached as Appendix I.

Properties of the diisooctyl terephthalates made, compared with literature values, are shown in Table VII.

Table VII

Properties of Diisooctyl Terephthalate

	Large Batches	Laboratory Batch	Literature[a]
Boiling Point, °F	-	-	258-281 at 4 microns
Refractive Index, n_D^{20}	1.5896	1.4897	Sp. Gr. 60/60 = 0.987
Sap. No., mg KOH/g (Theory 287)	279.4	279.0	286.0
Neut. No., mg KOH/g	0.3	Nil	-
Color	3-1/2 ASTM	+13 Saybolt	-
Lead Analysis, ppm	<1	<1	-
Flash Point, °F	420	425	-
Pour Point, °F	-75	-	-40
Viscosity, cs			
At 100°F	31.74	31.46	38.40
At 210°F	5.08	5.08	5.65
Viscosity Index	93	97	92

[a] P. V. Smith, R. G. Newberg, and D. W. Young, Ind. Eng. Chem., 42, 2576 (1950).

2.3 Synthesis of Alkylbiphenyls (R. O. Bolt and M. J. Schlatter)

The alkyl aromatic compounds were shown of interest as lubricant bases under "Available Fluids" (page 6). Previous screening work on AEC Contract AT(11-1)-174 indicated alkylbiphenyls, particularly the octadecyl (C_{18}) derivative, to be of possible use. In the present work, laboratory-scale preparations of C_{16-18} alkylbiphenyl were made for further evaluations. Work on variables in the biphenyl alkylation process was also conducted. A barrel-scale batch of C_{16-18} alkylbiphenyl was then made to provide base stock for extensive testing. Exploratory work also was undertaken on effects of varying olefin chain length and of introducing two or three small alkyl chains instead of a long chain in the biphenyl molecule.

2.3.1 C_{16-18} Alkylbiphenyls

General procedures used for the laboratory-scale alkylations (generally 200 ml quantities) are in Appendix II. Reactants and typical properties of products from the alkylations of biphenyl with 1-octadecene and C_{16-18} alpha-olefins are given in Table VIII Distillation of the crude products resulted in a marked reduction in pour point in some cuts with only a small reduction in viscosity. Some of the 10% distillation cuts had pour points of less than -50°F. Solids separated from the 50% to end point cuts on storage

TABLE VIII

PROPERTIES OF LABORATORY-SCALE BATCHES C_{16-18} AND C_{18} ALKYLBIPHENYL

1. Product No.	3470-07	3470-092	3470-093	3470-094	3470-095	3470-096	3470-097	3470-09	3470-17	3470-16	3274-12	3274-19	3274-19
Olefin	Mixed C_{16}-C_{18}[a]											1-Octadecene	
Solvent	None									$C_6H_5NO_2$	None	None	
Catalyst	$AlCl_3 \cdot CHCl_3$ (2:1)									$AlCl_3$	$AlCl_3 \cdot CHCl_3$ (2:1)	$AlCl_3 \cdot CHCl_3$ (2:1)	
Mole Ratio (Aromatic:Olefin:Catalyst)	2.75:1:0.1									2.75:1:0.05	4:1:0.1	4:1:0.1	
Distillation Fraction	Whole	10-20%	20-30%	30-40%	40-50%	50-60%	60-70%	30% Bottoms	Heart Cut 69 Wt. %	Whole	Whole	Whole	5-85%
2. Boiling Range, °F		455-466 at 2 mm	466-471 at 2 mm	471-472 at 2 mm	472-478 at 2 mm	478-482 at 2 mm	482-500 at 2 mm		430-500 at 2 mm				430-472 at 0.4 mm
3. Viscosity, cs													
At -40°F		48,027	47,754	47.177	47,737								
At 100°F	46.5	33.9	34.4	35.0	35.5	36.3	39.1	174	37.8	50.7	43.4	41.0	41.1
At 210°F	6.52	5.05	5.15	5.23	5.31	5.46	5.80	16.1	5.54	7.03	6.02	5.20	5.91
Viscosity Index	99	75	82	83	86	92	96	103	89	105	89	104	[illegible]
4. Pour Point, °F	-15	-55	-55	-55	-45	-35	Ppt.at Rm.Temp.	Ppt. at Rm.Temp.	-40	-10	-25	0	-20
5. Molecular Weight[b]											359	380	
6. Storage, Seeded													
At -20°F, 336 hours	cloud	haze	haze	haze	haze	heavy cryst. ppt.			cloud				
At -40°F, 168 hours	cloud	cloud	cloud	cloud	cryst. ppt.	solid			cloud				
7. Evaporation, %													
6-1/2 hours at 400°F											8.6	5	
8. Viscosity at Pour Point, cs	10,000	400,000	450,000		130,000	45,000							

a. Archer-Daniels-Midland alpha-olefin (75% C_{18}).
b. Freezing point method.

for one week at -40° F. Infrared spectrographic examination of these fractions showed that 4-alkylbiphenyl concentrations were highest in the cuts that crystallized.

A number of alkylations with C_{16-18} alpha-olefins were carried out to see if conditions used with the products of Table VIII could be modified to give bottoms samples with a lower pour point without adversely affecting viscosity or viscosity index. With aluminum chloride as catalyst, it was expected that the product would contain a large number of different hydrocarbon structures. These result from mono- and disubstitution of the biphenyl, formation of position isomers and isomers resulting from side chain isomerization. Such mixtures were desirable in that they should have lower pour points than the individual components. None of the variations of the original alkylation procedure tried yielded improved product properties. The data are summarized in Table IX and the procedures are in Appendix II.

A barrel batch of C_{16-18} alkylbiphenyl was made by the standard procedure[1]. About 475 pounds of alkylate (free of solvents and starting materials) was recovered. The product properties are summarized in Table X. The procedure followed in this preparation is given in Appendix III.

About 100 pounds of the alkylate was made into a lubricating grease[1]. Another 80 pounds was distilled to give a small precut, seven 4-liter distillate cuts, and about 7 liters of di- and (polyalkyl)biphenyl bottoms. The last fraction was clay treated and retained for evaluation. Several composites were made by combining various distillate cuts. The properties of these composites are also shown in Table X. The remaining 250 pounds of alkylate was filtered through clay and retained as a base stock for lubricant compounding.

2.3.2 Effects of Length of the Alkyl Group on the Properties of Alkylbiphenyls

These were studied in biphenyl alkylations under comparable conditions (note procedure in Appendix II) with C_{12-14}, C_{14-16}, C_{16-18}, and C_{20-22} alpha-olefins. Inspections of the whole alkylates after stripping off excess biphenyl are shown in Table XI. These show that the C_{16-18} side chain is about as long as can be used before the pour point of the alkylbiphenyl becomes too high for general use.

The C_{12-14} and C_{14-16} biphenyl alkylates were distilled and 10% cuts collected. Data are given in Table XII. As expected, products with lower viscosity and viscosity indexes resulted from decreased alkyl chain length as compared with the distilled C_{16-18} alkylbiphenyl (Table X, page 14). Lower pour points for the lower molecular weight products were also observed.

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[1] Costs were split half and half between this contract and AEC Contract AT(11-1)-174.

TABLE IX

BIPHENYL ALKYLATIONS WITH C_{16-18} ALPHA-OLEFINS

Experiment No.	4524-18B		3156-49			4524-14A		4524-7			4524-14E	
Reactants	g	Mole Ratio	g		Mole Ratio	g	Mole Ratio	g		Mole Ratio	g	Mole Ratio
Biphenyl	925	3	115		3	925	4	231		6	925	6
Solvent												
C_{16}-C_{18} α-Olefins	456	1	61		1	342	1	61		1	171	1
Catalyst and Modifiers	100% H_3PO_4			100% H_3PO_4		100% H_3PO_4			100% H_3PO_4		100% H_3PO_4	
	81.2	1.66	27.2		1.11	21.8	0.15	5.44		0.22	21.8	0.30
	BF_3			BF_3		BF_3			BF_3		BF_3	
	67.8	0.5	22.8		1.35	18.2	0.18	4.56		0.27	18.2	0.36
Reaction Conditions												
Temperature, °F	212-230			174-185		142-156			174-185		151-166	
Total Time, hours	0.7			5.5		4.0			5.5		3.0	
Olefin Addition Time, hours	0.3			1.4		1.0			1.4		0.67	
Product												
Total Alkylate, g	619		91.1			479		95.6			248	
Theory for 100% Mono-alkyl Product, g	764		99.5			573		99.5			287	
Sample No.	3443-48-1		4524-6-1	4524-11-1	4524-11-2	3443-40-7		3443-32-1	3443-32-2	3443-32-3	3443-45-1	
Boiling Range, °F	482+		392+	392-572	572+	415+		392+	392-572	572+	442+	
Boiling Range, °C	250+		200+	200-300	300+	213+		200+	200-300	300+	228+	
Pressure, mm	4		2	2.5	2.5	2		2	2	2	3	
% of Total Alkylate	100		100	84.9	15.1	100		100	93.7	6.3	100	
Fraction, Percentile	100		100	0-84.9	84.9-100	100		100	0-93.7	93.7-100	100	
Pour Point, °F			-15	-25		-5		-20	-25		-10	
Viscosity, 100°F, cs			36.4	36.31	154.2	41.54			33.97		39.33	
Viscosity, 210°F, cs			5.48	5.60	16.26	6.238			5.30		5.926	
Viscosity Index			93	99	115	107			96		103	

Experiment No.	4524-18A		4524-14B		4524-14F		4524-14C		4524-14D		4524-9		4524-10	
Reactants	g	Mole Ratio	g	Mole Ratio	g	Mole Ratio	g	Mole Ratio	g	Mole Ratio	g	Mole Ratio	g	Mole Ratio
Biphenyl	925	3	925	4	925	8	925	4	616	4	231	6	231	6
Solvent									Cl_3CCH_3		Benzene		Benzene	
									460	-	117	6	117	6
C_{16}-C_{18} α-Olefins	456	1	342	1	171	1	342	1	228	1	61	1	61	1
Catalyst and Modifiers	$AlCl_3$		$AlCl_3$		$AlCl_3$		$AlCl_3$		$AlCl_3$		100% H_3PO_4		$AlCl_3$	
	66.7	0.25	20	0.1	20	0.2	20	0.1	13.5	0.1	2.18	0.09	5.0	0.15
			$CHCl_3$		$CHCl_3$		Nitrobenzene				BF_3		$CHCl_3$	
			9.0	0.05	9.0	0.1	38.4	0.21			1.82	0.11	2.25	0.08
Reaction Conditions														
Temperature, °F	217-226		154-165		142-154		142-167		102-115		102-106		100-118	
Total Time, hours	1.6		3.7		3.0		3.6		3.0		2.0		3.7	
Olefin Addition Time, hours	0.6		1.2		1.0		0.85		1.0		0.9		0.8	
Product														
Total Alkylate, g	456		511		226		516		(c)		29.0		>90	
Theory for 100% Mono-alkyl Product, g	764		573		287		573				99.5		99.5	
Sample No.	3443-47-1		3443-43-1		3443-44-1		3443-42-7				3443-35-3	3443-35-4	3443-34-2	3443-34-3
Boiling Range, °F	419+		415+		419+		415+				320-410	410+	311-410	410+
Boiling Range, °C	215+		213+		215+		213+				160-210	210+	155-210	210+
Pressure, mm	3		2		2		2				9 2.5	2.5	8 2.5	2.5
% of Total Alkylate	100		100		100		100				41	59	20	80
Fraction, Percentile	100		100		100		100				0-41	41-100	0-20	20-100
Pour Point, °F	-10		-20 (a)		-20(a)		-5					(b)		-5
Viscosity, 100°F, cs	79.45		53.86		60.65		45.02				5.79	30.00		35.03
Viscosity, 210°F, cs	8.945		6.967		7.159		6.445				1.92	5.28		5.634
Viscosity Index	94		93		80		102					120		110

(a) Solid separated on standing.
(b) Not enough sample for pour.
(c) Very slow reaction as indicated by bromine number - product discarded.
(d) Archer-Daniels-Midland (75% C_{16}).

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TABLE I

PROPERTIES OF BARREL-SCALE BATCH OF C_{16-18} BIPHENYL[a,b]

Product Inspections									
Product No.	4571-6-35*	4524-28-2	4524-28-3	4524-28-4	4524-28-5	4524-28-6	4524-28-7	4524-28-8	2424-28-9
Description	Total Alkylate, Clay Treated	← C_{16}-C_{18} Alkylbiphenyl Distillate Fractions →							
Distillation Fraction, Vol. %		0-2.9	14.0	25.1	36.2	47.4	58.5	69.6	79.5
Boiling Range, °F		357-434	445	462	472	482	498	509	535
Boiling Range, °C		181-223	229	239	244	250	259	265	279
Pressure, mm		0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8
API Gravity, 60/60	22.4	23.8	22.2	22.2	22.5	22.6	22.5	22.4	22.4
Density, D_4^{20}	0.9160	0.907	0.917	0.917	0.915	0.915	0.915	0.916	0.916
Refractive Index, n_D^{20}	1.5274	1.5214	1.5298	1.5290	1.5280	1.5280	1.5275	1.5277	1.5278
Pour Point, °F	-20	+30	-55	-60	-60	-60	-35	-15	-5
Viscosity, cs									
At 100°F	55.11	17.64	32.76	35.53	36.33	38.45	40.45	43.11	47.06
At 210°F	7.070	3.426	4.824	5.158	5.263	5.507	5.783	6.067	6.503
At Pour	23,000	9,300	320,000	750,000	800,000	850,000	32,000	8,500	4,800
Viscosity Index	93	61	60	73	77	83	90	93	96
Flash Point, COC, °F	465	390	435	445	435	460	440	465	495
Fire Point, °F	515	440	500	500	500	520	530	550	550

Product Inspections					
Product No.	4571-18-19	4524-28-3 to 6	4524-28-3 to 7	4524-28-3 to 8	4524-28-3 to 9
Description	Distillate Bottoms, Clay Treated	Composites of Distillate Fractions: C_{16}-C_{18} Alkylbiphenyls			
Distillation Fraction, Vol. %	100	2.9-47.4	2.9-58.5	2.9-69.6	2.9-79.5
Boiling Range, °F	Bottoms	434-482	434-498	434-509	434-535
Boiling Range, °C		223-250	223-259	223-265	223-279
Pressure, mm	0.8	0.8	0.8	0.3	0.8
API Gravity, 60/60	22.8	22.4	22.4	22.4	22.4
Density, D_4^{20}	0.9146	0.9177	0.9170	0.9173	0.9172
Refractive Index, n_D^{20}	1.5260	1.5283	1.5231	1.5281	1.5280
Pour Point, °F	0	-55	-55	-45	-35
Viscosity, cs					
At 100°F	203.1	35.69	36.87	37.80	38.58
At 210°F	17.08	5.169	5.225	5.413	5.518
At Pour	36,000	500,000	520,000	140,000	50,000
Viscosity Index	97	73	71	79	83
Flash Point, COC, °F	585				
Fire Point, °F	645				

* DG-1269

a. No solvent, $AlCl_3$, $AlCl_3 \cdot CHCl_3$ (2:1) used; mole ratio aromatic:olefin: catalyst = 3.5:1:0.1

b. Archer-Daniels-Midland C_{16-18} alpha-olefins used (75% C_{16})

TABLE XI

PROPERTIES OF ALKYLBIPHENYLS[a]

Olefin	C_{20-22}[b]	C_{16-18}[b]	C_{14-16}[b]	C_{12-14}[b]
Catalyst	← $AlCl_3 \cdot CHCl_3$ (2:1) →			
Mole Ratio (Aromatic:Olefin:Catalyst)	3:1:0.15	3.5:1:0.15	3:1:0.15	3:1:0.15
API Gravity, 60/60	24.4	22.4	21.7	19.9
Density, D_4^{20}	0.9000	0.9160	0.9191	0.9286
Refractive Index, n_D^{20}	1.5182	1.5274	1.5328	-
Pour Point, °F	+35	-20	-50	-40
Viscosity, cs				
At 100°F	85.4	55.1	44.9	43.2
At 210°F	10.24	7.07	5.93	5.53
At Pour	900	23,000	500,000	190,000
Viscosity Index	109	93	77	58
Quantity, lb	0.4	475	2.5	2.2

a. Bottoms products after removing excess biphenyl.
b. Archer-Daniels-Midland alpha-olefins

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TABLE XII

PROPERTIES OF FRACTIONS OF [illegible] AND [illegible] ALKYLBIPHENYLS

Description																						
Experiment No.	8520-30														8520-3[illegible]								
Olefin	C[illegible]														C[illegible]								
Catalyst	AlCl₃-CHCl₃ (2:1)														AlCl₃-[illegible] (2:1)								
Solvent	None														None								
Mole Ratio (Aromatic:Olefin: Catalyst)	5:1:0.1														5:1:0.1								
% Yield	50														60								
Product Inspections																						
Product No.	4571-10-27	4571-21-1	4571-21-2	4571-21-3	4571-21-4	4571-21-5	4571-21-6	4571-21-7	4571-21-10	4571-16-[illegible]	4571-16-30	4571-21-1 to 10	4571-19-2	4571-19-3	4571-19-4	4571-19-5	4571-19-6	4571-19-7	4571-19-8	4571-19-9	4571-19-12	4571-19-13
Description	Total Alkylate[a]	← [illegible] Alkylbiphenyl Distillate Fractions →							← Polyalkylbiphenyls →			Composite Alkylbiphenyls	Total Alkylate[a]	← [illegible] Alkylbiphenyl Distillate Fractions →								Polyalkyl-biphenyls
Distillation Fraction, Vol %		0-10	20	30	40	50	60	70	81	91	100	[illegible]		0-10	20	30	40	50	60	70	78.[illegible]	100
Boiling Range, °F		365-406	408	[illegible]	[illegible]	425	43[illegible]	[illegible]	5[illegible]	[illegible]				[illegible]	433	430	442	[illegible]	[illegible]	45[illegible]	474	
Boiling Range, °C		185-208	209	21[illegible]	213	218.5	221	[illegible].5	2[illegible]	2[illegible]	Bottoms	1[illegible]		1[illegible]-22[illegible]	223	22[illegible]	228	230	2[illegible]	2[illegible]	245	Bottoms
Pressure, mm		2.0	2.0	2.0	2.0	2.0	2.0	[illegible]	[illegible].5	[illegible]	-	2.0		2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	-
API Gravity, 60/60	19.9	20.3	20.6	[illegible]	[illegible]	19.9	19.[illegible]	[illegible]		2[illegible].1		20.[illegible]	21.[illegible]	21.[illegible]	2[illegible]	21.[illegible]	2[illegible].2	[illegible].2	21.[illegible]	21.5	20.[illegible]	21.[illegible]
Density, d_4^{20}	0.9846	0.9[illegible]	0.9270	0.9278	0.9[illegible]	0.938	[illegible]	[illegible]		0.9[illegible]		0.9[illegible]	0.910	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Refractive Index, n_D^{20}		1.5[illegible]3	1.5[illegible]	1.5576	1.55[illegible]	1.55[illegible]	[illegible]	[illegible]		1.551[illegible]	1.5[illegible]	1.5[illegible]	1.5[illegible]	1.5[illegible]	1.55[illegible]	1.5[illegible]	[illegible]	[illegible]	[illegible]	1.5551	[illegible]	1.5[illegible]
Pour Point, °F	-4[illegible]	-55	-60	-55	-55	-55	-55	[illegible]	[illegible]	-25	+2[illegible]	-[illegible]	-4[illegible]	-[illegible]	-5[illegible]	-55	-5[illegible]	-5[illegible]	[illegible]	-5[illegible]	-55	-[illegible]
Viscosity at 100°F, cs	43.10	26.0[illegible]	26.[illegible]	26.[illegible]	26.[illegible]	2[illegible]	[illegible]	[illegible]		18[illegible]		[illegible]	[illegible]	29.4[illegible]	[illegible]	[illegible]	31.[illegible]	[illegible]	31.23	29.[illegible]	[illegible]	193.[illegible]
Viscosity at 210°F, cs	5.532	[illegible]6	5.[illegible]	[illegible]	5.4[illegible]	[illegible]	[illegible]	[illegible]		[illegible]		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	5.076	[illegible]	[illegible]	[illegible]
Viscosity at Pour, cs	130,000	510,000	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]		[illegible]		1,[illegible]	[illegible]	1,[illegible]	[illegible]	[illegible]	213,[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Viscosity Index	58	2	6	15	[illegible]	22	24	6[illegible]		[illegible]		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	56	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

a. Products distilled through a 5-foot "zigzag" column ([illegible]). Traces of biphenyl were removed at a reflux ratio of [illegible] when the alkylbiphenyl plateau was reached, the product was distilled rapidly at a [illegible] 1 or 1:2 reflux ratio.

b. Archer Daniels-Midland alpha-olefins (30% higher constituent).

2.3.3 Octylbiphenyls and Dialkylbiphenyls

Properties of the products from four alkylations of biphenyl with 1-octene are summarized in Table XIII. As predicted, the monoalkyl products had viscosities lower than those for C_{16-18} alkylbiphenyl and higher per cent evaporation at 400°F (Table VIII, page 11). However, the viscosity indexes were much poorer but the pour points were about the same as those for the C_{16-18} derivative. The di- and trioctylbiphenyls compared more favorably but were still inferior.

Other experiments to synthesize dialkylbiphenyls are shown in Table XIV. Alkylation of biphenyl with a 2:1 molar proportion of C_{12-14} alpha-olefins gave a "dialkyl" bottoms product after stripping off unreacted biphenyl and monoalkylbiphenyl. This product had a higher viscosity index and a lower pour point than were obtained for trioctylbiphenyl. The "dialkyl" bottoms from alkylation with C_{14-16} alpha-olefins had a 30°F higher pour point (to -5°F) than the C_{12-14} derivative. The trioctylbiphenyl and di(C_{12-14}) alkylbiphenyl were prepared in 200 ml quantities for evaluation as grease bases.

Samples of amylbiphenyl were alkylated with C_{12-14} and C_{16-18} alpha-olefins to get products containing both short and long side chains. Considerable migration of amyl groups occurred as shown by the boiling ranges cited in Table XIV. Thus, mixtures of molecules with no short chains and those with more than one short chain were obtained. Properties of fractions taken for testing are also summarized in the table.

2.4 Synthesis of Alkyl Diphenyl Ethers (A. C. Ettling)

These materials are cousins to the alkylbiphenyls. They were expected to have most of the advantages of the latter and have improved properties as well. Table XV shows the properties of the alkylated diphenyl ethers synthesized for this program. The general procedure of Appendix II was used as modified by the discussion under 2.4.4 "Procedures." The trioctyl and didodecyl derivatives were prepared to provide stocks of low volatility suitable for grease bases. The dodecyl and tetradecyl products appeared suited for hydraulic fluids.

2.4.1 Monoalkyl Diphenyl Ethers

Within the limits of this study the monoalkyl diphenyl ethers had decreasing pour points with increasing alkyl chain length up to 12 carbon atoms. Alkyl chains of greater than 12 carbon atoms showed increasing pour point with increasing length. As expected, the longer the alkyl group the higher the viscosity index. Table XVI illustrates these points.

TABLE XIII

PROPERTIES OF OCTYLBIPHENYLS

1. Product No.	3470-131	3470-132	3470-14	3470-141	3470-142	3470-143	3470-144	3470-44	3470-411	3470-442	4658-06
Olefin	← 1-Octene →										
Solvent	None		CS_2					None			None
Catalyst	$AlCl_3$		$AlCl_3$					$AlCl_3 \cdot CHCl_3$ (2:1)			$AlCl_3 \cdot CHCl_3$ (2:1)
Mole Ratio (Aromatic:Olefin:Catalyst)	1:2:0.05		1:2:0.1					1:3:0.15			3:1:0.1
Distillation Fraction	Monoalkyl	Dialkyl	Whole	Monoalkyl	Mono and Dialkyl	Dialkyl	Trialkyl	Whole	Dialkyl	Trialkyl	Monoalkyl
2. Boiling Range, °F	300-390 at 2.5 mm	390-480 at 2.5 mm		320-402 at 5 mm	402-424 at 5 mm	424-460 at 5 mm	460-526 at 5 mm		350-468 at 2 mm	468-540 at 2 mm	320-360 at 2 mm
3. Viscosity, cs											
At 100°F	17.9	73.4	60.2	16.4	20.1	51.1	99.5	141.0	59.2	171.4	15.0
At 210°F	3.00	7.57	6.99	2.96	3.91	5.04	9.42	11.4	6.37	12.9	2.74
Viscosity Index	-27	65	76	-11	-5	55	73	66	43	56	-30
4. Pour Point, °F	-50	-40	-50				-55	-30	-50	-20	-45
5. Refractive Index, n_D^{20}									1.5341	1.5292	1.5527
6. Evaporation, % 6-1/2 Hours at 400°F	87.7	22.8									
7. Spontaneous Ignition Temp., °F											790
8. Storage, Seeded											
At -20°F, 336 Hours	cloud	cloud	cloud	cloud	cloud	cloud	haze				
At -40°F, 168 Hours	cloud	cloud	cloud	haze	cloud	cloud	haze				

TABLE XIV

PROPERTIES OF ALKYLATED BIPHENYL AND AMYLBIPHENYL

	Alkylated Biphenyl						Alkylated Amylbiphenyl[e]		
1. **Product No.**	3470-41	3470-411	3470-412	3470-43	3470-431	3470-432	3470-49	3470-48	3470-481
Olefin	← Mixed C_{12}-C_{14}[a]			Mixed C_{14}-C_{16}[b] →			Mixed C_{12}-C_{14}[a]	Mixed C_{16}-C_{18}[c]	
Catalyst	← $AlCl_3 \cdot CHCl_3$(2:1) →						$BF_3 \cdot H_3PO_4$[d]	$AlCl_3 \cdot CHCl_3$(2:1)	
Mole Ratio (Aromatic:Olefin:Catalyst)	1:2:0.1			3:1:0.1			4:1:0.25	4:1:0.1	
Distillation Fraction	Whole	Monoalkyl	Dialkyl Bottoms	Whole	Heart Cut	Bottoms	Heart Cut	Heart Cut	Bottoms
2. **Boiling Range**, °F at 2 mm		386-500			398-474		404-500	442-528	
3. **Viscosity**, cs									
At -40°F					79,247		202,525		
At 100°F	97.6	35.5	134.8	48.8	33.2	229.2	59.1	103.2	502.9
At 210°F	10.4	5.06	13.2	6.20	4.80	16.8	6.76	9.37	31.3
Viscosity Index	97	63	99	75	53	83	66	66	99
4. **Pour Point**, °F	-60	-30	-35	-55	-60	-5	-55	-40	+5
5. **Molecular Weight**			444					417	776
6. **Index of Refraction**, n_D^{20}		1.5310	1.5191		1.5351		1.5158	1.5229	1.5087

a. Archer-Daniels-Midland (90% C_{12})
b. Archer-Daniels-Midland (90% C_{14})
c. Archer-Daniels-Midland alpha-olefins (75% C_{16})
d. 45.6 weight per cent BF_3
e. Sharples' Pentaryl A

TABLE XV

PROPERTIES OF ALKYLATED DIPHENYL ETHER

1.	Product No.	3470-241	3470-242	3470-25		3470-23		3470-27	3470-291	3470-292
	Olefin	← 1-Hexene →				← 2-Octene →				
	Catalyst	AlCl₃·CHCl₃ (2:1)		AlCl₃·CS₂ (1:2)		AlCl₃		AlCl₃·CS₂ (1:1)		
	Mole Ratio (Aromatic:Olefin:Catalyst)	1:2:0.5		1:2:0.1		1:2:0.1		1:2:0.1		
	Distillation Fraction	Monoalkyl	Dialkyl	Heart Cut	Bottoms	Heart Cut	Bottoms	Whole	70% Bottoms	56% Bottoms
2.	Boiling Range, °F	285-360 at 1.5 mm	360-500 at 1.5 mm	270-410 at 1.3 mm	410- at 1.3 mm	310-430 at 2 mm	430- at 2 mm	284- at 2 mm	357- at 2 mm	400- at 2 mm
3.	Viscosity, cs									
	At -40°F	-	-	-	-	-	-	-	-	-
	At 100°F	15.5	64.3	16.2	486.2	15.7	72.5	40.8	66.7	94.8
	At 210°F	2.85	8.75	2.97	23.4	3.01	8.11	5.71	7.81	9.78
	Viscosity Index	15	48	-5	80	20	94	84	88	88
4.	Pour Point, °F	-55	-40	-55	-20	-55	-50	-50	-45	-40
5.	Density, D_4^{20}	-	-	-	-	-	-	-	-	-
6.	Index of Refraction, n_D^{20}	-	-	-	-	-	-	-	-	-
7.	Flash, °F	-	-	-	-	-	-	-	-	-
	Fire, °F	-	-	-	-	-	-	-	-	-
	SIT, °F	-	-	-	-	-	-	-	-	-
8.	Evaporation, 6-1/2 hours at 400°F	-	42.0	-	-	-	-	-	-	-

1.	Product No.	3470-151	3470-152	3470-153	3470-154	3470-37	3470-371	3470-372	3470-373	3470-381	3470-382	3470-383
	Olefin	← 1-Octene →										
	Catalyst	AlCl₃ + CS₂ Solvent					AlCl₃·CHCl₃ (2:1)					
	Mole Ratio (Aromatic:Olefin:Catalyst)	1:2:0.1					1:2:0.1			1:3:0.15		
	Distillation Fraction	Whole			Bottoms	Whole	Monoalkyl	Dialkyl	Bottoms	Monoalkyl	Dialkyl	Trialkyl Bottoms
2.	Boiling Range, °F	284- at 5 mm	300-425 at 1.5 mm	425-520 at 1.5 mm	520- at 1.5 mm	277- at 2 mm	277-407 at 2 mm	407-482 at 2 mm	482- at 2 mm	230-410 at 2 mm	410-477 at 2 mm	477- at 2 mm
3.	Viscosity, cs											
	At -40°F	-	-	-	-	-	-	-	-	-	157,710	-
	At 100°F	34.1	13.1	32.9	474.5	33.3	15.6	56.8	121.9	17.8	58.8	159.9
	At 210°F	5.58	2.99	4.57	32.9	5.32	3.12	6.97	11.96	3.28	6.97	13.3
	Viscosity Index	118	20	77	107	77	22	73	94	29	77	97
4.	Pour Point, °F	-75	-60	-55	-30	<-60	<-60	-50	-40	<-60	-50	-50
5.	Density, D_4^{20}	-	-	-	-	-	-	-	-	-	-	-
6.	Index of Refraction, n_D^{20}	-	-	-	-	1.5140	1.5243	1.5090	1.5013	1.5191	1.5080	1.5002
7.	Flash, °F	-	-	-	-	-	-	-	-	-	-	-
	Fire, °F	-	-	-	-	-	-	-	-	-	-	-
	SIT, °F	-	-	-	-	-	-	-	-	-	-	-
8.	Evaporation, 6-1/2 hours at 400°F	45.1	-	23.4	-	-	-	-	-	-	-	-

(Continued Next Page)

TABLE XV

PROPERTIES OF ALKYLATED BIPHENYL ETHER

1. **Product No.**	4558-02	3470-33			3470-401	3470-402	3470-50		
Olefin	← 1-Dodecene →						Mixed C_{12}-C_{14}[d]		
Catalyst	← AlCl$_3$·CHCl$_3$ (2:1) →						AlCl$_3$·CHCl$_3$ (2:1)		
Mole Ratio (Aromatic:Olefin:Catalyst)	4:1:0.1	2:1:0.1			1:2:0.1		3:1:0.1		
Distillation Fraction	Bottoms or Whole	Whole	Heart Cut	Bottoms	Monoalkyl	Dialkyl	Whole	Heart Cut	Bottoms
2. **Boiling Range**, °F	380- at 2 mm	390- at 2 mm	390-430 at 2 mm	450- at 2 mm	376-477 at 2 mm	450-584 at 0.75 mm		380-450 at 2 mm	450- at 2 mm
3. **Viscosity**, cs									
At -40°F	11,008.0	-	-	-	13,151.0	95,610.0	-	9504.0	-
At 100°F	18.5	22.1	16.6	52.2	20.0	80.3	21.5	16.5	55.8
At 210°F	3.57	4.0[illegible]	3.34	7.5[illegible]	3.72	9.86	4.01	3.32	7.72
Viscosity Index	70	85	59	109	-7	110	88	66	111
4. **Pour Point**, °F	-75	-55	<-60	-60	-75	-50	-80	-75	-70
5. **Density**, D_4^{20}	0.9406	-	-	-	-	-	-	0.9430	-
6. **Index of Refraction**, n_D^{20}	1.5189	1.5159	1.5200	1.5058	-	1.4992	1.5167	1.5200	1.5001
7. **Flash**, °F	405	-	-	-	-	-	-	-	-
Fire, °F	455	-	-	-	-	-	-	-	-
SIT, °F	-	-	-	-	-	-	-	-	-
8. **Evaporation**, % 6-1/2 hours at 400°F	-	-	-	-	-	-	-	-	-

1. **Product No.**	3470-42			4558-03	3470-19	3470-20	3470-20[a]		
Olefin	Mixed C_{14}-C_{16}[c]			1-Tetradecene	Mixed C_{16}-C_{18}[b]		Mixed C_{16}-C_{18}[b]		
Catalyst	← AlCl$_3$·CHCl$_3$ (2:1) →						AlCl$_3$·CS$_2$ (1:2)		
Mole Ratio (Aromatic:Olefin:Catalyst)	3:1:0.1			4:1:0.1	2.75:1:0.1		2:1:0.05		
Distillation Fraction	Whole	Heart Cut	Bottoms	Bottoms or Whole	Whole	Heart Cut	Whole	Heart Cut	Bottoms
2. **Boiling Range**, °F		420-471 at 2 mm	471- at 2 mm	395- at 2 mm		450-503 at 3 mm		420-490 at 1.7 mm	
3. **Viscosity**, cs									
At -40°F		10041.0		13,056.0					
At 100°F	28.4	19.8	87.5	22.3	32.7	24.6	25.2	24.0	115.0
At 210°F	4.97	3.85	11.0	4.14	5.64	4.57	5.16	4.58	15.6
Viscosity Index	112	92	118	93	123	113	140	111	131
4. **Pour Point**, °F	-45	-60	-20	-70	+5	-10	+25	0	+30
5. **Density**, D_4^{20}	-	-	0.9026	0.9331	-	-	-	-	-
6. **Index of Refraction**, n_D^{20}	1.5120	1.5165	1.5009	1.5149	-	-	-	-	-
7. **Flash**, °F	-	-	-	445	-	-	-	-	-
Fire, °F	-	-	-	495	-	-	-	-	-
SIT, °F	-	-	-	-	-	-	-	-	-
8. **Evaporation**, % 6-1/2 hours at 400°F	-	-	-	-	-	13.6	-	-	-

a. Aromatic was Dowtherm A (74% diphenyl ether).
b. Archer-Daniels-Midland alpha-olefin (75% C_{18}).
c. Archer-Daniels-Midland (90% C_{14}).
d. Archer-Daniels-Midland (90% C_{12}).

Table XVI

Properties of Monoalkyl Diphenyl Ethers

Product No.	No. of Alkyl Carbon Atoms	Viscosity Index	Pour Point, °F
3470-241	6	-15	-55
3470-371	8	22	-65
4658-02	12	70	-75
4658-03	14	93	-70
3470-20	16-18	113	-10

2.4.2 Polyalkyl Diphenyl Ethers

These materials exhibited remarkably low pour points relative to the number of alkyl carbon atoms as shown in the following tabulation.

Table XVII

Properties of Polyalkyl Diphenyl Ethers

Product No.	Alkyl Groups	Viscosity Index	Pour Point, °F
3470-242	Dihexyl	48	-40
3470-372	Dioctyl	73	-50
3470-402	Didodecyl	110	-50
3470-383	Trioctyl	97	-50

2.4.3 Comparison of Products

Alkyl diphenyl ethers with less than 14 carbon atoms in a single alkyl group had higher viscosity indexes and lower viscosities and pour points than corresponding alkylbiphenyls. Table XVIII illustrates this point for two comparable products.

Table XVIII

Comparison of an Alkylbiphenyl With an Alkyl Diphenyl Ether

Product No.	3470-442	3470-383
Aromatic	Trioctylbiphenyl	Trioctyl Diphenyl Ether
Catalyst	$AlCl_3 \cdot CHCl_3$ (2:1)	
Viscosity, cs		
At 100°F	171.4	139.8
At 210°F	12.9	13.3
Viscosity Index	66	97
Pour Point, °F	-20	-50

However, for alkyl groups of 16 to 18 carbon atoms in length, alkylbiphenyls had lower pour points than the corresponding alkyl diphenyl ethers. It is notable that alkylation of a mixture of biphenyl and diphenyl ether (Dowtherm A: 73% biphenyl, 27% diphenyl ether) yielded a product which was close to that from diphenyl ether, indicating little alkylation of biphenyl.

Table XIX

Properties of Alkylated Dowtherm A and Biphenyl

Product No.	3470-17	3470-26	3470-20
Compound	C_{16-18} Biphenyl	C_{16-18} Dowtherm A	C_{16-18} Diphenyl Ether
Viscosity, cs			
At 100°F	37.8	24.6	24.6
At 210°F	5.54	4.54	4.57
Viscosity Index	89	111	113
Pour Point, °F	-40	0	-10

2.4.4 Procedures

Because diphenyl ether melts at 81°F (26.9°C), handling at moderate temperature was easy. Most of the alkylations of diphenyl ether were carried out using chloroform modified aluminum chloride catalyst (see Appendix II).

A few alkylations were made using aluminum chloride and carbon disulfide modified aluminum chloride catalysts. However, the chloroform method gave higher yields and less hazardous operation than the other catalysts. Temperature during alkylation was not critical. Olefin addition was started when the diphenyl ether was molten at 81°F (27°C) and the addition was completed in about 80 minutes, at which time the temperature was about 140°F (60°C).

2.5 Synthesis of Miscellaneous Alkyl Aromatics (A. C. Ettling)

In preliminary investigation of alkyl aromatics as lubricant bases, a number of alkylations of various types of aromatics were made. For the most part, viscosities and pour points needed further improvement. The alkylbenzenes, toluenes, naphthalenes, and alpha-methylnaphthalenes in Table XX had good viscosity characteristics but their pour points were generally too high to be of interest. Similarly, the alkylated metaterphenyls and partially hydrogenated terphenyl in Table XXI had high pour points and poor viscosity indexes.

2.5.1 Alkylbenzenes

Small samples of alkylbenzenes were available, from other projects at California Research, for obtaining a few physical properties. Four compounds had been prepared by alkylating benzene or an available alkylbenzene with 1-olefins using HF catalyst. Three of the compounds were relatively pure. Table XXII lists the viscosities and pour points of these alkylbenzenes.

Table XXII

Properties of Alkylbenzenes

Compound	Viscosity, [illegible]		Pour Point, °F
	At 100°F	At 210°F	
Ethyldecylbenzene	4.90	1.50	<-80
Dioctylbenzene	12.02	2.53	<-80
t-Butyldodecylbenzene	16.26	2.97	-80
Dodecylbenzene	4.69	1.48	<-85
2-Phenyldodecane	4.33	1.53	-20
6-Phenyldodecane	5.02	1.49	<-80
1-Phenyltetradecane	5.60	1.94	+45

The low pour points of five of the alkylbenzenes suggest their use as bases for hydraulic fluids. However, suitable polymers would be needed for improving their viscosity characteristics.

TABLE XX

PROPERTIES OF ALKYLATED AROMATICS*

1. Product No.	3274-13		3274-15	3274-17	3274-16		3274-11		3274-20	3274-18		3274-19	
Aromatic	Naphthalene		alpha-Methylnapnthalene				Benzene			Toluene			
Olefin	Mixed C_{16}-C_{18} [a]		Mixed C_{16}-C_{18}		1-Octadecene		Mixed C_{16}-C_{18}		C_{20}	Mixed C_{16}-C_{18}		1-Octadecene	
Solvent	None		None	None	None		None		None	None		None	
Catalyst Mole Ratio	$AlCl_3 \cdot CHCl_3$ (2:1)		HF	$AlCl_3 \cdot CHCl_3$ (2:1)	HF		$AlCl_3 \cdot CHCl_3$ (2:1)		$AlCl_3 \cdot CHCl_3$ (2:1)	$AlCl_3 \cdot CHCl_3$ (2:1)		$AlCl_3 \cdot CHCl_3$ (2:1)	
Mole Ratio (Aromatic:Olefin:Catalyst)	4:1:0.1		2:1:5	4:1:0.2	2:1:10		4:1:0.1		4:1:0.1	4:1:0.1		4:1:0.1	
Distillation Fraction	Whole	Heart Cut	Whole	Whole	Whole	Heart Cut	Whole	Heart Cut	Whole	Whole	Heart Cut	Whole	Heart Cut
2. Boiling Range, °F		404-504 at 1.4 mm				415-455 at 0.3 mm		336-385 at 2 mm			340-410 at 2 mm		360-422 at 2 mm
3. Viscosity, cs													
At 100°F	85.5		11.1	63.7	27.0	45.4	11.1	9.09	19.1	12.4	11.7	14.7	15.8
At 210°F	8.58		4.99	7.61	4.93	6.20	2.77	2.41	4.05	2.90	2.77	3.47	3.14
Viscosity Index	73		90	89	102	89	101	93	130	89	84	116	97
4. Pour Point, °F	-5	> Room Temp.	+10	+5	+30	-25	-20	-25	+25	-15	-30	+10	-5
5. Molecular Weight [b]			351	504	384		330		347	336		433	
6. Evaporation, % 6-1/2 hours at 400°F	9.3		21	22	8.2		50		30	64		40	
7. Index of Refraction, n_D^{20}								1.4814			1.4830		1.4820

* Work performed on Contract AT(11-1)-174.

a. Archer-Daniels-Midland alpha-olefin (75% C_{18}).
b. Freezing point method.

TABLE XXI

PROPERTIES OF ALKYLATED TERPHENYLS

	3470-13	3470-222	3470-22	3470-11	3470-21A	3470-21B	3470-06	3470-08	3470-47	
1. Product No.										
Aromatic	← m-Terphenyl →								HB-40[b]	
Olefin	← 1-Octene →						Mixed C_{16}-C_{18}[a]		1-Octene	
Solvent	CS_2			CS_2			None	CS_2	None	
Catalyst	$AlCl_3$			$AlCl_3$			$AlCl_3 \cdot CHCl_3$	$AlCl_3$	$AlCl_3 \cdot CHCl_3$	
Mole Ratio (Aromatic:Olefin:Catalyst)	1:1:0.06			1:2:0.05			3:1:0.1	1:1:0.1	2:1:0.05	
Distillation Fraction	Whole	Heart Cut	Btms.	Whole	Monoalkyl	Dialkyl		Whole	Whole	Heart Cut
2. Boiling Range, °F		430-490 at 1.4 mm			482-520 at 2 mm	505-534 at 1.5 mm				410-500 at 2 mm
3. Viscosity, cs										
At 100°F	178.8	227.0	708.0	550.0	294.0	545.0	Product	159.5	548.0	288.0
At 210°F	9.73	10.7	25.0	14.5	15.5	23.3	Was	14.7	18.1	12.4
Viscosity Index	-32	-10	35	-11	-12	81	Tar	100	-34	-45
4. Pour Point, °F	>Room Temp.	-5		-10	-5	0		>Room Temp.	-10	0
5. Evaporation, % 6-1/2 Hours at 400°F		11.6				3.2				
6. Storage, Seeded										
At -20°F, 330 Hours				gloss	cloud	cloud				
At -40°F, 150 Hours				gloss	gloss	gloss				

a. Archer-Daniels-Midland alpha-olefin (75% C_{18}).
b. Monsanto HB-40 (Partially Hydrogenated Terphenyl).

2.5.2 Diphenylnonane

The compound 1, 9-diphenylnonane was synthesized by the procedure given in Appendix IV. Some of its physical properties are as follows:

Table XXIII

Properties of 1, 9-Diphenylnonane

Viscosity at 100°F, cs	8.048
Viscosity at 200°F, cs	2.360
Viscosity Index	124
Pour Point, °F	-20
Density, D_4^{20}	0.9345
Index of Refraction, n_D^{20}	1.5290

The high viscosity index of this compound made it of interest. However, minor structural changes are warranted in order to lower the pour point. The synthesis of 1, 9-ditolylnonane and similar diphenyl or ditolylalkanes and isoalkanes is suggested. Such compounds may be useful as hydraulic fluids.

2.5.3 Aromatic Ethers

Three preparations of aromatic ethers were made from commercially available materials. The standard metathetical reaction between an alkyl halide and a metal phenate was used. These compounds had poor physical properties and were not of further interest. The data are as follows:

Table XXIV

Properties of Aromatic Ethers

Compound	Alkylbenzyl p-tert-Amyl-Phenyl Ether[a]	Dinonylphenyl Methyl Ether[b]	Alkylbenzyl p-Cresyl Ether[a]
Viscosity, cs			
At 100°F	252.7	492.9	94.87
At 210°F	11.05	16.56	6.049
Viscosity Index	-65	-46	-95
Pour Point, °F	0		-10
Gravity, °API	17.8	-	-
Boiling Range, °F	-	-	413-450 at 3 mm

a. Derived from chloromethylated dodecylbenzene (propylene tetramer).
b. From propylene nonylphenol (propylene trimer).

2.5.4 Coupling Biphenyls With Butadiene

Two experiments were carried out to determine whether high viscosity stocks suitable for grease bases and viscosity index improvers could be obtained: (1) by coupling biphenyl units with butadiene and (2) by coupling C_{16-18} alkylbiphenyl with butadiene. The reaction of butadiene and biphenyl, described in Appendix V, gave a product consisting of two biphenyl units linked by a four carbon unit derived from butadiene. A major proportion of a polymeric tar made of units derived from biphenyl and butadiene was also present. These two fractions were separated by distillation. The distilled fraction was too volatile to be of interest. The bottoms fraction was investigated as a V.I. improver (see V.I. improvers under Hydraulic Fluids).

Treatment of distilled C_{16-18} alkylbiphenyl with butadiene, also described in Appendix V, increased the viscosity at 210°F from 5 to 12 centistokes, raised the pour point from -55°F to -30°F and increased the viscosity index from 78 to 92. This product was too low in molecular weight for use as a V.I. improver. However, it may be usable as a grease base.

2.6 Synthesis of Dibenzyl Selenide

Dibenzyl selenide has been shown to be an inhibitor against oxidation and radiation damage[1] to organic fluids. It was of particular interest because it is more soluble than the usual dialkyl selenides in some of the better aromatic base oils. Approximately 10 pounds of the material was prepared by reacting sodium selenide with benzyl chloride. The procedure for this preparation is attached as Appendix VI.

2.7 Future Work

The synthesis of alkylbiphenyls, alkyl diphenyl ethers, and related fluids should be an important part of any further program to develop radiation resistant lubricants. The same general research areas discussed in this section should be pursued further. Procedures and processes need to be refined to get products with the stringent physical properties required by the lubricant specifications. For example, various distillate cuts of a crude alkylbiphenyl have properties sufficiently different from those of the crude that individual test work on the cuts is warranted.

Emphasis should be placed on heat stability in combination with radiation stability. Test work should guide the synthesis program in this respect so that optimum structures which are resistant to both these key considerations may be developed.

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[1] R. O. Bolt and J. G. Carroll, "Organics as Reactor Moderator Coolants: Some Aspects of their Thermal and Radiation Stabilities," Proceedings of the International Conference on Peaceful Uses of Atomic Energy in Geneva, August 8-20, 1955, Vol. 7, p. 546, United Nations (1956).

3. LUBRICATING GREASES[1]

(B. W. Hotten)

3.1 Introduction

The target specification for grease work is in Table XXV. In addition to radiation resistance, the target heat resistance requirements were very severe. Only one commercially available grease was known to meet the required bearing life at 450°F. This was a silicone oil gelled with a diarylurea. However, silicone oils were too weak in radiation resistance[2] to meet the requirements. Because the specification requirements were too severe for comparing properties and determining trends of behavior for reasonably available materials, most tests were run under more moderate conditions. Besides providing leads for further research, the results of tests under moderate conditions could be directly applicable if the requirements of the final design were less severe than anticipated.

3.2 Effects of Radiation on Conventional Greases

Commercially available greases and experimental greases containing commercially available ingredients were surveyed in initial work for resistance to radiation. Results on the properties of these greases from room temperature irradiations are shown in Table XXVI. The nonstandard screening test procedures used are summarized in Appendix VII.

All the greases tested showed large changes in consistency on exposure to radiation. As a general rule, the worked penetration indicated greases to soften in the early stages of irradiation - to about 5×10^8 r - and then harden. At about 5×10^9 r all the greases were very hard and brittle, like rosin. The ASTM Dropping Point did not change much. However, oxidation resistance, evaporation rate, and heat resistance generally worsened.

Corrosivity to copper was higher with exposed samples. Photographs of copper test strips are in Figure 3. The polyglycol grease (19E) was the worst in this test. Water resistance was not affected much. The effects of radiation observed probab · resulted from consistency changes. Bearing performance deteriorated in all irradiated samples. Low temperature torque increased whenever the unworked consistency hardened from irradiation. The effect of the greases in preventing gear wear did not differ much after irradiation, except for the diester grease (19F), which lost lubricity.

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[1] Much of the information obtained on AEC Contract AT(11-1)-174 was used in the research for the present contract (see "Radiation Resistant Greases," California Research-AEC Report No. 8 (AECU 3148), June 30, 1956).

[2] R. O. Bolt and J. G. Carroll, "Influences of Nuclear Radiation on Organic Fluids and Lubricants," submitted to Industrial and Engineering Chemistry.

TABLE XXV

TARGET SPECIFICATION FOR RADIATION RESISTANT LUBRICATING GREASE

	Original	Irradiated
1. Irradiation		
Dosage, 10^8 r	0	50
Temperature, °F	-	350
2. Dropping Point, °F, minimum	500(350)*	400(300)
3. ASTM Worked Penetration	260-310	200-375
4. Copper Corrosion		
Norma Hoffman Bomb: 100 hr at 212° F	No discoloration (Dark Brown)	-
5. Oxidation: Norma Hoffman Bomb 100 hr at 250° F (psi), maximum	5 (7.5)	-
6. Dirt Content, >25 microns, part./cc, max	7500	-
>75 microns, part./cc, max	1600	-
7. Water Resistance, MIL-L-3545, per cent loss, maximum	50 (60)	-
8. Bearing Performance, 10,000 rpm		
Hours at 450° F	500	-
350° F	(500)	100 (50)
9. Worked Stability		
Penetration after 100,000 strokes, max	375	-
10. Evaporation, weight loss after 22 hours at 400°F, per cent, max	4 (6)	-
11. Apparent Viscosity, poises		
at 40°F and at 12 sec^{-1}, maximum	15,000	-
at 0°F and at 12 sec^{-1}, maximum	-	15,000
12. Navy Gear Wear Test, 5 and 10-pound loads	Report	Report
13. Weight Change	-	6

*( ) indicates alternate minima.

TABLE XXVI

TEST RESULTS[a] ON IRRADIATED[b] CONVENTIONAL GREASES

	Test Method W-L-791e	Chevron[d] OMT Grease			Chevron[d] Industrial Grease Heavy											Polyglycol Grease				Diester Grease			RPM Aviation Grease No. 5	
									+ Organic Selenide				+ Dibenzothiophene											
1. Reference Number (2579-)		19A			19B				19C				19D			19E				19F			19G	
2. Sample Number		19A	20-1	21-1	19B	20-2	21-2	22-2	19C	20-3	21-3	22-3	19D	20-4	22-4	19E	20-5	21-5	22-5	19F	20-6	21-6	19G	20-7
3. Irradiation Dosage, 10⁸ r at 80°F		0	4.3	18.3	0	5.8	23.2	59	0	6.8	26.3	67	0	7.0	68	0	6.5	24.0	62	0	5.5	19.8	0	3.6
4. ASTM Penetration																								
a. Unworked	311.5	212	300	185	208	144	21	0	196	146	32	0	200	72	0	200	87	66	0	180	131	72	261	303
b. Worked 60 strokes	311.5	289	452	382	239	258	-	-	239	246	-	-	242	237	-	246	212	254	-	216	218	-	290	384
c. Worked 100,000 strokes	313.1	430			300				300				300											
5. ASTM Dropping Point, °F	1421.1	457	428	346	500+	500+	500+	500+	500+	500+	500+	500+	500+	500+	500+	460	500+	500+	500+	460	500+	500+	340	320
6. Oxidation - In bomb for 100 hours at 210°F, psi drop	3453-1	3	11		7.5	8	-	-	8	10	-	-	7	10	-	5	16			1	11	-	2	
7. Heat Resistance - Thin film; hours to harden at 300°F	(c)	600	600	700	600	600	-	-	600	500	-	-	600	600	-	350	300	70	-	350	600	-	100	100
8. Copper Corrosion - Appearance after 24 hours at 210°F	530.9	Slt. Stain	Slt. Stain	Med. Stain	Bright	Bright	-	-	Slt. Stain	Slt. Stain	-	-	Bright	Bright	-	Black	Black	Black	-	Black	Med. Stain	Dark		
9. Water Resistance																								
a. Per Cent Loss	3252.1	0	17.5		2	0			0	0			0	0		0	12.5			0	0		0	-
b. Boiling Water, life of 5 g. min	(c)	4	4	4	60+	60+	-	-	60+	60+	-	-	60+	60+	-	60+	60+		-	60+	60+	-	60+	60+
10. Evaporation - Per Cent Loss After 18 Hours at 300°F	(c)	4.7	8.1	9.3	2.2	2.9	-	-	3.2	4.7	-	-	7.3	6.7	-	19.8			-	5.0		-		
11. Bearing Performance																								
10,000 rpm; hours to failure																								
At 300°F		1300+	717 692	69 51	89+	94 319	-	-	1157	334 340	-	-	525	493	-				-			-		
At 250°F		-	-	-	-	-	-	-	-		-	-	-	-	-	3026	174 187				1815			
12. Low Temperature Torque																								
a. Seconds/revolution at 0°F	MIL-G-3278A	1	2	200	1	6	-	-	1	3.5	-	-	1	4.8	-	1	1		-			-		
b. °F for 10 sec/rev		-21	-22		-22	-3	-	-	-21	-11	-	-	-20	-6	-	-40	-15		-			-		
13. Gear Wear Test - Weight Loss/1000 cycles	MIL-G-3278A																							
a. At 5-lb load, mg		1.6	1.5		2.3	2.7	-	-	1.2	1.9	-	-	1.3	1.7	-	1.8	1.7		-	0.9	Stripped Gears	-	0.6	
b. At 10-lb load, mg		5.8	4.7		5.5	3.2	-	-	3.5	3.7	-	-	2.1	4.7	-	3.0	4.9		-	2.6		-	2.1	
14. Composition - Per Cent by Weight			Proprietary			Proprietary																	Proprietary	
Chevron Industrial Grease Heavy						100				94.9				94.9										
Terephthalamate Gelling Agent																	15				15			
Polyglycol PG 71																	79.9							
Di(2-ethylhexyl)sebacate																					79.9			
Didodecyl Selenide										5.0				-			5				5			
Dibenzothiophene										-				5.0			-				-			
Quinizarin										0.1				0.1			0.1				0.1			

a. Irradiations and 50% of test work performed on AEC Contract AT (11-1)-174.
b. MTR Canal Source; 150 grams of grease in metal can vented to air; about 80°F.
c. See Appendix VIII for description of this test.
d. Formerly Calol.

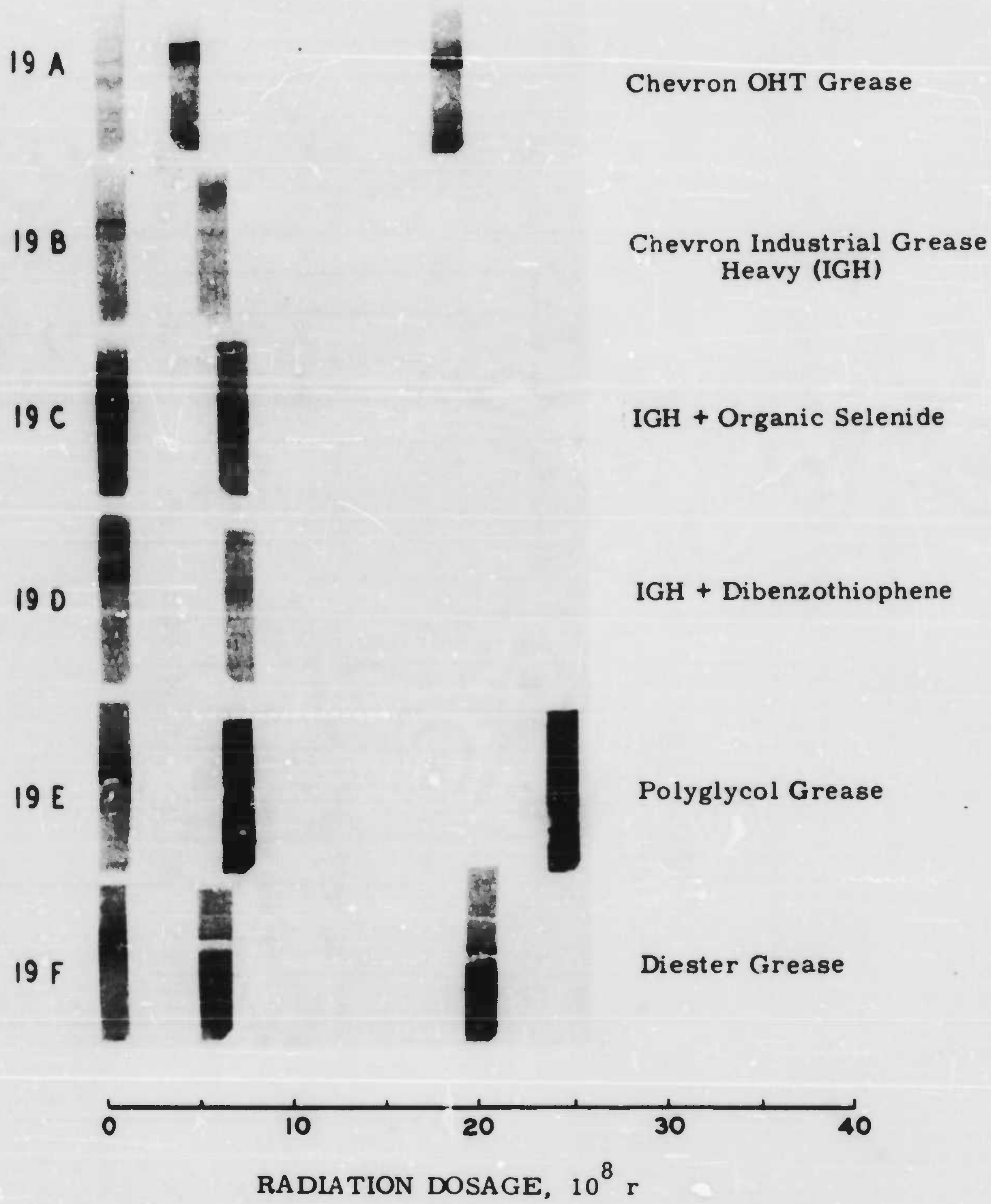

FIG. 3 - COPPER CORROSION OF IRRADIATED GREASES

In general, it was concluded that none of the conventional greases tested was promising to meet the contract specification. This conclusion was confirmed by reference to other work on a wider range of commercial greases[1]. However, the survey results gave useful information for research on experimental greases.

The terephthalamate[2] gelling agent present in Chevron[3] Industrial Grease Heavy, the polyglycol grease, and the diester grease allowed less softening in early stages of irradiation than the conventional soaps used in Chevron[3] OHT Grease and RPM Aviation Grease No. 5. Thus, it was apparent that the gelling agent had an effect on radiation resistance. The differences in the performance of greases in which the same gelling agent was used showed that the base oils also had an effect on radiation resistance. The two additives tried in the Table XXVI greases, didodecyl selenide and dibenzothiophene, did not reduce radiation damage sufficiently to make the greases containing them meet specification requirements. But didodecyl selenide improved bearing performance in unirradiated Grease 19C enough to be of further interest in experimental greases.

3.3 Formulation of Radiation Resistant Greases

3.3.1 Gelling Agents

The indication that terephthalamates had exceptionally good radiation resistance was studied further with the aid of a pair of more exactly comparable greases than were available in the preliminary survey. One of the greases was gelled with 14% sodium stearate and the other with 14% sodium N-octadecylterephthalamate. Both had a naphthenic mineral oil base with a viscosity of 450 SSU at 100° F. They were irradiated side by side in a cobalt-60 source. Samples were withdrawn at intervals for examination. Consistency changes are shown in Table XXVII.

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[1] "Radiation Resistant Greases," California Research-AEC Report No. 8 (AECU 3148), June 30, 1956.

[2] B. W. Hotten, "Synthesis and Properties of Unsymmetrical Derivatives of Terephthalic Acid and Their Use as Gelling Agents," submitted to Industrial and Engineering Chemistry.

[3] Formerly Calol.

Table XXVII

Comparison of Stearate-Gelled and Terephthalamate-Gelled Greases After Cobalt-60 Irradiation

	Sodium Stearate Grease		Sodium N-Octadecyl-Terephthalamate Grease	
Dosage, 10^8 r	P_0[a]	P_{60}[b]	P_0	P_{60}
0	252	309	246	263
0.9	256	347	271	289
1.9	252	389	265	282
5.1	286	liquefied	284	305
8.9	301	liquefied	278	307

a. ASTM unworked penetration.
b. ASTM worked penetration (60 strokes).

Both greases softened moderately in unworked penetration as radiation dosage accumulated. However, the stearate grease softened much more severely than the terephthalamate grease in worked penetration, which is of more functional importance. The change in worked penetration is plotted in Figure 4. The superiority of the terephthalamate led to its use as a gelling agent for oils which were specially synthesized to have improved radiation resistance.

3.3.2 Oils

Previous work showed that greases made from alkylbenzene oils had better radiation resistance than greases made from mineral oils[1]. However, the alkylbenzenes available were too volatile above 200°F for use in heat resistant greases. Thus, new alkyl aromatics were synthesized. Details of the syntheses are in Section 2 of this report.

Greases made from one of the new oils, octadecyl-alpha-methylnaphthalene (OMN, see Table XX, page 25), without and with didodecyl selenide, were compared for radiation resistance with mineral oil greases. All four greases were gelled with 12% sodium N-octadecylterephthalamate. Results of the tests are in Table XXVIII.

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[1] "Radiation Resistant Greases," California Research-AEC Report No. 8 (AECU 3148), June 30, 1956.

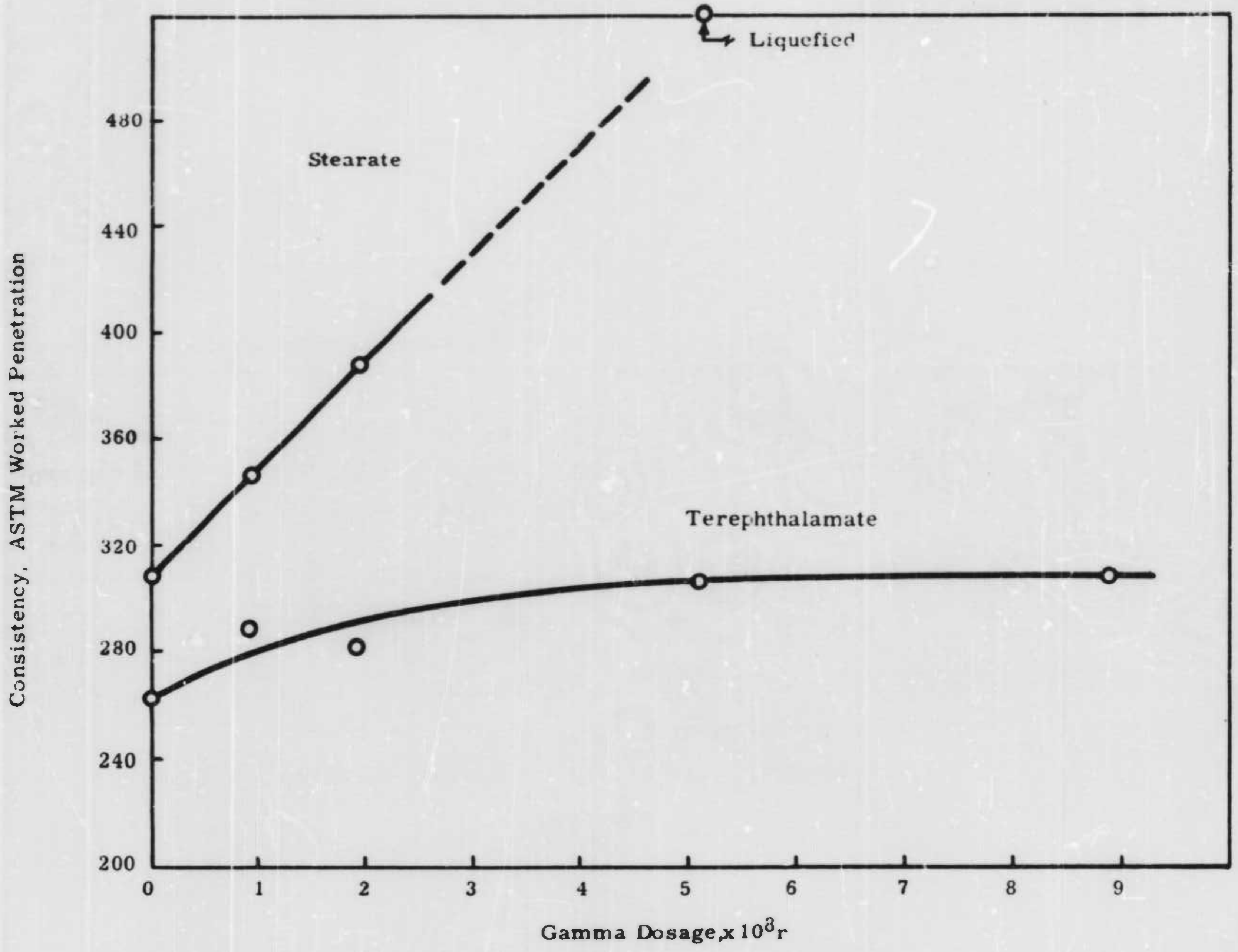


FIG. 4 - EFFECT OF IRRADIATION ON GREASE CONSISTENCY OF SODIUM STEARATE AND SODIUM N-OCTADECYLTEREPHTHALAMATE GREASES

TABLE XXVIII

COMPARATIVE RADIATION RESISTANCE OF ALKYLMETHYLNAPHTHALENE[a] AND MINERAL OIL GREASES GELLED WITH SODIUM N-OCTADECYLTEREPHTHALAMATE

	No Added Inhibitor							Inhibited with [illegible] Didodecyl Selenide						
Oil	Mineral Oil				Octadecyl-alpha-Methyl-naphthalene			Mineral Oil				Octadecyl-alpha-Methyl-naphthalene		
Grease No.	2579-19B				2579-21A			2579-19C				2579-21B		
Sample No.	19B	20-2	21-2	22-2	21A	21-8	22-8	19C	20-2	21-3	22-[illegible]	21B	21-9	22-9
Gamma Dosage, 10^8r	0	5.8	23.2	59	0	25.4	59	0	5.8	23.3	57	0	14.2	32.5
ASTM Penetration														
Unworked	208	144	21	0	231	191	0	196	146	52	0	269	242	227
Worked 60 strokes	239	258	-	-	254	389	-	239	245	-	-	269	336	276
Bearing Performance, 10,000 rpm, 300°F, hr (Method 331.1)	891	94	-	-	766, 378	582, 139	-	1157	504, 316	-	-	576, 2021, 1899	507, 437	141, 255

a. Formulation of this grease on AEC Contract AT (11-1)-174.

The uninhibited OMN grease was still soft at 26.4 x 10^8 r, but the mineral oil grease was a rubbery solid - too hard for a worked penetration test. The OMN grease finally solidified at 50 x 10^8 r. Bearing performance at 300°F of the OMN grease after 26.4 x 10^8 r was better than that of the mineral oil grease after only 5.8 x 10^8 r.

Before irradiation, the OMN grease containing 5% didodecyl selenide had considerably longer bearing life than the uninhibited OMN grease. After irradiation at 32.5 x 10^8 r, the OMN grease was still soft and reasonably useful in bearings. The mineral oil grease was hard and useless after 26.3 x 10^8 r.

Additional alkyl aromatic greases were made and, along with two mineral oil greases and a silicone oil grease, were irradiated at 250°F. Results are in Table XXIX. Chevron OHT Grease changed less in consistency at 250°F than at the room temperature irradiation reported in Table XXVI, page 31. At 250°F, it stiffened 43 points after 5 x 10^8 r, but at room temperature it softened 163 points in one case and to a liquid in the other. It softened only 21 points after 7 x 10^8 r at 250°F. Evidence from electron microsopic examination of irradiated greases indicates consistency changes at moderate doses to result from disintegration of the soap crystals of the gel lattice. Apparently radiation damage to the sodium soap of this grease is analogous to irradiative discoloration of glass. In both materials, higher temperatures permit areas of radiation damage in the crystal structure to heal soon after they form.

The other greases softened more at 250°F than at room temperature. Apparently their consistency change differed either in mechanism or in temperature sensitivity from that of Chevron OHT Grease. Didodecyl selenide and quinizarin did not protect Grease No. G-42-5 from softening, compared with uninhibited Grease No. G-42-6 (Table XXIX, page 37). Greases made from synthetic aromatic oils did not resist radiation damage at these doses any more than the commercial greases made from mineral oil; but the aromatic oil greases would be better at higher doses. The silicone oil grease did not polymerize noticeably at 8 x 10^8 r.

Dropping points were unchanged after irradiation except for Chevron OHT Grease. Its dropping point increased from 420°F to 500+°F at 3 x 10^8 r and remained at 500+°F after 7 x 10^8 r.

Navy High-Speed Bearing tests at 350°F were made on some of the greases that had been irradiated at 250°F. Chevron OHT Grease retained about one third of its original life after irradiation at 7 x 10^8 r. Chevron Industrial Grease Heavy retained about one fourth of its original life after 11.6 x 10^8 r. The octadecylbiphenyl grease, G-42-4, gave the best single bearing run of the irradiated greases, 164 hours after 14.3 x 10^8 r. The uninhibited C_{18} alkyl-alpha-methylnaphthalene grease, G-42-6 averaged 106 hours life after 13.8 x 10^8 r. The silicone grease did not perform well after irradiation at 8.4 x 10^8 r; it averaged 57 hours.

TABLE XXIX

EFFECT OF IRRADIATION AT 250° F ON GREASES

Grease			Gamma Dosage, 10^8 r	Penetration	High-Speed Bearing Life, hr at 350° F
Expt. No.	Fluid	Additives			
G-42-1	(Chevron OHT Grease)[b]	-	0	289	300 (av.)
			3.2	246	-
			7.0	310	116, 110
G-42-2	(Chevron Industrial[a] Grease Heavy)	-	0	239	144 (av.)
			4.9	43	-
			11.6	367	13, 63
G-42-3	C_{18} Alkyldiphenyl-methane[a]	Didodecyl Selenide-Quinizarin	0	258	139, 97
			5.6	323	-
			13.8	356	-
G-42-4	C_{18} Alkylbiphenyl[a]	-	0	267	123
			5.7	313	-
			14.3	360	94, 164
G-42-5	C_{18} Alkyl-alpha-methylnaphthalene[a]	Didodecyl Selenide-Quinizarin	0	260	-
			5.5	348	-
			14.3	425	-
G-42-6	C_{18} Alkyl-alpha-methylnaphthalene[a]	-	0	254	-
			5.1	250	-
			13.8	329	116, 95
G-42-7	Silicone-DC 550[c]	-	0	348	-
			8.4	410	96; 28
G-42-8	C_{16-18} Alkylbiphenyl[a]	Didodecyl Selenide	0	281	-
			7.8	320	-

a. Sodium terephthalamate gelling agent.
b. Sodium soap gelling agent.
c. Diarylurea gelling agent.

3.3.3 Barrel-Scale Batch CALRESEARCH 159

The octadecylbiphenyl grease was promising for further development and a 120-pound batch[1] was made. Its composition is in Table XXX.

Table XXX

Composition of Radiation Resistant Grease
CALRESEARCH 159

	Per Cent
C_{16-18} alkylbiphenyl	83
Sodium Terephthalamate	12
Didodecyl Selenide	5
Quinizarin	0.1

The properties obtained thus far are in Table XXXI. A small pilot batch of this grease formulation responded unexpectedly to irradiation; it stiffened 87 points after a dosage of 12 x 10^8 r at room temperature. Other greases containing the same gelling agent softened about 20 points when irradiated to the same degree. The bearing performance at 350°F on the pilot sample (av. 425 hours) was better than that of any commercial hydrocarbon oil grease thus far tested, but the large batch averaged 233 hours. The dropping point and work stability were far superior to those of ordinary sodium soap greases. However, copper corrosion, oxidation, and evaporation results did not meet specification requirements. Gamma irradiation tests at 350°F are in progress.

A sample of CALRESEARCH 159, along with two reference greases, was exposed in the Brookhaven Reactor. After a dosage of about 2 x 10^{18} slow[2] neutrons per cm^2, unworked ASTM penetrations were as follows (two samples each):

	Original	Irradiated
Chevron OHT Grease	212	53, 103
Chevron Industrial Grease Heavy	208	45, 45
CALRESEARCH 159	229	296, 296

The new grease thus showed improved resistance to combined reactor flux.

---

[1] Half was made under AEC Contract AT(11-1)-174.

[2] Less than about 0.47 ev. Fast neutrons and gamma radiation present in direct proportion. (Bolt, Carroll, Proc. Int. Conf. Peaceful Uses Atomic Energy 1955, Vol. 7, p. 546, United Nations (1956).

TABLE XXXI

PROPERTIES OF CALRESEARCH 159 GREASE

	Contract Specification Requirements		CALRESEARCH 159	
	Original	Irradiated	Original	Irradiated
1. Irradiation, Dosage, 10^8 r	-	50	-	
Temperature, °F	-	350	-	
2. ASTM Dropping Point, °F	500(350)^a min	400(300) min	500+	
3. ASTM Worked Penetration	260-310	200-375	261	
4. Copper Corrosion, Norma Hoffman Bomb; 100 hr at 212°F	No Discoloration	-	1 psi; not pass	
5. Oxidation, Norma Hoffman Bomb; 100 hr at 250°F, psi drop	5 (7.5)	-	9	
6. Dirt Content, >25 microns, part./cc	7500 max	-	-	
>75 microns, part./cc	1600 max	-	-	
7. Water Resistance, MIL-L-3545, % Loss	50 (60)	-	-	
8. Bearing Performance, 10,000 rpm				
Hours at 450°F	500	-	-	
Hours at 350°F	(500)	100 (50)	279, 188^b	
9. Worked Stability Penetration after 100,000 strokes	375 max	-	325	
10. Evaporation, Weight Loss After 22 hr at 400°F, %	4 (6) max	-	21	
11. Apparent Viscosity				
-40°F at 12 sec^{-1}	15,000 max	-	-	
0°F at 12 sec^{-1}	-	15,000 max	-	
12. Navy Gear Wear Test 5- and 10-pound loads	Report	Report	-	

a. ( ) indicate alternate requirements.

b. Small pilot sample: 481 and 375 hours.

Samples of CALRESEARCH 159 were sent to the following groups for evaluation:

Wright Air Development Center

General Electric Company, Schenectady, New York

General Electric, Air Nuclear Power Division, Evendale, Ohio

Vickers, Inc., Research and Engineering Center, Detroit, Michigan

Pratt and Whitney Aircraft, Hartford, Connecticut

3.3.4 Other Greases From Aromatic Oils

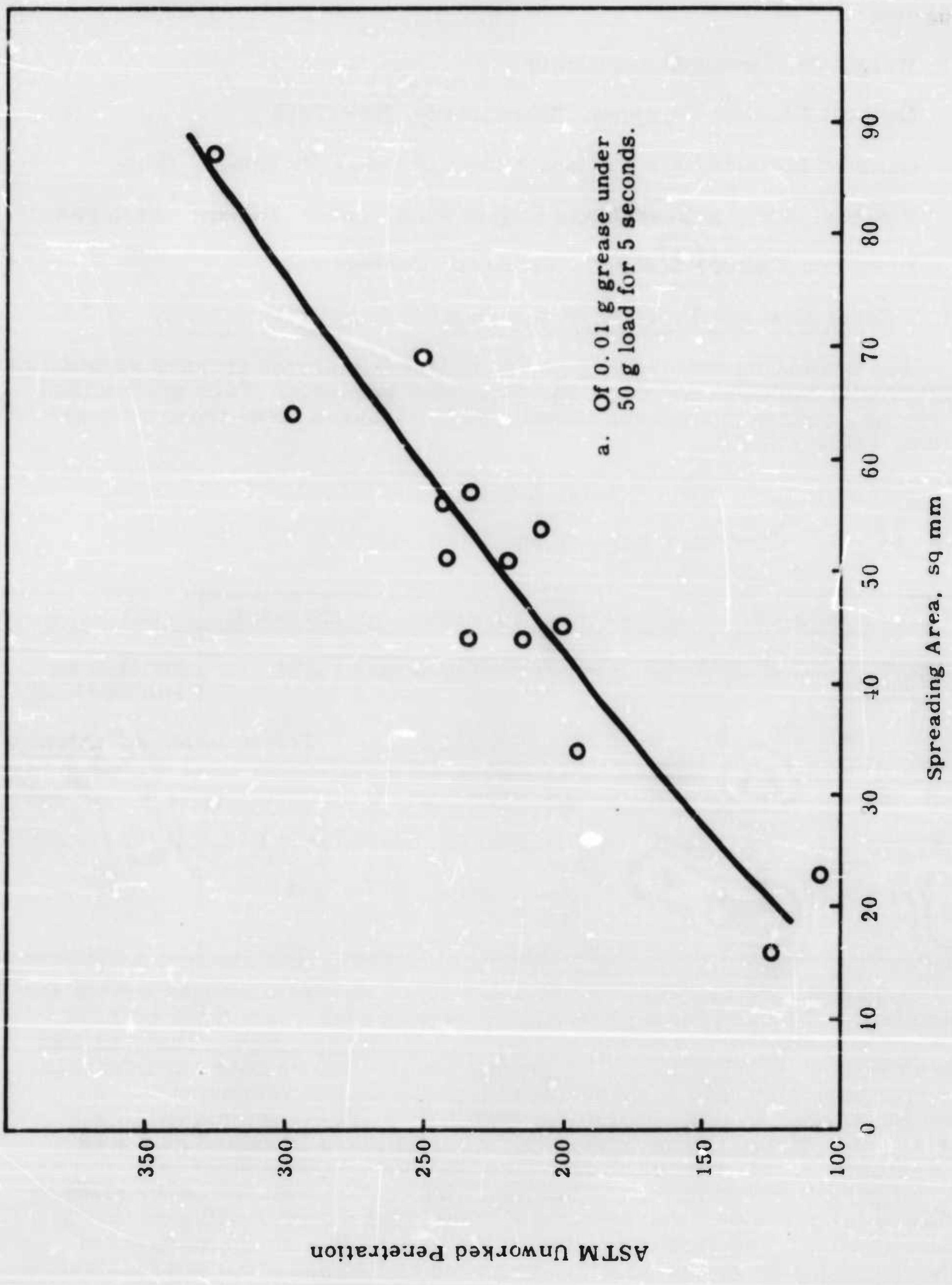
The promising results obtained on octadecylbiphenyl greases stimulated trial of other alkylbiphenyl and alkyl diphenyl ether products. Four synthesized oils and one new gelling agent were investigated. Greases made from them are described in Table XXXII.

Table XXXII

New Experimental Greases

Grease No.	2579-43	2579-47	2579-49A	2579-49B	2579-49C
Gelling Agent	Sodium N-Octadecylterephthalamate (12%)				Metal-free Amide (15%)
Oil	Dioctyl-biphenyl	Trioctyl-biphenyl	Didodecyl diphenyl ether	Trioctyldiphenyl Ether	
Additives	Didodecyl Selenide (5%) and Quinizarin (0.1%)				
ASTM Worked Penetration	241	244	260	203	233

A quantitative thin film test was developed as a preliminary screen for thermal stability of these greases. A film of each grease 1 mm thick by 2 cm wide by 5 cm long was spread on the bottom of an aluminum dish. The dish was heated in an oven at 350°F. An 0.01 g grease sample was removed at intervals and tested for consistency by a spreading test previously developed at California Research. In this consistency test 0.01 g grease is weighed in a globular mass on a glass microscope slide. A cover glass is rested gently on top of the globule. A cylindrical weight 1 cm in diameter on a shaft in a conventional grease penetrometer is lowered into contact with the cover glass, released, and let press on it for 5 seconds. The total weight resting on the cover glass is 50 g. The spreading area of the grease is a rough measure of its consistency. A correlation of spreading area and ASTM unworked penetration is in Figure 5.



a. Of 0.01 g grease under 50 g load for 5 seconds.

FIG. 5 - CORRELATION BETWEEN SPREADING AREA[a] AND ASTM PENETRATION

Curves showing the hardening rates of the five experimental greases are in Figure 6. The greases hardened mainly because of oil evaporation under these conditions. Evaporation was due partly to the inherent volatility of the oil and partly to cracking and oxidation. Among the alkylbiphenyl oils, trioctylbiphenyl gave a much longer lasting grease (No. 47) than dioctylbiphenyl (No. 43). Among the diphenyl ether oils, trioctyl diphenyl ether gave a grease (No. 49B) that hardened slower than a didodecyl diphenyl ether grease (No. 49A) during the first 100 hours; they hardened at about the same rate after the first 100 hours. Grease No. 49C contained a metal-free amide as the gelling agent in place of sodium N-octadecylterephthalamate used in the other four greases; it hardened faster than No. 49B, which was made from the same oil.

Trioctyl diphenyl ether appeared especially promising for further study. This oil, which is described more fully in Section 2, Table XV, page 20 had the following properties:

Viscosity, cs	
At 100°F	139.8
At 210°F	13.3
Viscosity Index	97
Pour Point, °F	-50

The pour point of -50°F makes it promising for the low temperature (-40°F) requirement of the contract specification.

3.4 Mechanism of Radiation Damage

A knowledge of the mechanism of radiation damage to lubricating greases is almost essential as a foundation for continued progress in the development of radiation resistant greases. Previous investigations[1] indicated that the initial softening that usually occurs in greases during irradiation results from mechanical breakdown of the gelling agent crystallites. The later hardening of greases corresponds to the hardening that occurs in oils alone as a result of polymerization[2] and cross linking. The effects on oils alone are being studied in other portions of the contract research. The effects on gelling agents were therefore emphasized in this portion.

3.4.1 Electron Microscopic Evidence

. The electron microscope has been the most valuable tool for direct study of dimensional changes in gelling agent crystallites.

Micrographs of gelling agents from the greases described in Section 3.3.1 are in Figures 7, 8, and 9.

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[1] "Radiation Resistant Greases," California Research-AEC Report No. 8 (AECU 3148), June 30, 1956.

[2] R. O. Bolt and J. G. Carroll, "Influences of Nuclear Radiation on Organic Fluids and Lubricants," submitted to Industrial and Engineering Chemistry.

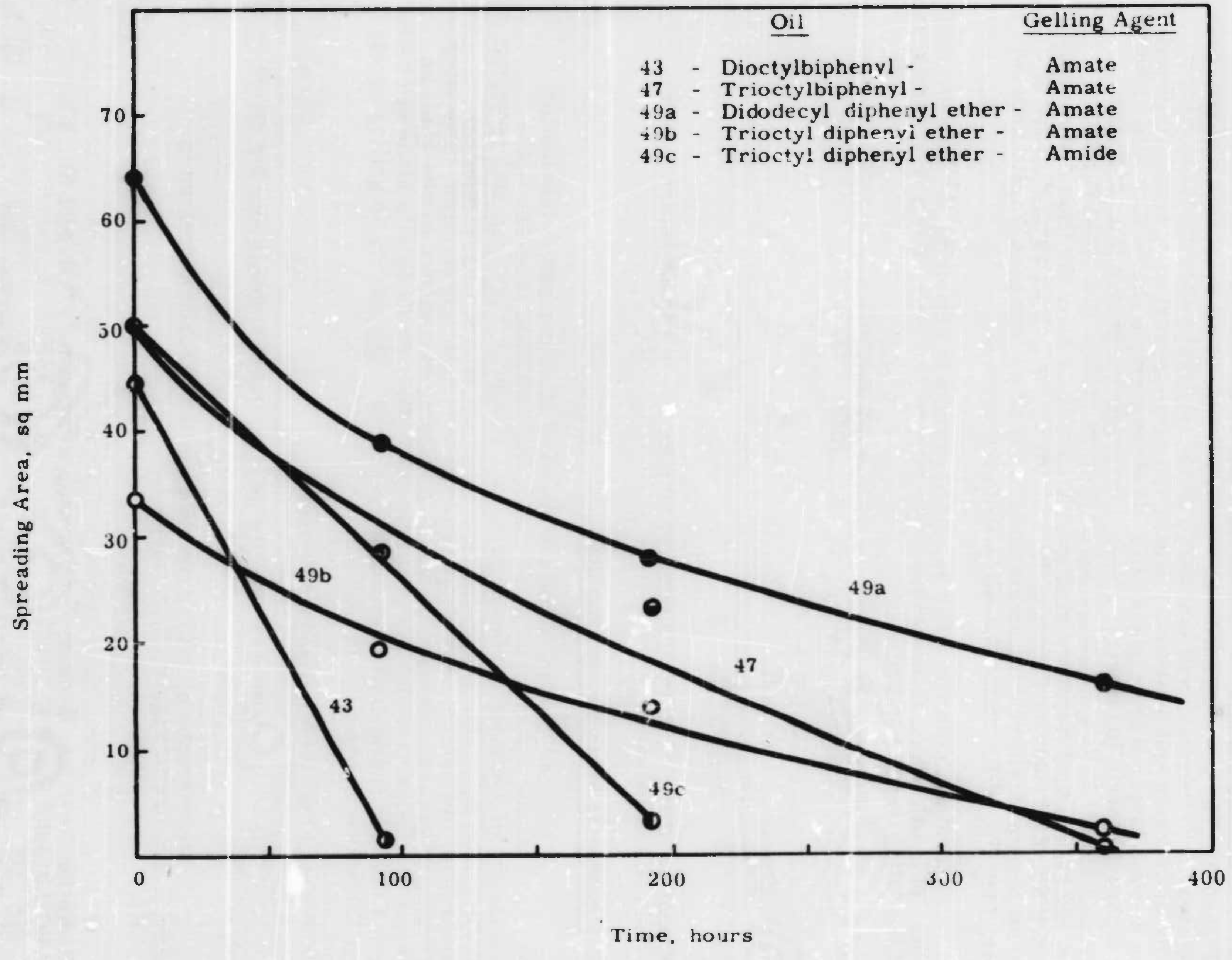
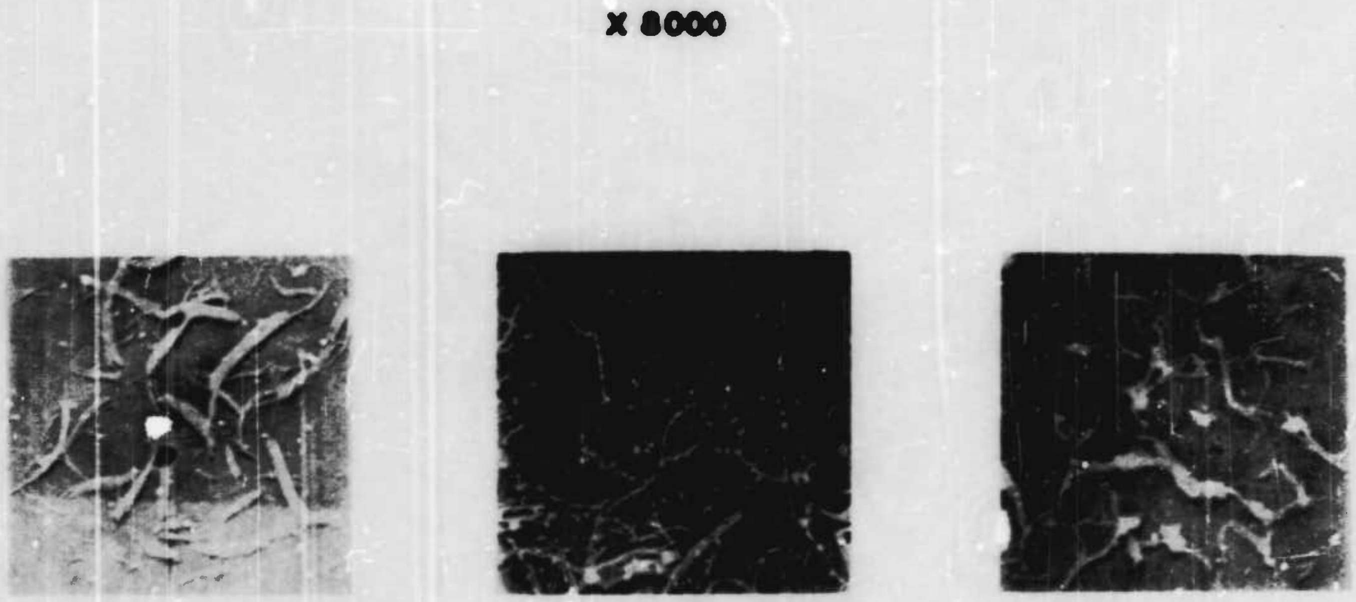


FIG. 6 - CONSISTENCY CHANGE AT 350°F OF THIN FILMS OF ALKYL AROMATIC OIL GREASES



0r $\qquad$ 0.89×10^8 r $\qquad$ 5.1×10^8 r

FIG. 7 - EFFECT OF CO-60 IRRADIATION ON CRYSTALLITE STRUCTURE OF SODIUM STEARATE GREASE

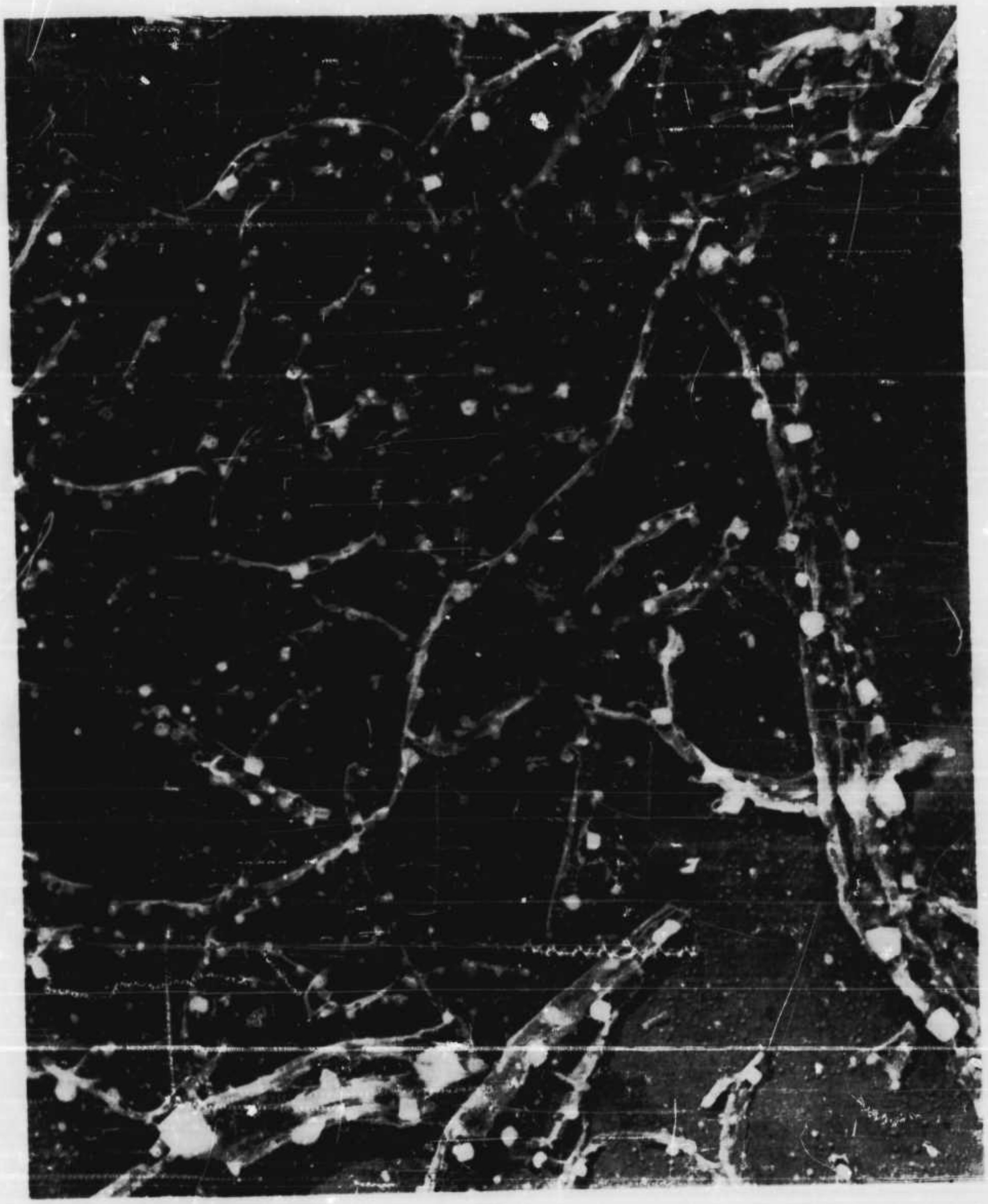
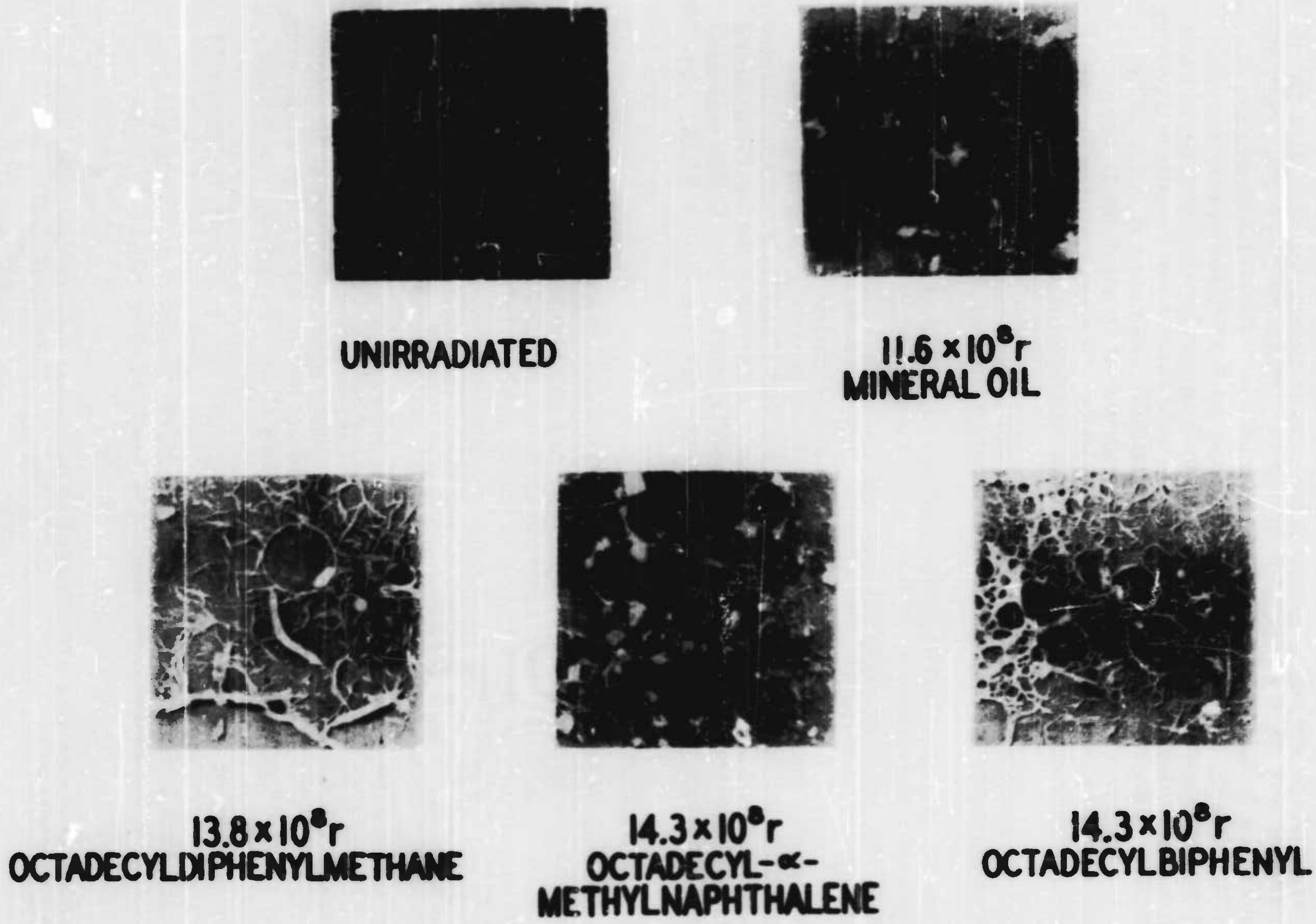


FIG. 8 - TUBERCLES IN AN IRRADIATED SODIUM STEARATE GREASE



UNIRRADIATED

11.6×10^8r
MINERAL OIL

13.8×10^8r
OCTADECYLDIPHENYLMETHANE

14.3×10^8r
OCTADECYL-α-
METHYLNAPHTHALENE

14.3×10^8r
OCTADECYLBIPHENYL

FIG. 9 - EFFECT OF CO-60 IRRADIATION ON CRYSTALLITE STRUCTURE OF SODIUM N-OCTADECYLTEREPHTHALAMATE GREASE·

The micrographs of the sodium stearate from grease irradiated at 0.89 x 10^8 r shown in Figures 8 and 9 are especially revealing. They show the outgrowth of many fine tubercles from the parent soap crystallites. These tubercles are more opaque to the electron beam in the microscope than is the parent soap. They may be an inorganic compound, such as sodium carbonate, that could have formed from elemental sodium, which in turn could form from bombarded sodium ions in the sodium stearate crystallite. The sample irradiated at 5.1 x 10^8 r shows fewer tubercles. They may have been rubbed off in handling or been converted into other products by further irradiation. The crystallites appear somewhat more irregular and fragmentary than those of the unirradiated grease.

The crystallites from the terephthalamate grease do not show obvious microscopic changes as a result of irradiation (see Figure 9, page 47).

The two greases just described were irradiated at room temperature. Some of the greases irradiated at 250° F, described in Table XXIX, page 37, were also examined with the electron microscope. The sodium soap from Chevron OHT Grease (Figure 10) was reduced to a much finer crystallite structure after 7 x 10^8 r. Two types of behavior are noticeable in the sodium N-octadecylterephthalamate greases (Figure 11). The crystallites of greases made from octadecyldiphenylmethane after 13.8 x 10^8 r and from octadecylbiphenyl after 14.3 x 10^8 r were still in fairly good shape. Apparently the oils containing two phenyl groups per molecule protected the gelling agent. Protection was also noticeable in the change in penetrations of the same greases (Table XXIX, page 37).

3.4.2 Irradiation of Dry Soaps

In one experiment, dry soaps were irradiated for 2.4 x 10^8 r and examined for changes in chemical composition and grease-forming properties. Results are in Table XXXIII. Perchloric acid titrations and bromine numbers did not reveal significant changes in any of the samples. Infrared absorption spectra gave slight evidence that free carboxyl groups formed in the sodium stearate and the lithium hydroxystearate, but not in the sodium terephthalamate. The typical spectra obtained are shown in Figure 12 for the sodium stearate.

All three gelling agents were made into greases with a naphthenic mineral oil. Preirradiation caused lithium hydroxystearate to yield a grease 3% softer, sodium stearate 30% stiffer, and sodium terephthalamate 10% softer than without irradiation. The effect of radiation on sodium stearate is surprising. Whole sodium stearate greases softened markedly upon irradiation; the grease made from preirradiated sodium stearate was much stiffer than normal. Electron micrographs of the grease at 8000 magnification are given in Figure 13. Sodium stearate showed the most modification in structure after irradiation. Thus, it appears that sodium stearate is particularly sensitive to radiolysis, but that the products formed can be recombined into an even more efficient gelling agent.

Sodium stearate was also examined by X-ray diffraction. Spacing data are in Table XXXIV

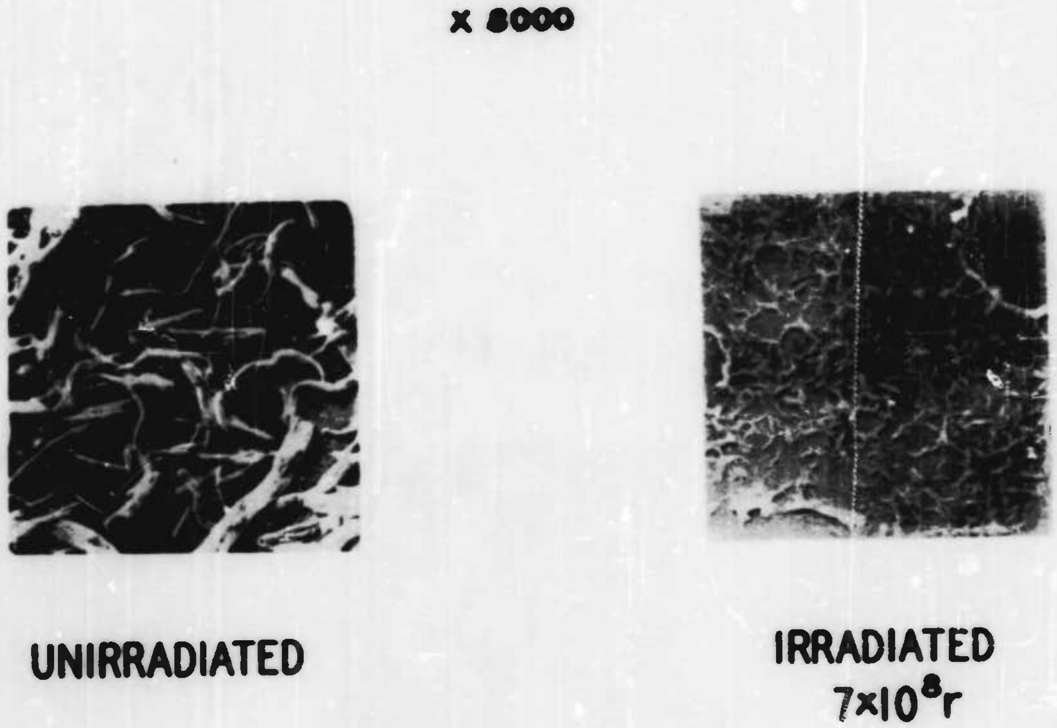


FIG. 10 - EFFECT OF GAMMA IRRADIATION AT 250°F ON CRYSTALLITE STRUCTURE OF CHEVRON OHT GREASE

FIG. 11 - EFFECT OF GAMMA IRRADIATION AT 250°F ON CRYSTALLITE STRUCTURE OF SODIUM N-OCTADECYLTEREPHTHALAMATE GREASES

TABLE XXXIII

EFFECTS OF GAMMA RADIATION ON DRY GELLING AGENTS

Gelling Agent	Lithium 12-Hydroxystearate		Sodium Stearate		Sodium (HTA)[b] Terephthalamate	
Product No.	2579-46C	2579-46F	2579-46A	2579-46D	2579-46B	2579-46E
Gamma Dosage[a], 10^8 r	0	2.4	0	2.4	0	2.4
Perchloric Acid Titration	-	No Change	-	No Change	-	No Change
Bromine No.	5	2	2	3	8	3
Infrared Absorption	-	Some $-CO_2H$	$-CO_2H$	Some $-CO_2H$	-	Slight Changes
Worked Penetration of Grease from 15% Gelling Agent in Naphthenic Mineral Oil	195	200	344	243	203	223

a. MTR Canal Source

b. Hydrogenated tallow amine

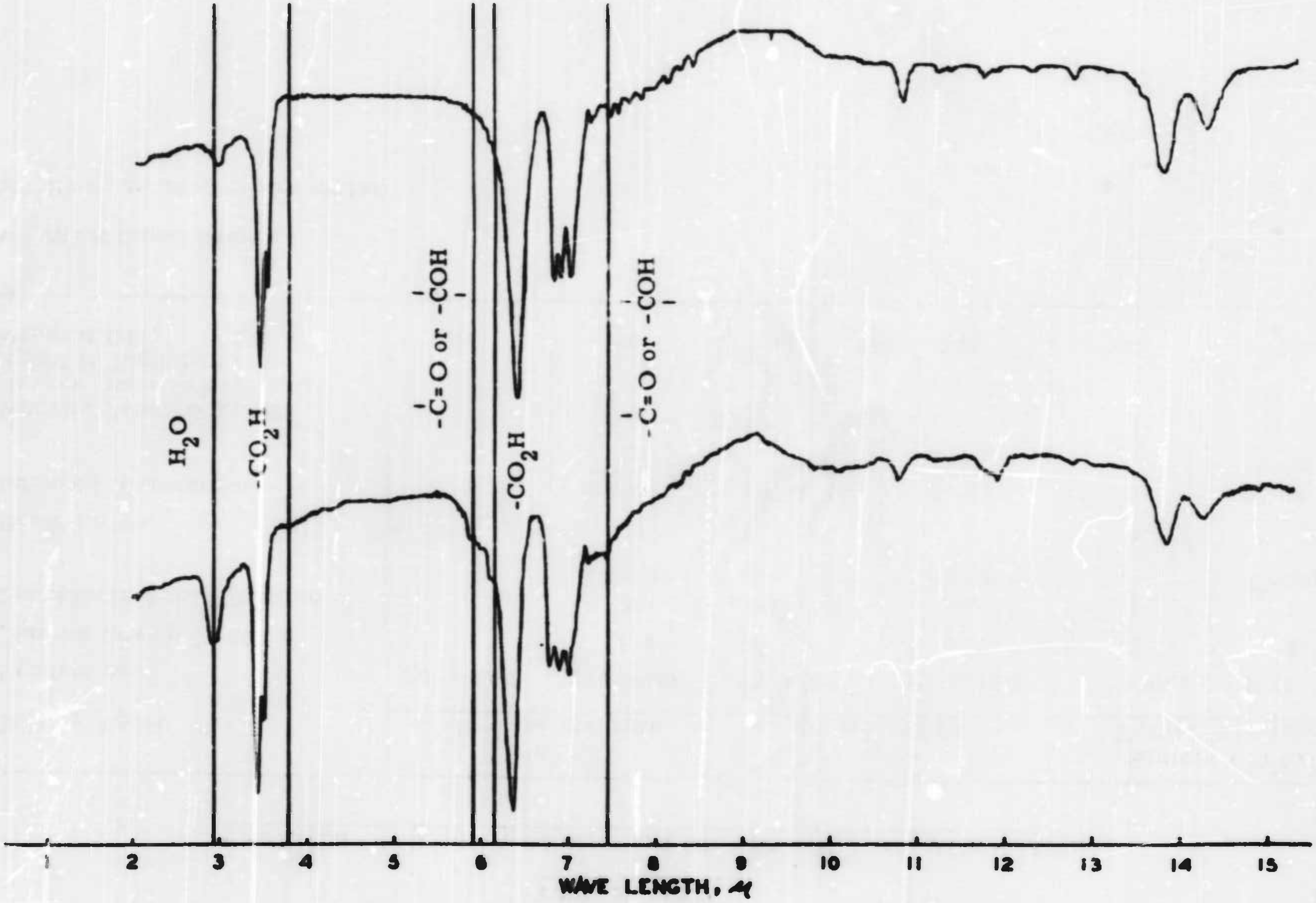


FIG. 12 - INFRARED SPECTRA OF SODIUM STEARATE (TOP) AND IRRADIATED SODIUM STEARATE (BOTTOM). INCREASED ABSORPTION IN IRRADIATED SOAP AT VERTICAL LINES.

SODIUM STEARATE

SODIUM(HTA) TEREPHTHALAMATE

LITHIUM 12-HYDROXYSTEARATE

GREASES FROM UNIRRADIATED SOAPS	GREASES FROM IRRADIATED* SOAPS

*2.4 × 10^8 R GAMMA DOSAGE

FIG. 13 - ELECTRON MICROGRAPHS OF GREASES

Table XXXIV

Effect of Gamma Radiation on X-Ray Diffraction Patterns of Sodium Stearate

Line	Sodium Stearate			Sodium Stearate After 2.4 x 10^8 r Gamma Irradiation		
	2 θ	d, Å	I (rel.)	2 θ	d, Å	I (rel.)
1	2.2	40.12	100	2.1	42.03	90
2	4.2	21.02	8	4.1	21.53	9.5
3	6.3	14.02	31	6.2	14.24	18
4	8.3	10.64	2	8.2	10.77	2
				9.1 (?)	9.71	1
5	10.5	8.42	8	10.3	8.58	4
6	14.7	6.02	1.5			
7 (wide)	19.0	4.67	3	18.9	4.69	3.5
				21.3	4.17	6 (overlap)
8 (wide)	22.0	4.037	7	22.3	3.98	6
9	24.8	3.587	1			
10	30	2.976	1	30.5	2.928	1.5
11	40	2.252	2	39.8	2.263	1.5

Differences are minor. Two questionable lines in the irradiated soap, at 9.1 Å and 21.3 Å, were not noticeable in the unirradiated soap. A weak line, No. 9, in the unirradiated soap was not noticeable in the irradiated soap. These results indicate that if the sodium ions were discharged and migrated from their original crystal sites during irradiation, they did so without much disturbance to the rest of the crystal structure. Any new compounds that may have formed from the displaced sodium must have been too finely divided or too small in quantity to be picked up by the X-ray beam.

3.4.3 Reversibility

Other research[1] has indicated that radiation softened greases are often reversible. They may recover their original consistency when reheated and cooled. The sodium stearate-naphthenic oil grease described in Table XXVII, page 34 after 5.1 x 10^8 r was heated to 400° F and pan cooled. Its work penetration recovered as follows:

Original grease	309
Gamma irradiated 5.1 x 10^8 r	Liquefied
Irradiated sample recooked	381

Thus, the radiolysis products recombined and regelled the grease.

---

[1] Hotten, B. W. and Carroll, J. G., "Mechanism of Radiation Damage to Greases," presented Am. Chem. Society Miami Meeting, April 1957.

3.5 In-Source Test Rigs (S. R. Calish)

Functional tests on radiation resistant lubricants have most often been performed on preirradiated fluids in equipment operating outside the radiation source. Results of such tests might differ from those obtained from equipment operating in the source. For example, operation of in-source bearing tests introduces a combination of such added factors as exposure of thin films to shear, heat, and metal surfaces in the radiation field. This was first emphasized by work in the reactor at the MTR with special motors.[1] Inspections after exposure revealed that lubrication failure occurred before such would have been predicted on the basis of static irradiations and subsequent functional tests. The evidence was not conclusive, but impetus was provided to design an "in-source bearing test rig."[2] In-source functional tests were also desired for another purpose. Greases were found in static tests to soften on irradiation before they hardened. The effect of bearing operation on this softening phenomenon could only be investigated with in-source rigs.

3.5.1 Equipment

The requirements for a simple bearing tester for in-source operation were based on size limitations of the radiation source, availability of equipment, availability of a power supply, and usefulness of data obtained. A standard Bodine Model NCI-13 capacitor motor was selected for the test unit because it was the proper size and immediately available in quantity. The motor employed two standard, grease lubricated, 8 mm bore bearings operating at 3350 rpm on 110-volt, 60-cycle power. As shown in Figure 14, a small, 10-bladed fan was provided for air circulation within the sealed container and for the slight load which it imposed on the motor and bearings.

The whole unit was sealed to prevent water intrusion during exposure in the MTR Canal Gamma Source. A flexible plastic vent line carried electrical leads from a control console. The console was provided to regulate the input voltage. It also indicated the current demand, provided a sonic indication of motor operation, and served as the terminal block and selector for power and thermocouple connections.

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[1] Pratt and Whitney tests on greases.

[2] A small electric motor test in a reactor was used in earlier work with oils; limited information was obtained (J. G. Carroll and R. O. Bolt, "Lubrication in the Presence of Nuclear Radiation," Lubrication Engineering, Vol. 12, No. 5, 305, 1956).

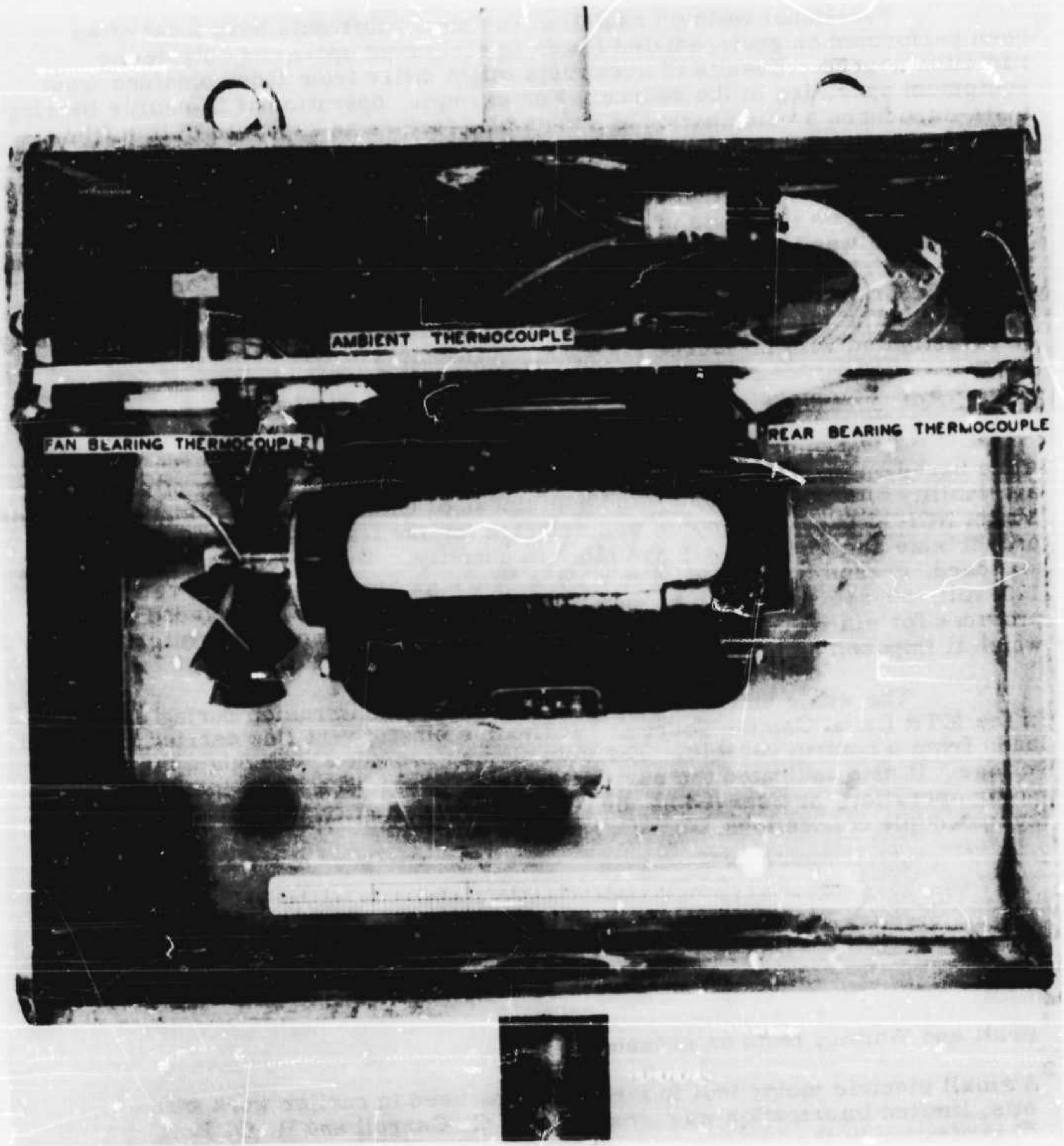

FIG. 14 - IN-SOURCE BEARING TEST MOTOR CANISTER

3.5.2 Results of Irradiations

Two units were employed and the motor bearings were packed with grease by hand. One motor was lubricated with Chevron OHT Grease and the other with a mixed C_{16-18} alkylbiphenyl gelled with sodium terephthalamate and containing a selenide oxidation inhibitor. The latter grease was a laboratory-scale batch of CALRESEARCH 159. A small sample of grease was exposed in a container placed beside the motor in each unit. Effects on these static samples were to be compared with those from the dynamic tests.

Both test rigs operated in a completely satisfactory manner for 500 hours, at which time the test was discontinued. At this point, the total gamma dosage was about 12 x 10^8 r. Measured temperatures (three positions for each motor) were under 80° F.

After irradiation, the canisters were opened and the motors inspected. All motor bearings turned freely and their greases were in good condition. The change in worked penetration of static samples is given in Table XXXV.

Table XXXV

Penetrations of Static Grease Samples
From Initial In-Source Bearing Tests

	Gamma Dosage, 10^8 r	ASTM Worked Penetration
2579-41 (Sodium HTA) Terephthalamate - C_{16-18} Alkylbiphenyl	0	281
	14.0	174
2579-19A (Chevron OHT Grease)	0	289
	12.5	220

The biggest change noted in the test equipment was hardening of the conventional insulation of the motor windings and electrical leads. Some corrosion was evident on the polished steel surfaces of the motor shaft, bearing mounts, and accessory equipment. This was much more pronounced in the case of the biphenyl grease.

Attempts were made to run the in-source motor rig to failure. The motor containing Chevron OHT Grease from the initial test was returned to the MTR undisturbed in its cannister. New bearings, lubricated with CALRESEARCH 159, were installed in the second motor before it was returned.

These nonfailure tests gave no information on the comparison of in-source functional tests with out-source functional tests on preirradiated greases. However, they did show that a grease such as Chevron OHT, which goes through a marked softening stage prior to hardening (see Table XXVI, page 31) on static irradiation, can operate in a bearing. Thus, static samples irradiated for the full dosage term (see Table XXXV) gave a reasonable picture of the usability of the greases.

After about 7 x 10^8 r additional irradiation, both canisters leaked water through the flexible plastic vent hose and the tests were discontinued. Failures were electrical due to water intrusion. The CALRESEARCH 159 motor turned freely, but the bearings were slightly rough. The Chevron OHT motor was completely free and smooth. Considerable rusting had occurred on all steel surfaces, but the bearings, because they were shielded, suffered little water damage.

The Chevron OHT Grease received a total of 20 x 10^8 r in both tests. Despite this high dosage, the commercial grease provided good service at the low temperatures involved.

3.5.3 Tests at Elevated Temperatures

To investigate simultaneously the effects of temperature and radiation, two new bearing rigs were constructed. The equipment, shown in Figure 15, was a modification of the first design in which heaters have been added and the motor housing cut away for increased air circulation. The test procedure and control setup were changed slightly to allow for heat control. Motors were rewound with Class H (silicone) insulation to permit high temperature operation. Units maintained 350° F in nonradiation tests. Initial irradiation tests will be with Chevron OHT Grease. It is planned to run the units to failure with these and CALRESEARCH 159 greases.

3.6 Summary of Conclusions

1. Conventional lubricating greases first soften (under about 5 x 10^8 r) and then stiffen (above about 5-10 x 10^8 r) under gamma irradiation.

2. Other important properties, such as bearing performance, corrosivity to copper, and oxidation resistance, also suffer on irradiation.

3. The early softening can be greatly reduced by the use of an aromatic gelling agent, sodium N-octadecylterephthalamate, in place of conventional soaps.

4. The later hardening can be postponed by the use of an aromatic oil, such as octadecyl-alpha-methylnaphthalene or octadecylbiphenyl, in place of the usual mineral oils.

5. A grease containing the terephthalamate and octadecylbiphenyl, along with the oxidation inhibitor, didodecyl selenide, is a promising prototype for development under the contract specification.

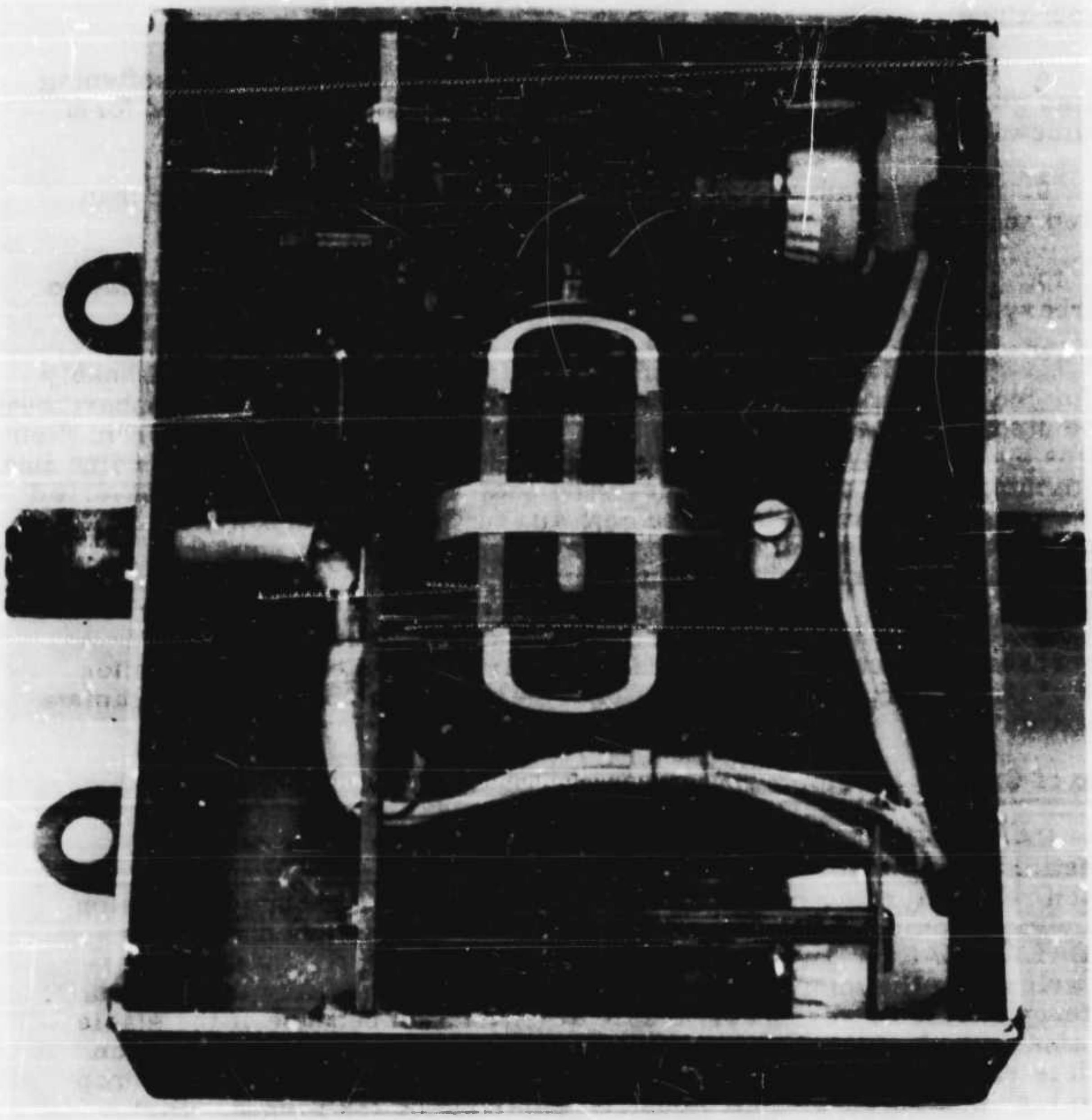

FIG. 15 - IN-SOURCE BEARING TEST MOTOR CANISTER WITH HEATERS

6. Alkyl diphenyl ether oils, such as the trioctyl derivative, are also promising oil types.

7. Heat damage and radiation damage are not additive up to 250°F. A grease irradiated while heated may be damaged less than one irradiated at room temperature.

8. As shown from electron microscopic studies, the early softening of irradiated greases results from disintegration of soap crystallites that form the gel framework.

9. Preirradiated soaps sometimes have better gelling power than unirradiated soaps.

10. Infrared analysis of irradiated dry soaps indicated the formation of free carboxylic acids.

11. The following mechanism of crystallite disintegration reasonably accounts for the experimental facts: Electrons formed during gamma bombardment of a grease discharge metal ions of the soap. The metal atoms migrate from their normal sites and are converted to oxide, hydroxide, or carbonate if they come into contact with moisture or carbon dioxide. The soap anion meanwhile is converted into a free radical by electron bombardment and further into carboxylic acid if in contact with moisture; but it is too big to migrate, at least until the crystallite is badly damaged by cation migration.

12. Dynamic in-source bearing tests and static irradiations of selected greases at about 80°F compare favorably for predicting the radiation resistance of these lubricants at 20×10^8 r. This may not hold for other gamma dosage regions.

3.7 Status of Grease Development

CALRESEARCH 159 was the grease most completely developed toward meeting the contract specification. Its properties relative to the specification requirements are given in Table I, page vi. Although irradiation tests on it were incomplete, previous experience with similar compositions indicated CALRESEARCH 159 may be usable at least to 10^9 r. Its dropping point was well above the minimum required, both before and after irradiation. Its consistency should be reasonably stable to irradiation because of the stable terephthalamate used as a gelling agent. It did not pass the copper corrosion test, which is exceptionally severe. Its bomb oxidation value of 9 pounds drop was not too high compared with the required minimum of 7.5 pounds. Dirt content was not checked, but should present no problem. Its water resistance was well above the requirement. Bearing performance of a pilot sample at 350°F before irradiation was about 80% of that required; the large batch had about 50% of the required life. The worked stability before irradiation was also exceptionally good. Its evaporation rate at 400°F was about four times the maximum permitted; there is little hope of meeting this requirement with an oil (other than a silicone) that also has a low pour point. Low temperature apparent viscosity was not tested but the grease should be usable at least to 0°F before and after irradiation to about 10^9 r. No trouble is expected with the Gear Wear Test before or after irradiation.

3.8 Future Work

The terephthalamate-alkylbiphenyl-selenide prototype grease should be further examined for all contract specification requirements and field tested as extensively as possible. New gelling agents should be broadly investigated; nonmetallics are of special interest for greater freedom from induced radioactivity.

New oils should also be investigated: alkyl diphenyl ethers are especially promising. Aromatic esters, aromatic polyethers, and aromatic silicones should be examined. Antiradiation additives should be studied systematically, especially for protection of the gelling agents. The mechanism of radiation damage to soaps and other gelling agents should be further studied, with purer compounds and more quantitatively than before, where possible. This is expected to furnish a background for more efficient formulation research.

4. GAS TURBINE LUBRICANTS

(R. L. Peeler and J. G. Carroll)

4.1 Introduction

The gas turbine lubricant specification is essentially a MIL-L-7808C fluid plus the ability to pass all tests after a radiation dosage of 10 x 10^8 r at 450°F. The requirements are in Table XXXVI as the "Phase III" fluid. To help in the step-wise development of this lubricant, two intermediate phases were set up. In these, the low temperature limit was relaxed from -65°F to 0°F and radiation dosages and temperature were also relaxed. Otherwise, requirements were unchanged.

Previous work[1] indicated coking and oxidation properties of MIL-L-7808 lubricants to deteriorate after gamma dosages of less than 10^8 r. Requirements for these two properties are difficult to pass even with unirradiated lubricants. Thus, in the contract work, emphasis was placed on finding base fluid and additive combinations, with suitable physical properties, to satisfy coking and oxidation tests. During the research the coking temperature requirement was increased so that coking tests were run mostly at 700°F rather than the initial 600°F.

4.2 Physical Properties

4.2.1 General

Table XXXVII lists physical properties of 14 fluids which were of interest for the gas turbine lubricant application. Eight of these fluids were commercially available while the other six were new materials prepared as described in Section 2 of this report. The fluids are grouped in the categories of hydrocarbons, ethers, and esters. The comparative advantages and disadvantages of each class were also described in Section 2, page 6. The viscosity-temperature properties (from measured values) of some of the more promising of these fluids are plotted in Figure 16. The Phase III viscosity temperature slope requirements were met only by the polyglycol diethers and aliphatic diesters.

For the reasons cited in Section 2 (page 7), the alkyl aromatic fluids were of particular interest as bases for new gas turbine lubricants. A brief summary of the effect of both the alkyl and aromatic groups on the physical properties of the alkyl aromatics is given in Table XXXVIII. The materials listed, with the exception noted, were distilled with a low separation efficiency. The good low-temperature properties obtained in these syntheses were largely the result of the formation of a mixture of isomers and any purification which would unduly concentrate pure isomers would have an adverse effect on pour point. The best combinations of viscosity, viscosity index, and pour point were found with the alkylbiphenyls and alkyl diphenyl ethers. The diphenyl ether derivatives had higher viscosity indexes than the alkylbiphenyls. Pour points of the ethers were lower than for the biphenyls until the C_{16-18} derivative was reached.

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[1] Johnson, R. H., and Ballentine, O. M., Technical Note, WADC 55-124, June 1955.

TABLE XXXVI

GAS TURBINE LUBRICANT REQUIREMENTS

	Phase I		Phase II		Phase III[a]	
	Original	Irradiated	Original	Irradiated	Original	Irradiated
1. Irradiation						
a. Dosage, 10^8 r		1		5		10
b. Temperature, °F		300		300		450
2. Oxidation-Corrosion, 347°F						
Weight Change, mg/cm^2						
Copper	+ 0.4 max		+ 0.4 max		+ 0.4 max	
Steel	∓ 0.2		∓ 0.2		− 0.2	
Aluminum	∓ 0.2		∓ 0.2		0.2	
Magnesium	∓ 0.2		∓ 0.2		0.2	
Silver Plate	∓ 0.2		∓ 0.2		0.2	
Titanium	∓ 0.2		∓ 0.2		0.2	
Appearance	pass		pass		pass	
Viscosity Change at 100°F, %	-5 to +15		-5 to +15		-5 to +15	
Neutralization No. Change	2.0 max		2.0 max		2.0 max	
3. Gear Test, lb/in.	2000 min		2000 min		2000 min	
4. Viscosity, cs						
At 210°F	3.0 min		3.0 min		3.0 min	
At 100°F	11.0 min		11.0 min		11.0 min	
At -65°F	13,000 max at 0°F		13,000 max at 0°F		13,000 max	
5. Pour Point, °F	-20		-20		-75 max	
6. Flash Point, °F	400 min		400 min		400 min	
7. Foaming	pass		pass		pass	
8. Coking at 600°F, mg	100 max		100 max		50 max	
9. SOD Lead Corr. at 325°F, mg/in^2	6.0 max		6.0 max		6.0 max	
10. Evaporation at 400°F, %	25 max		25 max		25 max	
11. SIT, °F	700 min		700 min		700 min	
12. Shell Four-Ball Wear	Determine		Determine		Determine	

a. As contained in Exhibit "A," Contract AF 33(616)-3184.

TABLE XXXVII

PROPERTIES OF GAS TURBINE LUBRICANT BASE STOCKS

	Viscosity, cs					Viscosity Index	Pour Point, °F	Flash Point, °F	Evaporation (6-1/2 hours At 400°F), %	Spontaneous Ignition Temperature, °F
	At -65°F	At -40°F	At 0°F	At 100°F	At 210°F					
I. **Requirements** (Unirradiated)										
a. Phase I	-	-	13,000 max	11.0 min	3.0 min	-	-20, max	400 min	25, max	700 min
b. Phase II	-	-	13,000 max	11.0 min	3.0 min	-	-20, max			
c. Phase III	13,000 max	-	-	11.0 min	3.0 min	(119)	-75, max			
II. **Hydrocarbons**										
a. Naphthenic White Oil	-	-	14,519	74.51	7.65	63	-30	435	19	735
b. C_{18-18} Biphenyl (Bottoms)	-	-	4,400^b	55.03	7.08	94	-25	360	8.6	730
c. C_{18-18} Biphenyl (Distilled)	-	61,664	2,400^a	36.54	5.27	76	-55	430	-	-
d. Dicotylbiphenyl	-	-	7,300^b	60.19	6.99	76	-50	-	22.8	800
III. **Ethers**										
a. Dioctyl Diphenyl Ether	-	157,713	5,500^a	58.82	6.97	77	-50	-	24.2	860
b. Tetradecyl Diphenyl Ether	-	13,656	-	22.26	4.14	93	-70	445	24.2	820
c. Ucon DLB 144E		16,550	790^a	32.37	7.16	162	-65	455	10.1	770
d. Polyglycol Diether (Dow PG 144)	5,512	-	103	8.88	2.75	168	<-80	370	34.7	-
IV. **Esters**										
a. Diisooctyl Azelate	6,986	-	-	12.36	3.39	169	<-80	405	17.8	770
b. Di(2-ethylhexyl)sebacate	8,224	-	-	12.66	3.34	156	<-80	430	14	-
c. Diisooctyl Phthalate	-	54,930	1,900^a	27.1	4.25	42	-55	410	23	-
d. Diisooctyl Terephthalate	-	49,624	1,900^a	31.7	5.09	93	-65	420	15.8	860
e. Hercoflex 600	-	7,791	-	24.3	4.77	132	<-80	470	7.2	775
f. Cresyl Diphenyl Phosphate	-	-	1,000^b	18.2	3.25	15	-35	475	15	-

a. Interpolated
b. Extrapolated

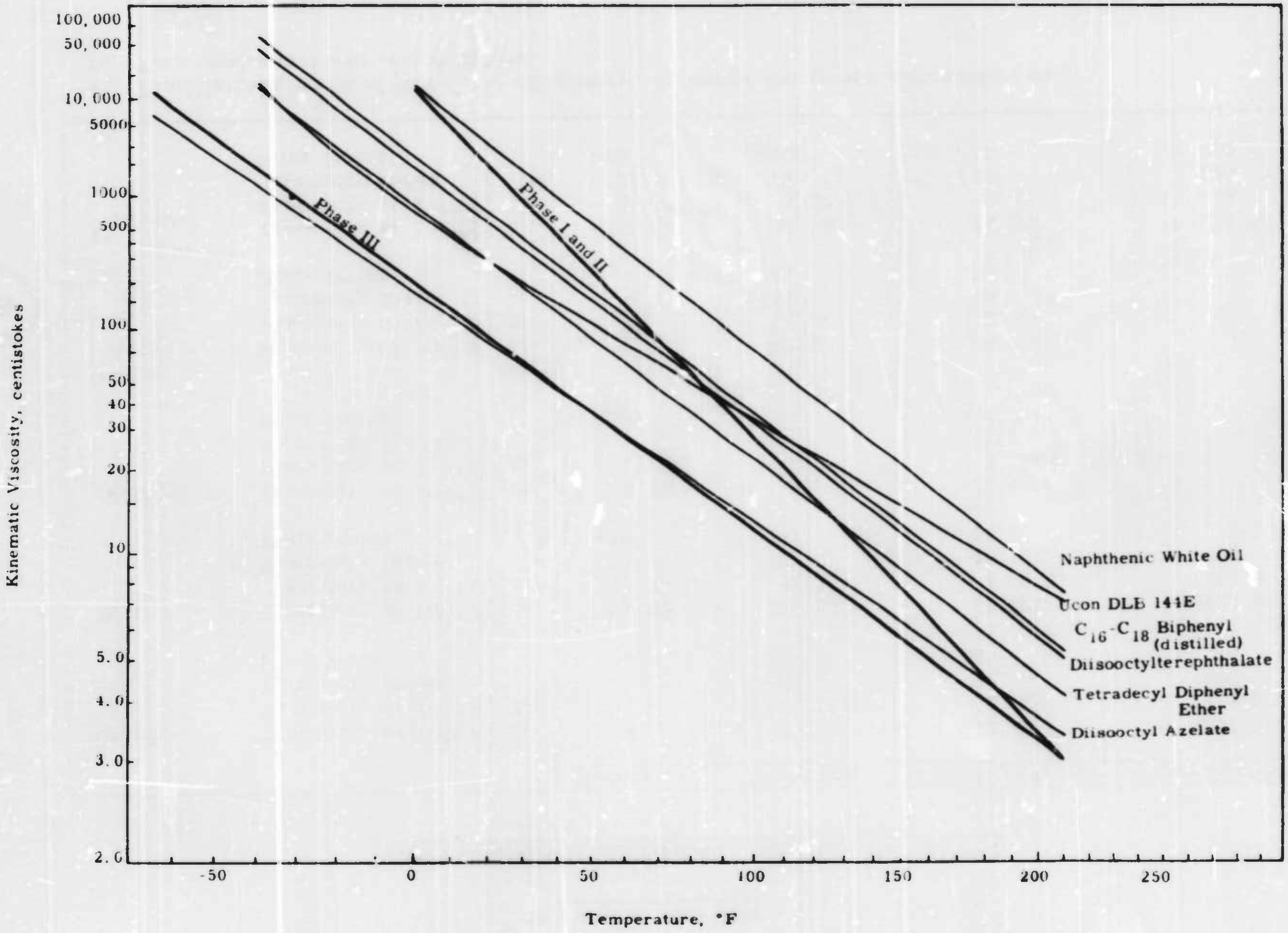

FIG. 16 - GAS TURBINE LUBRICANT VISCOSITIES

TABLE XXXVIII

PROPERTIES OF DISTILLED[a] ALKYL AROMATICS

		Benzene	Biphenyl	Diphenyl Ether	m-Terphenyl
Octyl -	Viscosity at 100°F, cs	-	17.91	13.0	227.1
	Viscosity at 210°F, cs	-	3.057	2.69	10.8
	Viscosity Index	-	-27	20	-50
	Pour Point	-	-50	-65	-5
Dioctyl -	Viscosity at 100°F, cs	12.02	51.14	56.80	642.8
	Viscosity at 210°F, cs	2.531	6.04	6.872	23.3
	Viscosity Index	11	55	73	21
	Pour Point	-80	-50	-50	0
Dodecyl -	Viscosity at 100°F, cs	4.331	-	16.57	-
	Viscosity at 210°F, cs	1.531	-	3.34	-
	Viscosity Index	-	-	69	-
	Pour Point	-20	-	-65	-
Tetra-decyl -	Viscosity at 100°F, cs	-	33.2	19.77	-
	Viscosity at 210°F, cs	-	4.80	3.85	-
	Viscosity Index	-	53	92	-
	Pour Point	-	-60	-60	-
C_{16-18} -	Viscosity at 100°F, cs	9.09	36.54	24.57	158.5[b]
	Viscosity at 210°F, cs	2.41	5.27	4.57	14.7
	Viscosity Index	92	76	113	100
	Pour Point	-25	-60	-10	70

a. Distillations were of low plate efficiency, intended for gross separation only.
b. This compound was not distilled.

The lower boiling fractions from distillation of the C_{16-18} biphenyl could be stored one week at -40°F without crystallization; the higher boiling fractions crystallized readily. Pour point was reduced from -25°F to -55°F by removing the high boiling (60-100%) fractions. Some loss in viscosity index resulted from this procedure. With the tetradecyl diphenyl ether, the bottoms product had a pour point at least as low as that of the distilled product. The bottoms showed no tendency to crystallize on storage at -65°F for 72 hours, seeded with a diphenyl ether crystal. The distilled tetradecyl diphenyl ether had a viscosity at -40°F of 10,041 cs.

4.2.2 Irradiation Tests

In order to screen a wide variety of potential base stocks for physical property changes on irradiation, some 32 fluids were exposed in the MTR gamma source at 80°F. The gamma dosages ranged from 0.3 to 10 x 10^8 r. Twenty ml of fluid and 1/4 by 1-inch corrosion specimens of aluminum and of 1020 steel were contained in glass vials. The vials were closed with plastic caps which were provided with a liner of aluminum foil. A drilled hole in the cap permitted escape of the evolved gas after pressure was sufficient to rupture the aluminum foil. No attempt was made to exclude air either before or during irradiation.

Didodecyl selenide was used as a radiation damage inhibitor with all hydrocarbons and with all ethers and esters in which it was soluble. Amine inhibitors were used in those fluids in which the selenide was not soluble. Previous work had already shown that (1) aromatics have better radiation stability than aliphatics[1, 2, 3, 4], and (2) aliphatics may be improved in radiation stability by the use of selected inhibitors, particularly the alkyl selenides[1]. The present series of irradiations amplified the previous work. Hydrocarbons showed much less radiation damage than the other two groups; ethers varied from good to poor, depending primarily on aromatic content; and the esters as a class were the poorest. The following sections present expanded discussions of these results.

4.2.2.1 Hydrocarbons

Table XXXIX shows the results of some physical property inspections on 13 hydrocarbons which were irradiated for up to 9 x 10^8 r. All fluids contained 5% didodecyl selenide. With only a few exceptions, the aluminum corrosion strips were bright for all fluids. The 1020 steel specimens contained in the sample vials during the irradiations usually showed a brown stain or coating. Attempts to identify the nature of the coating were unsuccessful. X-ray

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[1] R. O. Bolt and J. G. Carroll, "Influences of Nuclear Radiation on Organic Fluids and Lubricants," submitted to Industrial and Engineering Chemistry.

[2] C. S. Schoepfle and C. H. Fellows, "Gaseous Products from Action of Cathode Rays on Hydrocarbons," Industrial and Engineering Chemistry, <u>23</u>, 1396 (1931).

[3] R. O. Bolt and J. G. Carroll, "Organics as Reactor Moderator Coolants: Some Aspects of Their Thermal and Radiation Stabilities," Proceedings of the International Conference on Peaceful Uses of Atomic Energy in Geneva, August 8-20, 1955, Vol. 7, p. 546, United Nations (1956).

[4] E. L. Colichman and R. J. H. Gercke, "Radiation Stability of Polyphenyls," Nucleonics, Vol. 14, No.7, p. 50, July 1956.

TABLE XXXIX

INSPECTIONS ON IRRADIATED[a] HYDROCARBONS

Identity[b]	Gamma Dosage, 10^8 r	Appearance of Oil	Appearance of Metals Aluminum	Appearance of Metals Steel	Viscosity, cs At 100°F	Viscosity, cs At 210°F	Index of Damage,[e] T_{10}	Index of Damage,[e] V_{10}	Reference
1. Naphthenic White Oil	0				78.31	8.76	200	10	3341-16-2
	0.33	Clear	Pitted	Lt. Brown	67.35	7.51		9.5	G-63-1
	3.3	Clear	Pitted	Lt. Brown	131.7	11.65		13.4	G-64-1
2. 10-C Insulating Oil	0				10.26	2.71	102	10	3341-16-10
	0.33	Clear	Spotted	Lt. Brown	8.90	2.35		8.7	G-63-5
	3.3	Haze	Pitted	Brown	13.36	3.02		13.0	G-64-5
3. C$_{16-18}$ Benzene	0				12.86	3.22	114	10	3341-16-6
	0.33	White Parts.	Bright	Lt. Brown	11.97	2.98		9.3	G-63-2
	3.3	Lt. Floc	Bright	Brown	14.99	3.48		11.6	G-64-2
4. C$_{16-18}$ Toluene	0				14.80	3.46	124	10	3341-16-8
	0.33	Clear	Bright	Lt. Blue	13.41	3.13		9.0	G-63-4
	3.3	Lt. Floc	Lt. Pits	Brown	16.50	3.58		11.3	G-64-3
5. C$_{18}$ Toluene	0				17.82	4.03	132	10	3341-16-7
	0.33	White Parts.	Pitted	Brown	15.78	3.58		8.8	G-63-3
	3.3	White Parts.	Hvy Pits	Brown	20.18	4.18		10.9	G-64-3
6. C$_{18}$ Benzene	0				13.70	3.35	118	10	3341-16-24
	1.03	Clear	Bright	Lt. Blue	12.35	2.98		9.0	G-63-15
	9.13	Clear	Pitted	Brown	20.59	4.28		14.5	G-64-15
7. Mixed Alkylbenzenes (m.w. ~ 250)	0				7.77	2.15	95	10	3341-16-11
	0.61	Clear	Bright	Blue	6.50	1.85		8.6	G-63-6
	5.18	Clear	Bright	Blue-Brown	8.23	2.12		10.8	G-64-6
8. Dioctylmetaterphenyl	0				431.2	20.4	250	10	3341-22-7
	0.54	Clear	Bright	Brown	431.5	20.6		10.2	G-63-28
	5.30	Clear	Bright	Blue	526.9	23.6		11.1	C-64-28
9. C$_{18}$ Biphenyl	0				37.9	5.72	168	10	3341-22-1
	0.54	Clear	Lt. Spots	Brown	38.5	5.73		10.2	G-63-30
	5.80	Clear	Pitted	Brown	51.1	7.05		12.5	G-64-30
10. C$_{16-18}$ Biphenyl	0				34.98	5.38	163	10	3341-22-1
	0.84	Clear	-	-	35.95	5.48		10.4	G-63-20
	0.84	Clear	Bright	Lt. Brown	30.42	5.52		10.3	G-63-21
	0.84[c]	Clear	Bright	Lt. Brown	36.10	5.63		10.4	G-63-22
	7.65	Clear	-	-	54.42	7.35		14.7	G-64-20
	7.65	Clear	Bright	Brown	54.40	7.34		14.2	G-64-21
	7.65[d]	Clear	Bright	Brown	54.05	7.26		14.6	G-64-22
11. C$_{18}$ alpha-Methylnaphthalene	0				40.86	5.96	173	10	3341-22-2
	0.84	Clear	Bright	Brown	43.08	6.19		10.1	G-63-23
	7.65	Clear	Bright	Blue	83.01	9.55		16.7	G-64-23
12. Octylbiphenyl	0				17.28	3.10	125	10	3341-22-3
	0.84	Clear	Bright	Brown	17.24	3.08		10.0	G-63-24
	7.65	Clear	Pitted	Brown	20.73	3.47		12.0	G-64-24
13. Dioctylbiphenyl	0				62.23	7.19	186	10	3341-22-5
	1.15	Clear	Bright	Brown	64.23	7.26		10.3	G-63-26
	4.56	Clear	Bright	Blue	90.35	9.12		12.2	G-64-26

a. In 20-ml quantities in glass vials; MTR Canal Source.
b. Each containing 5% didodecyl selenide.
c. Copper - lt. peacock; silver - brown stain.
d. Copper - brown stain; silver - black coat.
e. See Table XL, page 69.

absorption edge spectroscopy failed to show the presence of selenium. X-ray diffraction showed only alpha-iron. Electron diffraction gave a pattern which indicated crystallinity, but the material could not be identified by comparison with available tables. The most probable composition is iron oxide.

The C_{16-18} biphenyl containing 5% didodecyl selenide was irradiated with no metals present; with aluminum and 1020 steel present; and with aluminum, 1020 steel, silver, and copper present. A comparison of weight changes of the specimens is shown in Table XL. Weight changes of all the metals were nominal, although the steel, copper, and silver all showed discoloration. The presence or absence of the metals did not affect the viscosity change of the fluid.

Table XL

Effect of Metal Catalysis on Irradiated C_{16-18} Biphenyl

Gamma Dosage, 10^8 r	0.85			7.7		
No. of Metals Present	0	2	4	0	2	4
Metal Weight Change, mg/cm^2						
Aluminum	-	-0.1	+0.1	-	0	-0.1
1020 Steel	-	0	+0.1	-	+0.1	+0.1
Copper	-	-	0	-	-	-0.1
Silver	-	-	+0.1	-	-	+0.1
Index of Damage, η_{10}[a, b]	10.4	10.3	10.4	14.7	14.2	14.6

a. η_{10} is the viscosity of an irradiated fluid in centistokes at the temperature, T_{10}, in °F at which the original viscosity is 10 centistokes.

b. By this means all fluids are referred to a common starting viscosity so that radiation-induced viscosity change may be compared directly for a given radiation dosage. A value of 10.0 = no change; $>$ 10.0 = viscosity increase; $<$ 10.0 = viscosity decrease.

As seen from Table XXXIX, page 68, two thirds of the fluids containing didodecyl selenide showed an initial viscosity decrease on irradiation. The alkyl aromatics evidenced the smallest increases in viscosity for the highest gamma dosages. The alkylbiphenyls were better than alkylbenzenes and toluenes, as expected on the basis of aromatic content. Dioctylbiphenyl showed a smaller viscosity increase than octadecylbiphenyl. Thus, the two short chains may impart greater radiation stability than one long alkyl group.

4.2.2.2 Ethers

Table XLI shows the results of some physical property inspections on eight ethers irradiated for up to 9 x 10^8 r. Didodecyl selenide was added to the aromatic ethers; the more soluble phenyl-alpha-naphthylamine was used in the aliphatic materials. Only the two diphenyl ethers caused a brown coating on steel. All aluminum specimens were bright. All oils remained clear after irradiation.

The four aliphatic ethers were considerably degraded after 9 x 10^8 r; two were gelled by this dosage. The lower the starting viscosity of these materials the better they performed. Thus, DLB 50 was the most resistant. Both Dioctyl- and C_{16-18} diphenyl ether displayed low viscosity changes after 5.8 x 10^8 r and appeared to be about as radiation stable as their hydrocarbon counterparts. The viscosity change with radiation dosage for several of these aromatic fluids is shown in Figure 17.

Two compounds deserve special mention: Bis(dimethylbenzyl) ether was less stable than would be expected from the high aromatic content. Apparently the benzyl ether linkage is reactive under the test conditions. Bis[(1, 1, 3, 3-tetramethylbutyl)phenyl] ether, had the lowest viscosity change at a high dosage of any of the materials tested including octyl diphenyl ether. The complex ether is a commercial product made by the alkylation of diphenyl ether with diisobutylene.

4.2.2.3 Esters

Table XLII shows the results of some physical property inspections on 11 esters (including silicon derivatives) which were irradiated for up to 9 x 10^8 r. Dialkyl selenide was used as an inhibitor in all fluids in which it was soluble except the silicates. Selenides tend to degrade hydrolytic and high temperature stability of the silicates. Therefore, amines were used in the silicate and also in the phosphates and the Hercoflex 600 (pentaerythritol) ester.

All of the aluminum specimens included in the irradiations were bright after exposure. The steel specimens were bright except for brown coats on the cresyl diphenyl phosphate (phenothiazine inhibited) and DC 703 (selenide inhibited). All fluids were clear after irradiation except for the cresyl diphenyl phosphate and the DC 703.

As a class the esters showed relatively poor radiation stability as indicated by η_{10}[1] values of about 20 for 5 x 10^8 r dosage versus about 11-12 for the hydrocarbons and ethers already discussed. The best ester was not as good as the worst of the hydrocarbons (note Table XXXIX, page 68). The viscosity change with irradiation of several of these fluids is shown in Figure 18.

4.3 Panel Coking Tests

These were run in the Model "C" coker as described in Specification MIL-L-7808C. Standard procedures were followed for the majority of tests. With fluids in short supply, as with irradiated samples, the procedure was varied as follows:

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[1] See Table XL, page 69 for explanation.

TABLE XLI

INSPECTIONS ON IRRADIATED[a] ETHERS

Identity	Additive	Gamma Dosage, 10^8 r	Appearance of Oil	Appearance of Metals		Viscosity, cs		Index of Damage[b]		Reference
				Aluminum	Steel	At 100°F	At 210°F	T_{10}	I_{10}	
1. Bis[(1,1,3,3-tetramethylbutyl)-phenyl] Ether	5% Didodecyl Selenide	0				572	14.14	220	10	3341-16-25
		1.15	Clear	Bright	Bright	519	13.20		9.2	G-63-16
		2.56	Clear	Bright	Bright	524	14.83		10.3	G-64-16
2. Dioctyl Diphenyl Ether	5% Didodecyl Selenide	0				47.08	6.20	174	10	3341-22-5
		0.54	Clear	Bright	Brown	47.19	6.20		10.3	G-63-26
		5.90	Clear	Bright	Brown	64.69	7.70		12.2	G-64-26
3. C_{16-18} Diphenyl Ether	5% Didodecyl Selenide	0				22.04	4.48	145	10	3341-22-6
		0.54	Clear	Bright	Brown	22.08	4.40		10.2	G-63-9
		5.90	Clear	Bright	1/3 Brown	30.81	6.04		14.7	G-64-27
4. Bis(dimethylbenzyl) Ether	5% Didodecyl Selenide	0				10.45	2.50	102	10	3341-16-15
		0.61	Clear	Bright	Bright	9.96	2.31		9.7	G-63-9
		5.19	Clear	Bright	Bright	15.94	2.90		15.5	G-64-9
5. Ucon LB-135	5% Phenyl-alpha-naphthylamine	0				34.02	6.16	170	10	3341-16-19
		1.03	Clear	Bright	Bright	47.00	7.57		12.7	G-63-12
		9.13	Clear	Bright	Bright	1243.5	boils		-	G-64-12
6. Ucon DLB-144E	5% Phenyl-alpha-naphthylamine	0				38.24	7.42	183	10	3341-16-21
		1.03	Clear	Bright	Bright	45.64	8.04		11.3	G-63-13
		9.13	Gel	-	-	-	-		high	G-64-13
7. Ucon DLB-50	5% Phenyl-alpha-naphthylamine	0				9.83	2.45	94	10	3341-16-22
		1.03	Lt. Cloud	Bright	Bright	10.02	2.75		11.0	G-63-14
		9.13	Clear	Bright	Bright	53.07	9.19		61.8	G-64-14
8. Polyglycol Diether (Dow PG 65)	5% Phenyl-alpha-naphthylamine	0				67.47	10.55	215	10	3341-16-23
		1.03	Clear	-	-	83.65	12.28		12.2	G-63-35
		9.13	Gel	-	-	-	-		high	G-64-35

a. In 20-ml quantities in glass vials; MTR Canal Source.
b. See Table XL, page 70.

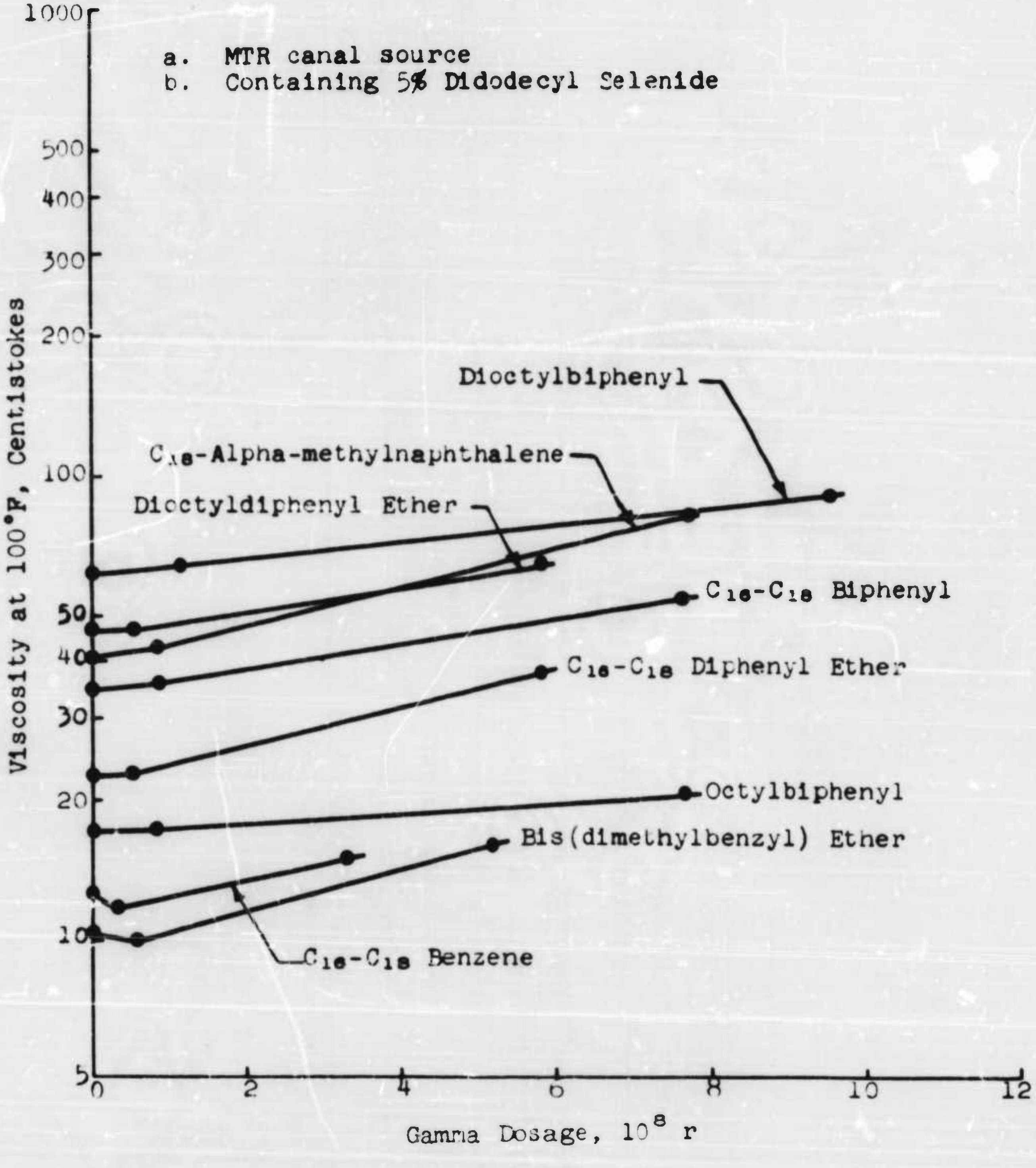

FIG. 17 - VISCOSITY CHANGE OF IRRADIATED[a] ETHERS[b] AND AROMATICS[b]

TABLE XLII

INSPECTIONS ON IRRADIATED[a] ESTERS AND SILICON COMPOUNDS

Identity	Additive	Gamma Dosage, 10^8 r	Appearance of Oil	Appearance of Metals		Viscosity, cs		Index of Damage[b]		Reference
				Aluminum	Steel	At 100°F	At 210°F	T_{10}	η_{10}	
1. Tridecyl Azelate	5% Didodecyl Selenide	0				35.86	6.71	175	10	3341-16-16
		0.61	Clear	Bright	Bright	34.34	6.37		9.6	G-63-10
		5.18	Clear	Bright	Bright	100.2	13.04		22	G-64-10
2. Diisooctyl Terephthalate	5% Didodecyl Selenide	0				29.34	4.96	156	10	3341-22-8
		0.54	Slt.Haze	Bright	Bright	31.40	5.10		10.5	G-63-29
		5.80	Slt.Haze	Bright	Bright	66.15	8.28		19	G-64-29
3. Diisooctyl Phthalate	5% Didodecyl Selenide	0				27.64	4.56	151	10	3341-16-17
		1.03	Clear	Bright	Bright	28.70	4.56		10.4	G-63-11
		9.13	Clear	Bright	Bright	166.2	13.56		40	G-64-1
4. Diisodecyl Phthalate	5% Didodecyl Selenide	0				41.35	5.80	169	10	3341-16-18
		1.15	Clear	-	-	42.86	5.77		10.3	G-63-34
		9.56	Clear	-	-	341.6	20.26		45	G-64-34
5. Dibutyl Phthalate	5% Phenothiazine	0				10.89	2.42	104	10	3341-18-3
		1.15	Clear	Bright	Bright	11.80	2.58		11	G-63-19
		9.56	Clear	Bright	Bright	26.53	4.18		25	G-64-19
6. Hercoflex 600	5% Phenothiazine	0				27.03	4.93	154	10	
		1.15	Lt. Floc	Bright	Bright	33.87	5.74		10.2	G-63-17
		9.56	Clear	Bright	Bright	379.3	30.33		80.2	G-64-17
7. Cresyl Diphenyl Phosphate	5% Phenothiazine	0				20.16	3.45	135	10	3341-18-2
		1.15	Cloudy	White	Brown	32.90	4.80		15	G-63-18
		9.56	Opaque	Deposit	Brown	481.8	22.73		138	G-64-18
8. Tricresyl Phosphate	5% Phenothiazine	0				35.48	4.33	154	10	3341-18-4
		0.61	Clear	-	-	53.82	5.55		13.7	G-63-36
		5.18	Very Dark	-	-	673.6	26.95		96	G-64-36
9. Hexa(2-ethylbutoxy)disiloxane	5% Phenyl-alpha-naphthylamine	0				11.71	3.85	112	10	3341-16-12
		0.61	Slt.Haze	Bright	Bright	15.91	4.83		13	G-63-7
		5.18	Clear	Bright	Bright	1273	Gassy		high	G-64-7
10. 1,1,3,3-Tetra(2-ethylbutoxy)-1,3-diphenyldisiloxane	2% p,p'-Dioctyldiphenylamine	0				17.23	4.53	133	10	3468-8-5
		0.33	Clear	-	-	18.49	4.79		10.7	G-63-37
		3.3	Clear	-	-	44.74	9.39		25	G-64-37
11. DC 703 Fluid	5% Didodecyl Selenide	0				25.69	5.77	160	10	3341-16-13
		0.61	Clear	Bright	Brown	24.30	5.28		9.3	G-63-8
		5.18	Haze	Bright	Brown	60.09	10.02		20	G-64-8

a. In 20-ml quantities in glass vials; MTR Canal Source.
b. See Table XL, page 70.

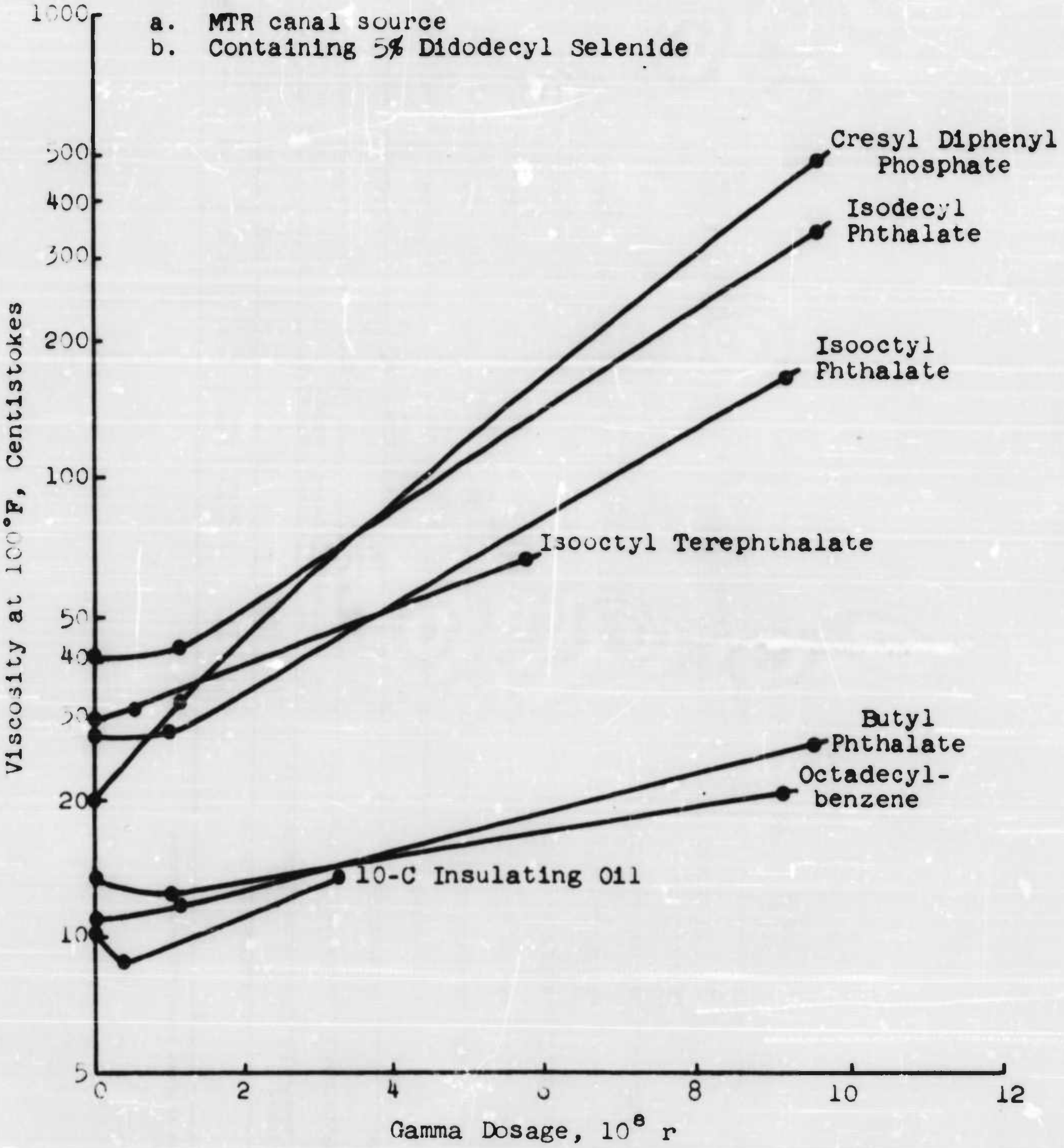

FIG. 18 - VISCOSITY CHANGE OF IRRADIATED[a] BASE STOCKS

1. Tests were for 4 hours rather than 8 hours.
2. An aluminum "false bottom" was inserted in the coker sump in order to reduce the holdup of fluid. Most of the tests were made at 700°F; only a few were made at 600°F.

4.3.1 Coking Tests on Unirradiated Fluids

Results of a series of panel coking tests on mineral oil blends are shown in Table XLIII.

Table XLIII

Coking Tests on Mineral Oils
Model "C" Coker - 8 Hours

Base Stock	Additive	Coke, mg at	
		600°F	700°F
1. Naphthenic White Oil	5% Tricresyl Phosphate + 2% Didodecyl Selenide	0	1215
2. Naphthenic White Oil	5% Tricresyl Phosphate + 2% Phenyl-alpha-naphthylamine	185	-
3. Naphthenic White Oil	2% Didodecyl Selenide + 2% Dibenzyl Selenide	- -	567, 1157 823
4. Naphthenic White Oil	5% Tricresyl Phosphate + 5% Acryloid 794 + 2% Didodecyl Selenide	0	2295
5. Naphthenic White Oil	2% Paranox 441	-	402
6. Naphthenic Pale Oil	5% Tricresyl Phosphate + 2% Didodecyl Selenide	6	1395

At 600°F, either a naphthenic white oil or a naphthenic pale oil gave very low coke deposits with dialkyl selenide inhibitors. With phenyl-alpha-naphthylamine, the white oil gave a considerable deposit, indicating the contribution of the additive to the total deposit. At 700°F, high deposits formed even in the presence of selenides. The deposits were, on the average, larger in the presence of tricresyl phosphate.

Coking tests at 700°F on several unirradiated synthetic lubricants are shown in Table XLIV. Uninhibited diisooctyl terephthalate and C_{16-18} biphenyl deposited over 500 mg of coke in the 8-hour test. Additives were ineffective in improving the coking of the ester. However, the alkylbiphenyl responded favorably to amine phenolic and selenide inhibitors. The last were the most effective, although a low coke value resulted from a single test with Paranox 441.

TABLE XLIV

PANEL COKING TESTS ON SYNTHETIC LUBRICANTS MODEL "C" COKER

8 Hours at 700° F

Base Stock	Additives	Coke, mg
Polyglycol Diether (PG 65)	2% Phenyl-alpha-Naphthylamine	346
Ucon DLB 144E	2% Dibenzyl Selenide	210
Ucon DLB 144E	2% Didodecyl Selenide	582
Ucon DLB 144E	2% Phenyl-alpha-Naphthylamine	1950
Cresyl Diphenyl Phosphate	0.5% Phenothiazine	468
Hercoflex 600	0.5% Phenothiazine	567
Diisooctyl Phthalate	0.5% Phenothiazine	1690
Diisooctyl Terephthalate	None	503
Diisooctyl Terephthalate	2% Dibenzyl Selenide	537
Diisooctyl Terephthalate	0.5% Phenothiazine	785
C_{16-18} Biphenyl	None	646
C_{16-18} Biphenyl	2% Didodecyl Selenide	173
C_{16-18} Biphenyl	5% Didodecyl Selenide	218, 191
C_{16-18} Biphenyl	2% Dibenzyl Selenide	419
C_{16-18} Biphenyl	2% Dibenzyl Selenide	246[a]
C_{16-18} Biphenyl	5% Dibenzyl Selenide	263
C_{16-18} Biphenyl	2% Phenyl-alpha-Naphthylamine	453
C_{16-18} Biphenyl	2% Paranox 441	184
C_{16-18} Biphenyl	0.5% Phenothiazine	382
C_{16-18} Biphenyl (distilled)	2% Dibenzyl Selenide	144
C_{16-18} Biphenyl (distilled)	None	1092
Dioctyl Diphenyl Ether	2% Dibenzyl Selenide	18[b]
Dodecyl Diphenyl Ether	2% Paranox 441	404[a]
Tetradecyl Diphenyl Ether	2% Paranox 441	368[a]

a. Four-hour run with "false bottom" in sump.
b. Three-hour 40-minute run with "false bottom" in sump.

The data of Table XXXIV are insufficient to distinguish between dibenzyl selenide and didodecyl selenide. The former was somewhat more effective in Ucon DLB 144E, while the latter was better in the alkylbiphenyl.

4.3.2 Coking Tests on Irradiated Fluids

A series of base stock and inhibitor combinations was irradiated in the MTR canal gamma source at about 80°F and nominal dosages of 5 and 14 x 10^8 r. Air had access to the fluids during exposure. Panel coking tests were run on the irradiated materials for comparison with data on original fluids. Results are shown in Table XLV.

The feature of these tests was the lower coke values of the selenide-inhibited blends after irradiation than before. In contrast, phenothiazine and dibenzothiophene blends showed very large increases in coking on irradiation. The selenide-radiation interaction in reducing coke deposits is most significant in that it may provide a means to reverse a major detrimental effect of radiolysis. Although the beneficial effect of selenides on coke deposition was apparent with all base stocks, it was greatest with the polyglycols. As a result, the polyglycol-dibenzyl selenide formulation approached the 700°F final coking requirement before and after the prescribed dosage of 10 x 10^8 r. (See Appendix VIII for a discussion of the role of selenium additives.)

Several tests were also run at 600°F to determine whether some adverse effect might be found at the lower temperature which was absent at the higher. Good performance was noted here also; the selenide-inhibited oils tested met the 50 mg coke requirement both before and after irradiation. An additional irradiation under similar conditions was carried out on a C_{16-18} biphenyl-dibenzyl selenide blend. Although a limited supply of stock permitted only a 2-hour run, the low level of coking obtained at the end of this time indicated that, in this base stock also, the selenide reduced coking following irradiation.

In the eight irradiated dibasic acid esters containing selenides, a red precipitate was noted. A sample of diisooctyl azelate containing dibenzyl selenide which was irradiated to 14 x 10^8 r was selected for further tests. The oil was centrifuged, the precipitate washed with n-pentane, and then it was examined by X-ray diffraction and X-ray fluorescence. The sample was mainly selenium. The only diffraction pattern obtained appeared to be that of lead formate. The selenium was therefore presumed to be present in the red amorphous form. Selenium analysis of the oil before and after the centrifuging failed to show any detectable difference. Thus, the insolubles represented only a very small proportion of the selenium present. No precipitate formed with the irradiated blends containing selenide in either the polyglycol or the C_{16-18} biphenyl.

The viscosity data of Table XLV also show that the selenides are more effective inhibitors in all three base fluids. The rank in decreasing order of effectiveness is as follows: dibenzyl selenide $>$ didodecyl selenide $>$ phenothiazine $>$ dibenzothiophene. The poor performance of dibenzothiophene is of note as previous work ascribed good effects to this compound above 700°F[1].

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[1] R. O. Bolt and J. G. Carroll, "Organics as Reactor Moderator Coolants: Some Aspects of Their Thermal and Radiation Stabilities," Proceedings of the International Conference on Peaceful Uses of Atomic Energy in Geneva, August 8-20, 1955, Vol. 7, p. 546, United Nations (1956).

TABLE XLV

TEST RESULTS ON IRRADIATED[a] GAS TURBINE LUBRICANT BLEND

Formulation													4-Hour Panel Coking Test[c]			
Base Fluid	Additive	% By Weight	Gamma Dosage, 10^8 r	Viscosity, cs 100°F	Viscosity, cs 210°F	Index of Damage[b] T_1, °F	η_1	T_{10}, °F	η_{10}	Pour Point, °F	Appearance	Evaporation, % 6-1/2 Hr at 400°F	mg of Coke 600°F	mg of Coke 700°F	Oil Consumption, ml 600°F	Oil Consumption, ml 700°F
1a. Polyglycol Diether (PG 144)	Didodecyl Selenide	5	0	9.82	2.73	408	1.00	92	10.0	-55	-	34.7	-	194	-	430
			5.6	18.[illegible]	4.52		1.42		20.0	-60	Clear	-	-	395	-	190
			11.1	32.4	5.79		1.93		[illegible]	-50	Clear	39.6	-	62	-	240
b.	Dibenzyl Selenide	5	0	9.23	2.70	405	1.00	92	10.0	<-80	-	36.2	19	114	140	315
			5.6	15.4	4.05		1.57		17.6	<-80	Clear	-	41	11	125	225
			14.3	23.5	5.50		1.63		20.8	<-80	Clear	30.9	-	26	-	235
c.	Phenothiazine	2	0	9.46	2.82	412	1.00	90	10.0	<-80	-	-	-	2435	-	470
			5.6	28.0	6.40		1.77		50.0	-80	Clear	-	-	8070	-	330
			14.3	75.0	14.1		2.13		220.0	-70	Clear	-	-	7790	-	285
d.	Dibenzothiophene	5	0	9.14	2.74	405	1.00	94	10.0	<-80	Clear	-	-	2201	-	490
			5.5	54.0	7.40		2.05		[illegible]	<-80	Clear	-	-	3190	-	365
			14.6	259.0	40.2		7.45		285.0	-65	Clear	-	-	8909	-	245
2a. Di(2-ethylhexyl) Sebacate	Didodecyl Selenide	5	0	12.5	3.31	434	1.00	114	10.0	-30	-	-	-	431	-	165
			5.6	25.0	5.44		1.38		19.0	-50	Red ppt.	-	-	118	-	245
			11.1	52.3	9.24		1.95		38.5	-60	Red ppt.	-	-	1207	-	90
b.	Dibenzyl Selenide	5	0	12.2	3.23	430	1.00	112	10.0	<-80	-	16.5	0	700	90	275
			5.6	18.7	4.07		1.16		12.8	<-80	Red ppt.	-	17	178	120	180
			11.1	27.6	5.98		1.54		21.6	<-80	Red ppt.	31.6	-	506	-	210
c.	Phenothiazine	2	0	13.2	3.39	[illegible]	1.00	116	10.0	<-80	-	-	-	1532	-	[illegible]
			5.6	35.0	6.90		1.63		25.7	<-80	Clear	-	-	5720	-	145
			14.3	83.1	13.7		2.68		57.0	-65	Clear	-	-	4750	-	95
d.	Dibenzothiophene	5	0	12.7	3.28	430	1.00	114	10.0	<-80	-	-	-	266	-	325
			5.5	49.5	8.78		1.93		30.0	<-80	Clear	-	-	2722	-	120
			14.0	175	23.8		3.75		123.0	-70	Clear	-	-	6512	-	70
3a. Diisooctyl Azelate	Didodecyl Selenide	5	0	12.2	3.30	443	1.00	112	10.0	-30	-	-	-	54	-	290
			5.6	22.9	5.07		1.28		19.2	-45	Red ppt.	-	-	27	-	250
			11.1	43.2	7.59		1.53		33.2	-60	Red ppt.	-	-	747	-	155
b.	Dibenzyl Selenide	5	0	11.8	3.26	440	1.00	110	10.0	<-80	-	25.4	0	628	110	175
			5.6	15.4	3.88		1.09		13.0	<-80	Red ppt.	-	30	139	110	165
			14.3	21.8	4.[illegible]		1.30		18.0	<-80	Red ppt.	37.0	-	248	-	175
c.	Phenothiazine	2	0	12.9	3.42	446	1.00	115	10.0	<-80	-	-	-	129	-	185
			5.5	27.7	5.85		1.41		20.7	<-80	Clear	-	-	3307	-	155
			14.0	90.2	15.[illegible]		2.56		66.0	-65	Clear	-	-	6987	-	145
d.	Dibenzothiophene	5	0	12.3	3.30	440	1.00	112	10.0	<-80	-	-	-	489	-	210
			5.5	37.5	7.45		1.69		29.5	<-80	Clear	-	-	2732	-	170
			14.0	180.0	23.7		3.46		132.0	-70	Clear	-	-	6016	-	130
4. C_{16}-C_{18} Biphenyl	Dibenzyl Selenide	2	0	51.8	6.81	-	-	181	10.0	-	-	-	-	246	-	175
			7.5	76.8	8.87	-	-	-	13.6	-	-	-	-	56[d]	-	50

a. 25-ml quantities in vented aluminum containers; MTR Canal Source.
b. η_1 (η_{10}) is the viscosity of an irradiated fluid in centistokes at that temperature T_1 (T_{10}) in °F at which the original viscosity is 1 (10) centistokes.
c. Using "false bottoms" to reduce sump capacity; standard procedure.
d. Two-hour test.

Pour points of the blends containing didodecyl selenide were relatively high due to the tendency of the additive to precipitate on cooling. As a result of irradiation, the pour points of these blends decreased. The pour points of the other blends were not greatly affected, although there was a tendency for the pour points to rise at the highest radiation dosage.

Evaporation of the polyglycol-selenide blends did not change much following irradiation. The blends of the two diesters with dibenzyl selenide increased to a greater degree in evaporation following irradiation. The result is that the diesters, originally superior, match the polyglycols after irradiation.

4.4 Oxidation Stability Tests on Unirradiated Fluids

The oxidation and corrosion test requirement at 347° F is, with the coking test, the most difficult of the specification tests to pass. Results of oxidation-corrosion work are reported in Table XLVI.

In the presence of dialkyl selenide inhibitors, heavy corrosion of copper and silver specimens occurred. Steel, aluminum, and magnesium were not adversely affected by didodecyl selenide. Magnesium was occasionally affected with dibenzyl selenide. Neglecting metal corrosion, satisfactory fluids were prepared from diisooctyl phthalate, diisooctyl terephthalate, octadecylbenzene, naphthenic white oil, dodecyl diphenyl ether, and tetradecyl diphenyl ether. Among the unsuitable fluids were two experimental products: amyldodecylbiphenyl, and cracked naphtha alkylated diphenyl ether.

The detrimental effect of the selenides on the stability of the silicate esters was shown by the poor performance of hexa(2-ethylbutoxy)disiloxane. When inhibited with amine-type inhibitors, this material can successfully operate at 400° F (see 8200 Fluid Table III, page ix). Several materials in Table XLVI were borderline in viscosity change. This might be improved by a better choice of inhibitors. Among them were Ucon DLB 144E (which also had high neutralization number), octadecylbenzene, C_{16-18} toluene, and C_{16-18} biphenyl. The failure of the latter to give a satisfactory result was surprising. The sample tested was the bottoms product which also might contain significant amounts of such impurities as olefin dimer and dialkylbiphenyls. Further work on this material is warranted.

A number of oxygen absorption measurements at 340° F were also carried out as a measure of the relative effectiveness of the various oxidation inhibitors. Results are shown in Table XLVII. These results show that several additives, including didodecyl selenide were effective in C_{16-18} biphenyl. base stock. In contrast, dibenzyl selenide gave only poor inhibition in this as well as in the other three stocks tested. This is believed related to the greater chemical reactivity and poorer thermal stability of dibenzyl selenide in comparison with didodecyl selenide. The former readily decomposed on heating in this temperature range or in the presence of light to give a red deposit, apparently amorphous selenium.

TABLE XLVI

OXIDATION AND CORROSION TESTS

72 Hours at 347°F - MIL-L-7808C

Base Stock	Additives	Metal Weight Change, mg/cm²					Neutralization No.		Viscosity Change, %		Evaporation[c] %	Sample No.	Insolubles, %	
		Copper	Steel	Silver	Magnesium	Aluminum	D 664[a]	[illegible][b]	100°F	210°F			Pentane	Benzene
C_{18}-C_{18} Diphenyl	2% Didodecyl Selenide	-	-0.03	-	-0.02	+0.04	1.1	1.03	+17.0	+7.4	1.4	4535-29-1	-	-
C_{18}-C_{18} Biphenyl	2% Didodecyl Selenide	-12.6	0	-22.2	0	+0.01	2.1	0.58	+19.4	+23.4	1.3	4535-29-1	0.2	0.49
C_{18}-C_{18} Biphenyl	2% Dibenzyl Selenide	-	+0.01	-	-0.04	+0.10	2.1	1.25	+33.7	+18.5	2.2	4535-29-2	-	-
C_{18}-C_{18} Biphenyl	2% Dibenzyl Selenide	-35.3	+0.05	-49.5	+0.05	+0.05	5.6	1.88	+54.9	+30.4	3.5	4535-29-2	9.0	0.92
C_{18}-C_{18} Biphenyl	0.5% Phenothiazine	-0.08	+0.24	+0.10	+0.05	+0.10	4.7	1.20	+21.8	+11.9	2.3	4535-29-3	5.3	1.02
C_{18}-C_{18} Biphenyl	Sat. Phenothiazine	-0.11	+0.18	+0.02	-0.01	+0.21	4.3	.39	+19.9	-14.1	1.4	4511-11-4	3.4	0.96
C_{18}-C_{18} Biphenyl	2% Phenyl-alpha-Naphthylamine	+0.06	-0.03	-0.07	0	+0.02	3.0	2.83	+30.6	+19.3	2.5	4535-29-4	-	-
C_{18}-C_{18} Biphenyl	2% Paranox 441	-0.17	-0.04	-0.02	0	0	2.2	2.45	+25.9	+14.0	-	4535-29-5	-	-
C_{18}-C_{18} Biphenyl	2% Dibenzyl Selenide + 0.01% Quinizarin	-51.1	+0.03	-58.7	+0.06	0.31	4.3	3.9	+44.6	+23.8	1.3	4535-29-6	-	-
Amyldodecylbiphenyl	2% Dibenzyl Selenide	-	+0.07	-	+0.06	+0.04	2.8	0.43	-21.2	-15.1	0.9	4535-29-11	-	-
Dioctyl Diphenyl Ether	2% Dibenzyl Selenide	-	+0.06	-	0	+0.03	1.0	0.43	+19.6	+10.1	2.3	4535-29-13	1.39	0.37
Cracked Naphtha Diphenyl Ether	2% Dibenzyl Selenide	-	+0.02	-	+0.01	-0.01	3.4	0.40	+180.6	+83.1	1.1	4535-29-12	1.9	0.65
Diisooctyl Terephthalate	2% Dibenzyl Selenide	-	-0.05	-	+0.10	+0.02	0.8	0.74	+43.6	+22.7	4.0	3341-27-1	-	-
Ucon DLB 144E	2% Dibenzyl Selenide	-	+0.06	-	+0.07	+0.03	8.6	0.75	-7.6	-16.5	4.1	4535-29-7	1.0	0.89
Ucon DLB 144E	2% Dibenzyl Selenide	-40.5	+0.02	-46.7	+0.26	+0.06	17.7	92.1	-24.1	-35.1	-	4535-29-7	-	-
Hexa(2-ethylbutoxy)disiloxane	5% Didodecyl Selenide	-	+0.10	-	-8.34	+0.13	1.7	0.49	+51.5	29.2	-	3341-23-3	-	-
Diisooctyl Phthalate	0.5% Phenothiazine	0	+0.08	+0.08	+0.07	+0.08	0.77		+3.3	+2.5	-	3341-12-10	1.1	0.59
C_{12} Benzene	0.5% Phenothiazine	+0.03	+0.10	+0.05	+0.11	+0.10	0.87		+1.8	+1.6	-	3341-13-13	1.0	0.32
Bis(dimethylbenzyl) Ether	1% Phenyl-alpha-Naphthylamine	-1.2	-0.20	-0.08	-32.8	-0.02	18.7		+86.5	+36.8	-	3341-13-15	11.5	0.79
Ucon DLB 144	2% Phenyl-alpha-Naphthylamine	+0.06	+0.11	+0.12	-0.10	+0.05	5.3		+12.0	-14.1	-	3341-13-16	4.1	4.8
Diisooctyl Terephthalate	5% Dibenzyl Selenide	-28.1	+0.02	-5.26	-2.43	+0.02	1.9		+1.7	+1.6	1.5	3341-19-1	-	-
C_{18}-C_{18} Toluene	0.5% Phenothiazine	+0.01	+0.03	+0.02	+0.02	+0.01	8.6		+26.7	+15.1	1.6	3341-19-3	2.8	0.44
Naphthenic White Oil	2% Didodecyl Selenide + 5% Tricresyl Phosphate	-0.59	+0.09	-39.2	+0.07	+0.08		3.6	+40.8	-	1.3	3341-20-1	-	-
Naphthenic White Oil	2% Phenyl-alpha-Naphthylamine + 5% Tricresyl Phosphate	+0.13	+0.08	+0.04	+0.06	+0.08		0.29	+0.7	-	1.2	3341-20-3	-	-
Naphthenic Pale Oil	2% Didodecyl Selenide + 5% Tricresyl Phosphate	-0.3	-0.01	-29.6	+0.13	+0.13		0.23	+49.7	-	-	3341-20-6	-	-
Diisooctyl Terephthalate	2% Didodecyl Selenide	-10.95	+0.03	-4.06	0	+0.01	0.48		+14.0	-7.40	-	3341-23-7	0.02	0.02
C_{12} Diphenyl Ether	2% p,p'-Dioctyldiphenylamine	-3.51	-0.22	0	-10.35	+0.01	2.0	-	+25.1	-	1.8	4606-39-5	-	-
C_{14} Diphenyl Ether	2% Paranox 441	-0.25	+0.01	+0.06	+0.29	+0.01	0.36	-	+6.3	-	1.6	4606-39-3	-	-
C_{12} Diphenyl Ether	2% Paranox 441	-0.19	+0.02	+0.02	+0.26	+0.0[illegible]	0.25	-	+7.0	-	1.0	4606-39-1	-	-

a. ASTM Method D 664.
b. F.S. VV-L-791e Method.
c. During test (72 hours at 347°F).

TABLE XLVII

OXYGEN ABSORPTION MEASUREMENTS ON LUBRICANT BLENDS

Temperature 340° F

Base Oil	Additives	Time to Absorb 1000 cc O_2/100 g Oil, Hours
C_{16-18} Biphenyl	2% Didodecyl Selenide	27.0
C_{16-18} Biphenyl	2% Dibenzyl Selenide	7.75
C_{16-18} Biphenyl	0.5% Phenothiazine	19.5
C_{16-18} Biphenyl	2% Phenyl-alpha-naphthylamine	15.25
C_{16-18} Biphenyl	2% Paranox 441	18.5
C_{16-18} Biphenyl, Distilled	2% Dibenzyl Selenide	1.85
Diisooctyl Terephthalate	2% Dibenzyl Selenide	5.5
Diisooctyl Terephthalate	0.5% Phenothiazine	19.5, 35.0
Ucon DLB 144E	2% Dibenzyl Selenide	3.5

4.5 Other Tests on Unirradiated Fluids

4.5.1 Lead Corrosion

Results of SOD lead corrosion tests performed are shown in Table XLVIII. Excessive corrosion was not encountered with any of the inhibitors used.

Table XLVIII

SOD Lead Corrosion Test Results
325° F, 1 Hour

Base Stock	Additive	Weight Loss, mg/sq in.
C_{16-18} Biphenyl	2% Didodecyl Selenide	1.2
C_{16-18} Biphenyl	2% Dibenzyl Selenide	0.4
C_{16-18} Biphenyl	0.5% Phenothiazine	0.5
C_{16-18} Biphenyl	2% Phenyl-alpha-Naphthylamine	0.3
C_{16-18} Biphenyl	2% Paranox 441	0.9
Ucon DLB 144E	2% Dibenzyl Selenide	2.1

4.5.2 Rubber Swell

Rubber swelling measurements were made with several of the new aromatic fluids. Results are shown in Table XLIX.

Table XLIX

Rubber Compatibility of
Alkyl Aromatics - 70 Hours at 250° F

	Rubber	Volume Change, %
C_{16-18} Biphenyl	H	+11.3
C_{16-18} Biphenyl	R	+120.7
C_{16-18} Biphenyl	MIL-R-7362	-4.3
C_{16-18} Biphenyl	MIL-P-5516A	+21.4
C_{16-18} Biphenyl	MIL-P-18017A	+10.4
C_{16-18} Biphenyl	Poly FBA[a]	-2.2
Diisooctyl Terephthalate	MIL-R-7362	+16.6
C_{12} Diphenyl Ether	MIL-P-18017A	+17.5
C_{14} Diphenyl Ether	MIL-P-18017A	+11.7
0-1A[b]	MIL-R-7362	+3.8
0-1A	MIL-P-5516A	+36.9
0-1A	MIL-P-18017A	+19.1
0-1A	Poly FBA[a]	+3.1

a. Linear 8210-70-X.
b. Base is alkylbenzene of approximately 250 m.w.

The alkyl aromatics caused more swelling than the petroleum base lubricants but less than the aliphatic diester lubricants. With a material such as C_{16-18} biphenyl, MIL-P-18017A rubbers would probably be satisfactory. This would also be true for materials of a high aromatic content such as dodecyl diphenyl ether and tetradecyl diphenyl ether. With diisooctyl terephthalate, the diester rubber MIL-R-7362 appeared suitable. This same rubber also would probably be usable with the lower molecular weight oil 0-1A.

On the basis of these swelling tests, selection of packings for use with the alkyl aromatic oils does not appear more difficult than for currently used lubricants.

4.6 Fluids Sent to Other Organizations for Tests

Because many of the types of base materials used in the gas turbine oil development were new, some work was required to determine whether they had unusual lubricity properties. Thus, samples of C_{16-18} biphenyl and diisooctyl terephthalate were sent to Southwest Research Institute for evaluation in "Ryder" type gear testing machines. Results are not yet available.

The possible use in jet engines of selenide inhibitors depends on their compatibility with bearing materials at high temperature. To determine to what extent existing bearings and other engine parts could tolerate this inhibitor, two samples of white oil were shipped to the Power Plant Laboratory at WADC for test work including operation in a J-57 engine. One sample contained a selenide while the other contained phenyl-alpha-naphthylamine. Tricresyl phosphate was added as an antiwear additive because of the questionable lubricity of white oils. Results are expected in the near future. The composition of these blends was as follows.

	53888-R	53889-R
Naphthenic White Oil, Wt. %	93	93
Tricresyl Phosphate	5	5
Didodecyl Selenide	2	-
Phenyl-alpha-Naphthylamine	-	2

Thirty gallons each of two similar experimental gas turbine lubricants were included for irradiation in the Systems Panel Irradiation Test No. 2 at Convair, Fort Worth. Extensive specification test work is anticipated with these to determine the effects of irradiation. The compositions of these fluids were as follows:

	G14809	G14810
Naphthenic White Oil, Wt. %	98	98
Didodecyl Selenide	2	-
Paranox 441	-	2
	100	100

4.7 Status of Gas Turbine Lubricant Development

The aliphatic diesters and polyglycol diethers are the base materials most suited for fluids to meet the nonirradiation Phase III requirements. However, they do not have acceptable radiation stability. This property can be improved by the use of selected additives, but the indicated ultimate solution for both the thermal and radiation stability problems is to use the more resistant aromatic base materials.

With both the aliphatic and aromatic base oils the dialkyl selenides are the most effective oxidation and radiolysis inhibitors. This inhibitor is unique in reducing coke deposits at 700°F in oils both before and after irradiation. However, the selenides give high corrosion of copper and silver in the specification oxidation and corrosion test. All data obtained on the most important base oils and formulations from these are summarized in this section.

Table L summarizes data on fluids based on a polyglycol diether. From this base material, a fluid might ultimately be formulated which could withstand the 10^9 r Phase III radiation requirement. It would be superior in this regard to an aliphatic diester base fluid. Table LI summarizes data on fluids from naphthenic white oil. Such a base might produce a fluid for use at a dosage of about 3×10^8 r. The ready availability of these materials makes them of continuing interest.

Of the radiation resistant materials synthesized, tetradecyl diphenyl ether has the best combination of physical properties. Table LII summarizes data on all the fluids made from this material. Radiation stability with this ether, reasoned from information on analogous compounds, is expected to be improved by a factor of 5 over that for the aliphatic compounds. Oxidation stability of the ether, with Paranox 441 as the inhibitor, approaches specification requirements. However, with this additive, 700°F coking was high.

Table LIII gives data on C_{16-18} biphenyl and Table LIV summarizes diisooctyl terephthalate information. The biphenyl has the better radiation stability of the two but low temperature properties are slightly poorer. The 700°F coking of the biphenyl derivative was lower than that of other aromatics tested. With selenide inhibitor, the biphenyl showed the reduction of coking following irradiation noted with other base oils. These three classes of aromatics, the biphenyl, diphenyl ether, and terephthalate derivates, appear the most promising for radiation resistant gas turbine lubricants.

4.8 Conclusions and Future Work

1. Conventional polyglycols and diesters, if suitably inhibited, show fair radiation resistance. The important coking properties of the polyglycols are less sensitive to radiation damage than are those of the diesters. Suitably inhibited polyglycols and diesters will undoubtedly have a range of usefulness as radiation resistant lubricants. This range may be 10^8 to 10^9 r. Future work should seek to define further the usefulness of these materials. Other conventional fluids such as phosphates, silicates, and pentaerithrytol esters should be abandoned for the gas turbine fluid application due to poor thermal and/or radiation stability.

TABLE [illegible]

SUMMARY OF DATA ON [illegible]

Additive, %[a]																					
Type	None	2 DDS		2 DBS	2 PAN	[illegible] PAN			[illegible] DPS			[illegible] SO		5 ZDDPP 2 DBS		[illegible] DBS		0.1 AAP 2 DBS		[illegible] SOLX 2 DBS	
1. Radiation Dosage, 10^8 r	0	[illegible]			[illegible]	0	1.[illegible][b]	[illegible].1[illegible][b]	0	0.4[illegible][c]	2.42[c]	0	[illegible][d]	0	[illegible].5[d]	0	[illegible][d]	0	[illegible][d]	0	[illegible][d]
2. Viscosity, cs																					
210°F	[illegible].18					7.42	8.04	Gel	[illegible].88	[illegible].7[illegible]	7.1[illegible]	7.27	4.5[illegible]	[illegible]	12.84	[illegible]	11.4[illegible]	[illegible]	17.[illegible]2	[illegible].72	1[illegible].4[illegible]
100°F	[illegible]					38.24	43.64	Gel	30.11	23.[illegible]4	32.1[illegible]	32.01	19.4[illegible]	[illegible].71	91.56	23.12	56.7[illegible]	[illegible]	11[illegible]	[illegible].71	1[illegible]1.[illegible]
0°F	[illegible]																				
-40°F	[illegible]																				
Viscosity Index	1[illegible]2																				
3. Pour Point, °F	-[illegible]																				
4. Flash Point, °F	4[illegible]																				
5. AIT, °F	[illegible]																				
6. Evaporation, % [illegible]-1/2 hours at [illegible]°F	1[illegible].1																				
7. Panel Coking, mg [illegible] hours at [illegible]°F		21[illegible]		[illegible]2	1[illegible]																
8. Oxidation-Corrosion [illegible]																					
72 hours at [illegible]°F																					
Wt. loss, mg/cm - Cu		-	-[illegible]		+[illegible].06																
Fe		+[illegible]	+[illegible].02		+[illegible].11																
Ag		-	-[illegible]		+[illegible].12																
Mg		+[illegible].07	+[illegible].2[illegible]		+[illegible].1[illegible]																
Al		+[illegible].0[illegible]	+[illegible]		+[illegible].05																
Neut. No. - Initial		[illegible]	1[illegible]		[illegible].3																
Final		[illegible].0[illegible]	[illegible]2.1		-																
Viscosity Change, %																					
210°F		-1[illegible]	-[illegible].1		-1[illegible]																
100°F		-[illegible]	-24.1		-12.[illegible]																
Evaporation, %		4.1	-																		
Insolubles																					
Pentane		[illegible]	-		4.5																
Benzene		0.80	-		4.6																
9. Oxygen Absorption, [illegible]°F Hours to absorb 1000 ml O_2/g Oil		3.5																			
10. Corrosion During Irradiation																					
At 80°F - Cu						-	nil	nil													
Fe						-	nil	nil													
11. Gas Evolved During Irradiation ml Gas/ml Oil										1.4	6.6										
Gas Constituents, %																					
Hydrogen											91.6										
Methane											6.3										
CO_2											0.3										
Propane											0.9										
Propene											0.[illegible]										
Butane											0.3										
											100.0										

a. Additive Code:
DDS - Didodecyl Selenide
DBS - Dibenzyl Selenide
PAN - Phenyl-alpha-naphthylamine
DPS - Diparaffin Sulfide
ZDDPP - Zinc Dialkyl Dithiophosphate
SO - Sulfurized Olefin
AAP - Amine Salt of Phosphoric Acid
SOLX - Santolube [illegible]

b. In 20-ml quantities in vented glass vials; MTR Canal Source.
c. In 10-ml quantities in 410 stainless steel capsules sealed under helium; MTR Canal Source.
d. In 52[illegible]-ml quantities in vented aluminum containers; MTR Canal Source.
e. Interpolated.

TABLE 11

SUMMARY OF DATA ON FLUIDS BASED ON NAPHTHENIC WHITE OIL

Additive,a % By Wt., Type Property or Test	None -	2% DDS 5% TCP	2% PAN 5% TCP	5% DDS			2% DDS 2% DBS	2% DDS 5% 704A 5% TCP
1. Radiation Dosage, 10^8 r	0	0	0	0	0.33b	3.3b	0	0
2. Viscosity, cs								
210°F	7.65			8.76	7.51	11.65		
100°F	74.51			78.31	67.35	131.7		
0°F	14,510							
-40°F	-							
Viscosity Index	63							
3. Pour Point, °F	-30							
4. Flash Point, °F	435							
5. SIT, °F	735							
6. Evaporation, % 6-1/2 hours at 400°F	10							
7. Panel Coking, mg								
8 hours at 700°F		1215	-				567, 1157, 823	2295
8 hours at 600°F		0	185				-	-
8. Oxidation and Corrosion								
Temperature, °F		347	347					
Time, hours		72	72					
Wt. Loss, mg/cm^2, Cu		-0.59	+0.13					
St		+0.08	+0.08					
Ag		-39.2	+0.04					
Mg		+0.07	+0.06					
Al		+0.08	+0.08					
Neut. No. D-664		-	-					
5105		3.6	0.29					
Viscosity Change, %								
100°F		+40.8	+6.7					
210°F		-						
Evaporation, %		1.3	1.2					
9. Corrosion During Irradiation								
At 80°F - Al				-	Pitted	Pitted		
St				-	Brown	Brown		

a. Additive Code:
DDS = Didodecyl Selenide
DBS = Dibenzyl Selenide
PAN = Phenyl-alpha-naphthylamine
TCP = Tricresyl Phosphate
704A = Acryloid 704

b. In 20-ml quantities in glass vials; MTR Canal Source.

TABLE LII

SUMMARY OF DATA ON FLUIDS BASED ON TETRADECYL DIPHENYL ETHER

Additive, % By Wt.	None	2% PAR[a]
1. Radiation Dosage, 10^8 r	0	0
2. Viscosity, cs		
At 400°F	1.12	
210°F	4.13	
100°F	22.26	
0°F	-	
-40°F	13,656	
Viscosity Index	93	
3. Pour Point, °F	-70	
4. Flash Point, °F	440	
5. SIT, °F	820	
6. Evaporation, % 6-1/2 hours at 400°F	24.2	
7. Vapor Pressure at 400°F, mm Hg	2.0	
8. Panel Coking, mg 4 hours at 700°F		368
9. Oxidation and Corrosion		
Temperature, °F		347
Time, hours		72
Wt. Loss, mg/cm^2, Cu		-0.25
Steel		+0.01
Ag		+0.06
Mg		+0.29
Al		+0.01
Neut. No. D-664		0.36
5105		-
Viscosity Change, %		
100°F		+6.3
210°F		-
Evaporation, %		1.6

a. Additive Code: PAR = Paranox 441.

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[illegible]

SUMMARY OF DATA [illegible]

BASED ON [illegible]

Additive[a], % wt. Type	None	PAN	PAN	PT	DDS	DPS	None	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
1. Radiation Dosage, 10⁸ r	0	0	0	0	0	0	0	0	0	0	[illegible]	[illegible]	[illegible]
2. Viscosity, cs													
210°F	7.08						5.27				[illegible]		
100°F	[illegible]						[illegible]				[illegible]		
0°F	[illegible]						[illegible]						
-40°F							[illegible]						
-65°F													
Viscosity Index	7[illegible]						[illegible]						
3. Pour Point, °F	-2[illegible]						-[illegible]						
4. Flash Point, °F	[illegible]						4[illegible]						
5. SIT, °F	[illegible]												
6. Evaporation, % 6-1/2 hours at 400°F	9.0												
7. Panel Coking, mg													
[illegible] hours at [illegible]°F [illegible] hours at [illegible]°F	680	186	455	382	819 [illegible]f		1042	144	263	173	[illegible]		
8. Oxidation-Corrosion [illegible] hours at [illegible]°F mg/cm² - Al		0	+0.02	-0.11 -0.2[illegible]	[illegible]	[illegible]				[illegible]	[illegible]		
St		-0.0[illegible]	-0.[illegible]	-0.2[illegible] +0.1[illegible]	[illegible]	[illegible]				[illegible]			
Cu		[illegible]	-0.[illegible]	[illegible] -0.11	[illegible]	[illegible]					[illegible]		
Ag		[illegible]	[illegible]	-0.[illegible]	[illegible]	[illegible]					[illegible]		
Mg		[illegible]	[illegible]	-0.2[illegible]	[illegible]	[illegible]				[illegible]			
Neut. No., D-[illegible]		2.[illegible]	3.[illegible]	4.[illegible]	[illegible]	[illegible]				1.1	2.[illegible]		
[illegible]		2.4[illegible]	2.[illegible]	1.2[illegible] 0.[illegible]	1.[illegible]	1.[illegible]				1.[illegible]	[illegible]		
Viscosity Change, % 210°F		+14.5	+15.[illegible]	+11.[illegible] +14.[illegible]	+1[illegible]	+3[illegible]				[illegible]	[illegible]		
100°F		+2[illegible]	+31.[illegible]	+21.[illegible] +[illegible]	[illegible]	[illegible]				[illegible]	[illegible]		
Evaporation, %			2.[illegible]	2.[illegible] 1.[illegible]	[illegible]	[illegible]				1.[illegible]	1.[illegible]		
Insolubles, % Pentane		[illegible]	[illegible]	[illegible]	-	[illegible]				[illegible]	[illegible]		
Benzene		[illegible]	[illegible]	0.[illegible] 0.[illegible]	-	[illegible]					[illegible]		
9. SOD Lead Corrosion [illegible]°F, 1 hour, mg/sq in.		0.0	0.[illegible]	0.5		0.6				1.2			
10. Shell Four-Ball Wear Scar in mm - [illegible] kg 10 kg 40 kg							0.46e 0.[illegible]0 0.84						
11. Rubber Swell [illegible] hours at 2[illegible]0°F Vol. Change, % H	+11.[illegible]												
R	+12[illegible]												
MIL-R-[illegible]2	-4.[illegible]												
MIL-P-[illegible]A	21.4												
MIL-P-1[illegible]A	10.4												
Poly FHA	-2.2												
12. Oxygen Absorption Time in hours to absorb 1[illegible] cc [illegible] oil at [illegible]°F		18.5	15.25	13.5	7.75					27.0			
13. Corrosion During Irradiation At [illegible]°F, mg/cm² - Al St											[illegible]		
14. Gas Evolved During Irradiation, ml gas/ml oil												1.4	2.1
Composition, %													
Hydrogen													[illegible]
Methane													[illegible]
CO₂													0.4
Ethane													0.8
Ethene													0.6
Propene													[illegible]
Butane													[illegible]
Butene													[illegible]

a. Additive Code:
DDS = Didodecyl Selenide
DPS = Diphenyl Selenide
PAN = Phenyl alpha-naphthylamine
PAR = Paranox 441
PT = Phenothiazine
[illegible] = Sulfurized Olefin
[illegible] = [illegible]ntoiate [illegible]

b. In 20-ml quantities in vented glass vials, MTR [illegible].

c. In 10-ml quantities in 410 stainless steel capsules, sealed under helium, MTR [illegible].

d. In [illegible] quantities in vented aluminum containers, [illegible].

e. Extrapolated.

f. [illegible] test.

g. [illegible] data.

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TABLE [illegible]

SUMMARY OF DATA ON

[illegible]

Additive, %, Type	None Literature[a]	New Laboratory Preparation [illegible]	New Barrel Preparation [illegible]	1 [illegible]	1 [illegible]	0.5 PT	2 [illegible]	3 [illegible]	2 ← DDS	5 →	[illegible]	[illegible]	0.1 ASP 2 DBS	
1. [illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible][c]	[illegible][c]	[illegible]	7.[illegible][d]	[illegible]	7.[illegible][d]
2. Viscosity, cs														
210°F	[illegible]	[illegible]	[illegible]					4.[illegible]	[illegible]	8.2[illegible]	4.8[illegible]	[illegible]	4.[illegible]	9.[illegible]
100°F	[illegible]	41.[illegible]	[illegible]					[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	20.[illegible]	72.[illegible]
0°F			1,[illegible]											
-40°F			[illegible]											
Viscosity Index	[illegible]	97	[illegible]											
3. Pour Point, °F	[illegible]	-	[illegible]											
4. Flash Point (Cleveland), °F	-	42[illegible]	4[illegible]											
5. AIT, °F			[illegible]											
6. Boiling Point, °F (at [illegible] microns)	[illegible]	-	-											
7. Refractive Index, n_D^{20}	-	1.[illegible]	1.[illegible]											
8. Density, 20°	-	0.[illegible]	[illegible]											
9. Specific Gravity, 60/60	[illegible]	-	-											
10. Lead Analysis, ppm	-	<1	<1											
11. Neut. No., mg of KOH/g	-	nil	[illegible]											
12. Sap. No., mg KOH/g ([illegible])	[illegible]	279	279.4											
13. Color	-	[illegible] Saybolt	3-1/2 ASTM											
14. Evaporation, % [illegible] hours at [illegible]°F		[illegible]												
15. Panel Coking, mg [illegible] hours at [illegible]°F			[illegible]	537		789								
16. Oxidation-Corrosion (MIL-L-[illegible]) 72 hours at [illegible]°F														
mg/cm² - Cu				-	-28.1		-10.95							
St				-0.05	+0.02		+0.03							
Ag				-	-5.26		-4.06							
Mg				+0.10	-2.43		0							
Al				+0.02	+0.02		+0.01							
Neut. No. D-974				6.8	1.9		0.48							
5104				5.74	-		-							
Viscosity Change, % 210°F				+22.7	+1.8		+7.40							
100°F				+43.6	+1.7		+14							
Evaporation, %				4.0	1.5		-							
17. Oxygen Absorption at 340°F Hours to absorb 1000 cc O_2/100 g Oil				5.5		19.5 35.0								
18. Rubber Swell, % 70 hours at 250°F Mil-R-7362			16.6											
19. Corrosion During Irradiation At 80°F - Al									nil	nil				
St									nil	nil				

a. P. V. Smith, R. G. Newberg, and D. J. Young, Ind. Eng. Chem., 42, 2576 (1950).
b. Additive Code:
DDS - Didodecyl Selenide
DBS - Dibenzyl Selenide
PT - Phenothiazine
SO - Sulfurized Olefin
ASP - Amine Salt of Phosphoric Acid
c. In 20-ml quantities in vented glass vials; MTR Canal Source.
d. In 625-ml quantities in vented aluminum containers; MTR Canal Source.
e. Interpolated.

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2. Alkyl aromatic materials have both good radiation and heat stability. Acceptable fluids for 10^9 r and higher should be possible from these materials. Therefore, emphasis on this type of compound should be continued in future work. The development should follow the course of formulation, testing of critical properties, reformulation, irradiation, and subsequent testing. Complete specification tests should be run progressively on formulations which continue to be promising. Specifically, the materials for extensive test work should include the following as well as new aromatics, e.g., diphenyl alkanes, developed from synthesis programs.

a. The C_{16-18} biphenyl which was shown to have good radiation stability.

b. Tetradecyl diphenyl ether which has the best physical properties of any aromatic prepared thus far.

c. Diisooctyl terephthalate which has the best radiation stability and best physical properties of any aromatic ester studied thus far.

3. Regarding inhibitors, the superiority of alkyl selenides as radiation damage and coking inhibitors was shown. The main disadvantage of these materials is their degree of compatibility with copper and silver bearing materials at high temperature. In most fluids systems, the selenides will increase radiation resistance by a factor that may be as great as two. Other inhibitors, such as phenolic and amine types, are not as effective as the selenides in imparting stability to radiation and/or oxidation. Further evaluation of inhibitors in alkyl aromatic systems will be required to obtain optimum stability to oxidation, radiation, and heat.

5. HYDRAULIC FLUIDS

(R. L. Peeler)

5.1 Requirements

The target specification for the radiation resistant hydraulic fluid is shown in Table LV. The Phase III, or final, fluid was essentially a MIL-H-8446 fluid but with an additional requirement of withstanding a radiation dosage of 50 x 10^8 r at 350°F. This final product was intended for operation between -65°F and 400°F. Two intermediate phases allowed a stepwise approach to the target properties. Thus, Phases I and II called for dosages of 5 and 10 x 10^8 r, respectively, with a corresponding reduction in viscosity and low temperature requirements.

The most restrictive aspect of the specification was considered to be the vapor pressure of 100 mm at 400°F on the irradiated oil. As organic liquids evolve gas during irradiation[1], some method of gas removal aboard ANP aircraft may be required. The final vapor pressure of the irradiated fluid will depend primarily on the effectiveness of this gas removal system. The viscosity limitations of the specification were also considered restrictive. The Phase III requirements could be met only by a few classes of synthetic lubricants, if a low vapor pressure at 400°F was to be maintained.

5.2 Tests on Unirradiated Fluids

5.2.1 Selection of Base Materials

The physical properties of several prospective base stocks are summarized in Table LVI in comparison with the contract requirements. The viscosity properties of several of the best of these are in Figure 19. Although the dimethyl silicones had excellent physical properties, their poor radiation stability[1] and unfavorable wear history eliminated them from further consideration. Methyl phenyl silicones, such as DC-703, were expected to show better radiation resistance than that of dimethyl silicones[1]. Chlorinated silicones were eliminated because of the general corrosivity of halogenated materials on irradiation[2].

[1] "Radiation Resistant Lubricants - Their Development and Status," (California Research-AEC Report No 7) TID 5186, June 30, 1954 (CONFIDENTIAL).

[2] "The Effects of Fission Radiations on Lubricants and Lubrication," (Final Report, California Research-NEPA Project) Report No. NEPA 1844, April 30, 1951. (SECRET)

TABLE LV

HYDRAULIC FLUID TARGET REQUIREMENTS

	Phase I		Phase II		Phase III	
	Original	Irradiated	Original	Irradiated	Original	Irradiated
1. Irradiation						
Dosage, 10^8 r	-	5	-	10	-	50
Temperature, °F		80		250		350
2. Viscosity, cs						
At -65°F, maximum	-	-	-	-	2500	Report
At -30°F, maximum	4000	20,000	4000	Report	(2500)^a	-
At 400°F, minimum	1.0	1.0	1.5	1.0	2.5	1.0
3. Pour Point, °F, maximum	-40	Report	-40	Report	-75 (-40)	-65 (-10)
4. Vapor Pressure, mm Hg at 400°F, maximum	100	Report	100	Report	100	100
5. Spontaneous Ignition Temperature, °F, minimum	500	Report	500	Report	700 (500)	500
6. Irradiation Stability						
Acid Number, maximum		5		5		5
Weight Change, mg/cm², maximum						
Copper		± 0.8		Report		± 0.4 (± 0.6)
Silver		± 0.8		Report		± 0.4 (± 0.6)
Steel		± 0.6		Report		± 0.4 (± 0.6)
Aluminum		± 0.6		Report		± 0.4 (± 0.6)
Sludge, %		Report		Report		None (0.5 max)
7. Oxidation-Corrosion, 48 hours, 0.5 l. air/hr at °F	250	250	400	400	400	400
Weight Change, mg/cm², maximum						
Copper	± 0.8	± 0.8	Report	Report	± 0.2	± 0.2 (± 0.4)
Silver	± 0.8	± 0.8	Report	Report	± 0.2	± 0.2 (± 0.4)
Steel	± 0.6	± 0.6	Report	Report	± 0.2	± 0.2 (± 0.4)
Aluminum	± 0.6	± 0.6	Report	Report	± 0.2	± 0.2 (± 0.4)
Viscosity at 400°F, cs, minimum	0.5	0.5	Report	Report	0.5	0.5
Pour Point, °F, maximum	0	0	Report	Report	-20	-20
8. Hydrolytic Stability						
"Coke Bottle" Test, 48 hours, 200°F	No sludge	Report	No sludge	Report	-	-
Pressure Bomb, 24 hours at 400°F with 0.5% water	-	-	-	-	No sludge	Report
9. Wear Test, piston pump, 100 hours at 100°F	Report	Report	Report	Report	MIL-H-8446	MIL-H-8446

a. ( ) indicate alternate minima.

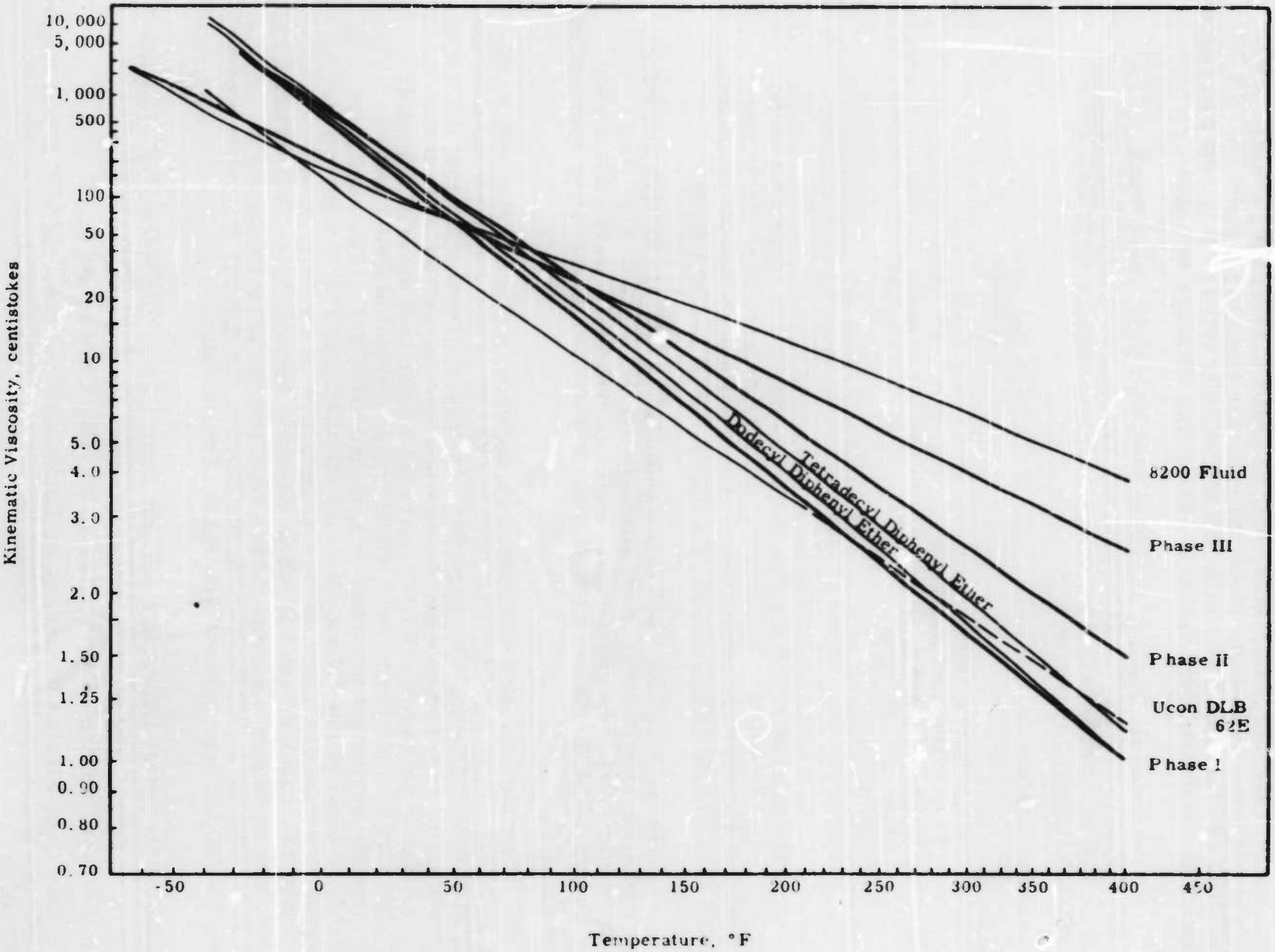

FIG. 19 - VISCOSITIES OF SEVERAL PROSPECTIVE HYDRAULIC FLUIDS

The available fluids which met the Phase III viscosity requirements were Oronite 8200 and 8515 Fluids, both of which were based on hexa(2-ethylbutoxy)disiloxane. The 8200 fluid had superior viscosity properties. The 8515 fluid was the 8200 fluid with 15% di(2-ethylhexyl) sebacate added to improve compatibility with synthetic rubbers. Pertinent data are in Table LVI.

A general purpose, radiation resistant fluid, identified as O-1A[1], was developed previously[2]. This material was based on mixed alkylbenzene (m. w. ~ 250) and had shown excellent radiation resistance up to 50 x 10^6 r. It had the following composition:

	Wt. %
Alkylbenzene 250	74.45
Poly-alpha-Methylstyrene	15.00
Polybutene 128	5.50
Didodecyl Selenide	5.00
Quinizarin	0.05
	100.00

The high pour point of +15° F for this fluid was due to the separation of the didodecyl selenide at low temperatures; the alkylbenzene base stock itself had good low temperature properties. Thermal stability was not optimum with the Alkylbenzene 250 because of a highly branched alkyl group.

Because earlier work had shown the polyglycols to have somewhat better radiation stability than most aliphatic synthetic lubricants[3], two commercially available Ucon fluids, DLB 62E and 144E, were included for investigation. The former met Phase I viscosities, while the latter approached Phase II.

Of the aromatic compounds synthesized in this contract effort, the alkyl diphenyl ethers had the best combination of viscosity and low temperature properties (see Table XXXVII, page 64). Dodecyl diphenyl ether met the 400° F viscosity requirements and closely approached the -30° F limit for Phase I. Vapor pressure at 400° F, although higher than those of currently used high temperature fluids, was within the specification limits and was approximately equivalent to that of MIL-O-5606 at 275° F. Decreasing the length of the alkyl group did not decrease the viscosity at low temperature markedly, because of the corresponding reduction in viscosity index (see Table XV, pages 20 and 21). The viscosity curves of the distilled octyl, dodecyl, and tetradecyl diphenyl ethers all appeared to rotate around a point at 10,000 cs at -40° F. For these reasons, the dodecyl derivative was chosen for further test work on this class of materials.

[1] "Radiation Resistant Lubricants - Their Development and Status," (California Research-AEC Report No. 7) TID 5186, June 30, 1954 (CONFIDENTIAL).

[2] By California Research Corporation under AEC Contract AT(11-1)-174.

[3] "The Effects of Fission Radiations on Lubricants and Lubrication," (Final Report, California Research-NEPA Project) Report No. NEPA 1844, April 30, 1951 (SECRET).

TABLE LVI

PROPERTIES OF PROSPECTIVE BASE STOCKS FOR HYDRAULIC FLUID USE

	Viscosity, Centistokes						Viscosity Index[c]	ASTM Pour Point, °F	Vapor Pressure At 400°F, mm Hg	Spontaneous Ignition Temperature, °F
	At -65°F	At -40°F[c]	At -30°F[c]	At 100°F	At 210°F[c]	At 400°F				
Requirements - Unirradiated										
Phase I	-	-	4000 max.	10.1	3.27	1.0 min.	80	-40 max.	100 max.	[illegible]00 min.
Phase II	-	-	4000 max	26.8	5.3	1.5 min.	145	-40 max.	100 max.	[illegible] min.
Phase III[a]	2500 max.	-	(2500)	26.2	7.6	2.5 min.	182	-75(-40) max.	100 max.	700(500) min.
Hexa(2-ethylbutoxy(disiloxane	719	-	-	11.17	4.00	1.6•	250	Below -100	1.0	720
7200 Fluid	2234	-	-	33.20	11.59	3.82	-	Below -100	1.0	720
9515 Fluid	2357	-	-	24.30	8.21	2.04	188	Below -100	1.0	720
Alkylbenzene[b]	-	-	1015	6.21	1.73	0.62•	-	Below -80	88.0	800
Fluid 0-1A	-	-	-	16.94	3.46	1.06•	83	+20	88.0	1000
Dow Corning 703 Fluid	-	-	45,249	25.63	5.47	1.6•	156	-40	0.9	940
Ucon DLB 62E	-	1200	610	10.86	3.18	1.15•	177	-80	-	
Ucon DLB 144E	-	16,550	7200	32.57	7.16	2.06•	162	-65	7.8	770
Dodecyl Diphenyl Ether	-	11,503	4800	18.47	3.57	1.00	70	-75	25.0	830
Tetradecyl Diphenyl Ether	-	15,556	6000	22.26	4.14	1.12	95	-70	2.0	820
10C Insulating Oil	-	-	850	8.20	2.17	0.77•	66	Below -80	51.0	720
Bis(dimethylbenzyl)ether	-	-	2000•	9.36	2.16	0.75•	8	-55	11.0	905
Dibutyl Phthalate	-	2028	-	9.64	2.29	0.77•	36	-75	18.1	790
Octadecylbenzene	-	-	200•	11.45	2.79	0.93•	95	-40	4.0	-

a. ( ) indicate alternate minima.
b. Mixed alkylbenzenes, molecular weight ca. 250.
c. Not a specification requirement.

• Extrapolated values.

A low viscosity naphthenic petroleum oil was also a possible base stock as were dibutyl phthalate and bis(dimethylbenzyl) ether, low viscosity commercially available materials. The use of these depended upon the availability of a suitable viscosity index improver. A long chain alkylbenzene completed the list from Table LVI (page 95). This material had the best physical properties of any of the alkylbenzenes prepared in the present effort (see Table XX, page 25 and XXII, 24).

5.2.2 Viscosity Index Improvers

Blends with a number of possible V.I. improvers in low viscosity base stocks were prepared to determine their thickening effectiveness. The data are shown in Table LVII. Previous work[1] had shown that the polymethacrylates were among the least radiation stable viscosity index improvers. Polybutenes were somewhat better, while polystyrenes were the most resistant.

The results show that polybutenes were sufficiently effective to meet Phase II viscosity requirements (excepting radiation). The polystyrenes (Piccolastic A-5) and poly-alpha-methylstyrenes (Dow Resin V-9) caused thickening of the fluid but did not improve V.I. An attempt to use the viscous liquid, bis(1, 1, 3, 3-tetramethylbutylphenyl) ether as a thickener resulted in some thickening but a pronounced viscosity index decrease.

Several experimental olefin polymers were also investigated as possible V.I. improvers. The polypropylenes were of interest as their structure was less highly branched than that of the polyisobutylenes. It was thought that this might produce improved radiation and thermal stability. The materials tested were the relatively low molecular weight, solvent extracted fractions from a synthesis of high molecular weight polymer. Relatively poor V.I. improvement was shown by the fractions tested. In addition, five of the polymers of highest molecular weight precipitated from solution after storage for one month at room temperature.

An experimental polymer bottoms from an attempted preparation of 1, 3-bis(4-biphenylyl)butane (see Section 2.5.4, page 28) was also tested. Although the material was soluble in the C_{16-18} biphenyl base stock, no V.I. improvement was obtained.

5.2.3 Stability Tests

The hydrolytic stability of the alkyl diphenyl ethers was of considerable interest because of the emphasis being placed on this type of compound as an unthickened hydraulic fluid base stock.

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[1] "Radiation Resistant Lubricants - Their Development and Status," (California Research-AEC Report No. 7) TID 5186, June 30, 1954 (CONFIDENTIAL)

TABLE LVII

VISCOSITY OF POLYMER-CONTAINING BLENDS

Base Stock	Wt. % Additive	Additive	Viscosity, cs At 100°F	Viscosity, cs At 210°F	Viscosity Index
10-C Insulating Oil	0		[illegible]	2.17	[illegible]
	5	Polybutene 128	15.42	3.195	116
	10	Polybutene 128	21.91	4.68	149
	15	Polybutene 128	35.29	6.75	145
	20	Polybutene 128	56.11	[illegible]	140
10-C Insulating Oil	5	Piccolastic A5	8.99	2.27	58
	10	Piccolastic A5	9.88	2.29	51
Dibutyl Phthalate	0		[illegible]	2.29	[illegible]
	5	Paratone	13.79	3.41	141
	10	Paratone	22.24	5.21	170
Dibutyl Phthalate	5	Piccolastic A5	10.82	2.44	30
	10	Piccolastic A5	12.20	2.59	21
	20	Piccolastic A5	15.79	2.98	11
Alkylbenzene 250[b]	0		6.21	1.73	-
	5	Dow Resin V-9	8.13	1.98	[illegible]
	10	Dow Resin V-9	12.56	2.63	19
Alkylbenzene 250	10	Polybutene 128	15.64	3.57	126
	15	Polybutene 128	28.15	5.47	141
	20	Polybutene 128	43.42	7.72	140
Alkylbenzene 250	5	Paratone	10.59	2.74	118
	10	Paratone	16.56	4.15	177
Alkylbenzene 250	5	Piccolastic A5	6.96	1.83	-
	10	Piccolastic A5	7.78	1.94	-
Alkylbenzene 250	15	Indopol H-300	15.87	3.40	95
	20	Indopol H-300	22.35	4.27	108
Alkylbenzene 250	5	Vistanex LM-MH	27.31	6.27	170
	10	Vistanex LM-MH	119.9	22.20	146
Alkylbenzene 250	25	Bis(1,1,3,3-tetramethylbutylphenyl) Ether	11.54	2.44	2
Bis(dimethylbenzyl) Ether	0	-	9.35	2.16	8
	25	Bis(1,1,3,3-tetramethylbutylphenyl) Ether	15.73	2.88	-14
Octadecylbenzene	0	-	11.42	2.79	95
	10	Polybutene 128	25.70	5.42	148
C_{16}-C_{18} Biphenyl	0	-	55.03	7.08	94
	5	Polypropylene 1	107.7	12.29	112[a]
	5	Polypropylene 2	175.7	18.85	121[a]
	10	Polypropylene 3	77.1	8.74	[illegible]
	5	Ethylene Propylene Copolymer	243.8	25.1	124[a]
	5	Ethylene-Butylene Copolymer	126.1	15.7	120[a]
	5	Poly-1-butene	118.8	14.3	122[a]
	5	Butadiene-Biphenyl Polymer	[illegible]	7.93	97

a. Precipitate on standing one month at room temperature.
b. M.W. ~ 250.

Results from a special test[1] are shown in Table LVIII.

Table LVIII

Hydrolytic Stability of Dodecyl Diphenyl Ether
20 Hours at 400°F, 6% Water

Insolubles, %	Nil
Copper Weight Change, mg/cm^2	-0.1
Appearance of Copper	Bright
Viscosity Change at 100°F, %	-0.7
Viscosity Change at 210°F, %	-0.1

Under the conditions used, there was no evident change in the dodecyl diphenyl ether. Thus, this type of compound had excellent stability at 400°F in the presence of water. It should meet the contract requirements in this regard.

Oxidation and corrosion tests under the MIL-H-8446 conditions were run on several fluids. Results are reported in Table LIX. Of the materials tested, DC 703 Fluid, dibutyl phthalate, 10-C Insulating Oil (petroleum oil), and dodecyl diphenyl ether appeared to be suitable for use as high temperature fluids as far as oxidation was concerned. The optimum compounding was not reached in the few tests made. Thus, several of the results were outside the MIL-H-8446 specification limits.

Difficulties encountered in the oxidation-corrosion tests were a tendency toward sludging of the petroleum oil and the failure of the Paranox 441 in the dodecyl diphenyl ether to prevent copper corrosion at 400°F. Further work on high temperature oxidation inhibitors should be performed, although the importance of this property is decreasing in newer high temperature hydraulic systems because of more careful design to exclude air.

5.3 Results of Irradiations

5.3.1 Physical Property Changes

Two series of irradiations (G-59 and G-60) were made to determine viscosity changes and rates of gas evolution from a series of compounded potential base stocks. Selenides were used almost exclusively to protect against oxidation and radiolysis. In view of the beneficial effects of the selenides, these combinations represent for the present the maximum capability of the base stocks.

---

[1] Ten ml of fluid was rotated at 5 rpm in a 22 ml Parr Peroxide Bomb for 20 hours at 400°F in the presence of 0.6 ml water and a 1/4 x 1/2 inch copper strip. The bombs exposed a 94% nickel surface and a copper gasket to the fluid.

TABLE LIX

RESULTS OF OXIDATION-CORROSION TESTS

72 Hours at 400°F - 5 l. air/hour

Fluid	% Additive	Sample No.	Metal Corrosion, mg/cm²					% Viscosity Change at		Neutralization Number mg KOH/gram	Insolubles, %	
			Al	Fe	Cu	Ag	Mg	100°F	210°F		Pentane	Benzene
DC 703	1 Phenyl-alpha-Naphthylamine	3341-13-14	-0.03	-0.03	-0.02	+0.02	-	-	-	-	-	-
Dibutyl Phthalate	0.5 Pheno-thiazine	3341-13-17	+0.25	+0.17	-0.12	+0.06	-	-	-	-	-	-
DC 703	5 Didodecyl Selenide	3341-23-4	-0.22	-0.02	-	-	+0.08	+25.8	+13.9	1.6	-	-
10-C Insulating Oil	5 Didodecyl Selenide	3341-23-5	+0.57	+0.70	-	-	+1.12	+13.8	+5.0	2.6	4.80	2.10
Dodecyl Diphenyl Ether	2 Paranox 441	4699-17-1	+0.09	+0.12	-4.54	+0.15						

The exposures were carried out at 250° F on about 10 ml of liquid in sealed capsules of 410 stainless steel[1]. The capsules were purged of air and refilled with helium prior to sealing. Irradiations were made in the MTR canal gamma source. Viscosity change was measured on the liquid remaining in the capsule following irradiation. The increase in pressure in the capsules was measured. In several cases, the evolved gas was saved and analyzed by mass spectrometry to determine its nature. The results of these irradiations are shown in Tables LX (silicon-containing compounds) and Table LXI (hydrocarbons).

Data from Table LX show OS-45-1, a selenide inhibited silicate, to change less in viscosity than either the 8200 or 8515 Fluids. Changes for the latter two fluids did not become important until 1-2 x 10^8 r was reached. MIL-O-5606 showed a large viscosity decrease at a relatively low dosage which is characteristic of radiolysis of materials containing polymer thickeners. Fluid 0-1.5A (a more highly thickened version of the O-1A described on page 94) showed a similar but less marked loss. In hexa(2-ethylbutoxy)disiloxane, didodecyl selenide and dibenzyl selenide reduced the viscosity change from that of the disiloxane base stock or that of the base compounded with p, p'-dioctyldiphenylamine. In one case, the blend containing didodecyl selenide was solid at the end of the test. The reason is not clear, although contamination with water during some stage of the filling or testing operation is a possibility. The viscosity stability of DC 703 Fluid was greatly improved by the addition of the selenide inhibitor. Another high V.I. silicone, F-4209, suffered an extremely large loss of viscosity, presumably due to rapid depolymerization of a high molecular weight fraction of the fluid.

Data from Table LXI show Ucon DLB 144E, 10-C Insulating Oil, and decalin, all inhibited with didodecyl selenide, to have good viscosity stability at the 3 x 10^8 r level. However, by far the best stability was shown by the aromatic materials: C_{16-18} biphenyl, octylbiphenyl and tetralin inhibited with didodecyl selenide. With these three compounds the change was less than 5% at the highest dosage (approximately 3 x 10^8 r). This is shown graphically in Figure 20.

Data from Table LXI on the stability of blends of polymeric V.I. improvers in octylbiphenyl have been plotted in Figure 21. The dotted portions of the curves were drawn on the basis of past experience which is described in Appendix IX. Of the three additives investigated, the polymethacrylate (Acryloid HF-855) decomposed most rapidly, the rate of viscosity loss being roughly equivalent to that shown by MIL-O-5606 fluid. The depolymerization begins at a low dosage and the viscosity decreases almost to that of the base oil. The polybutene blend was more stable. Even at 3 x 10^8 r only 12% of its initial viscosity was lost. This may be an acceptable amount for some applications. The poly(alpha-methylstyrene) [Dow Resin V-9] was very stable to radiation as far as viscosity change was concerned.

Gas evolution data for the fluids of major interest are in Figure 22. The values at and below 1 ml/ml should be taken as indicative only, as the over-all accuracy of the measuring equipment results in an error

[1] N. P. Shiells, R. O. Bolt, and J. G. Carroll, "Safe Containers Hold Organics for Irradiations," Nucleonics, 14, No. 8, p. 54-57, August 1956.

TABLE LX

IRRADIATIONS OF SILICON CONTAINING HYDRAULIC FLUIDS

Base Oil	Additive	Gamma[a] Dosage, 10^8 r	Appearance After Irradiation		Viscosity, Centistokes		Gas Evolution ml Gas/ ml Oil	Index of Damage[b]		Reference
			Oil	Capsule	100°F	210°F		T_{10}	η_{10}	
8200 Fluid	-	0	-	-	31.58	11.02	-	222	10.0	G-14496
		0.22	OK	OK	30.79	10.62	1.0		9.9	G-59-2
		0.34	OK	OK	29.86	10.14	2.0		9.4	G-59-11
		1.18	OK	OK	30.24	9.953	5.9		9.0	G-60-2
		3.00	OK	OK	48.09	14.68	12.0		13.4	G-60-11
8515 Fluid	-	0	-	-	23.78	8.039	-	182	10.0	G-14224
		0.22	OK	OK	23.78	7.966	1.0		9.9	G-59-1
		0.34	OK	OK	23.37	7.712	2.0		9.7	G-59-10
		1.18	Lt. Floc Ppt.	Dark Coat	25.68	7.723	6.6		9.9	G-60-1
		3.00	OK	OK	33.97	9.635	15.0		12.6	G-60-10
OS-45-1	-	0	-	-	12.21	3.951	-	114	10.0	G-14357
		0.22	OK	OK	10.32	3.211	0.7		8.5	G-59-3
		0.34	OK	OK	9.681	2.969	1.8		8.0	G-59-12
		1.18	OK	OK	10.56	3.100	5.5		8.6	G-60-3
		3.00	OK	OK	13.58	3.875	14.5		11.0	G-60-12
Hexa(2-ethylbutoxy)disiloxane	-	0	-	-	11.17	3.999	-	108	10.0	DG-1231
		0.33	Contains H_2O	Rusted	11.93	3.788	3.0		10.5	G-59-13
		3.44	OK	OK	26.72	8.110	13.0		25.8	G-60-13
	5% Didodecyl Selenide	0	-	-	10.71	3.769	-	105	10.0	G-22-11
		0.28	OK	Rusted	10.63	3.687	1.0		9.9	G-59-4
		1.83	Gel	Black Coat	-	-	7.0		-	G-60-4
	5% Dibenzyl Selenide	0	-	-	10.22	3.249	-	101	10.0	3341-24-1
		0.28	OK	OK	10.29	3.622	1.0		10.1	G-59-5
		1.83	OK	OK	12.10	4.156	5.5		12.0	G-60-5
	5% p,p'-Dioctyldiphenylamine	0	-	-	12.46	4.071	-	116	10.0	3341-24-2
		0.28	Few Specs	OK	12.89	4.161	1.4		10.4	G-59-6
		1.83	OK	OK	18.13	5.414	7.8		19.4	G-60-6
DCF-4209	-	0	-	-	72.55	30.05	-	437	10.0	
		0.30	Light Haze	OK	8.317	3.573	2.0		1.4	G-59-18
		4.75	OK	OK	11.28	4.026	18.0		1.4	G-60-18
DC 703 Fluid	-	0	-	-	25.63	5.467	-	157	10.0	G-14178
		0.30	OK	OK	31.02	6.399	0.7		12.0	G-59-16
		4.75	OK	OK	145.0	24.54	1.0		49.5	G-60-16
	5% Didodecyl Selenide	0	-	-	22.52	5.061	-	150	10.0	3341-22-13
		0.30	OK	OK	22.48	5.035	0.3		10.0	G-59-17
		4.75	OK	OK	26.03	5.539	1.4		11.3	G-60-17

a. MTR canal gamma source at 80°F in 410 stainless steel capsules sealed under helium.

b. η_1 (η_{10}) is the viscosity in centistokes of an irradiated fluid at that temperature T_1 (T_{1c}) in degrees F at which the original fluid is one centistoke.

TABLE LXI

IRRADIATIONS OF HYLROCARBON-TYPE HYDRAULIC FLUIDS

Base Oil	Additive	Gamma[a] Dosage, 10^8 r	Appearance After Irradiation		Viscosity, Centistokes		Gas Evolution ml Gas/ ml Oil	Index of Damage[b]				Reference
			Oil	Capsule	100°F	210°F		T_1	η_1	T_{10}	η_{10}	
MIL-O-5606		0	-	-	14.23	5.10	-			131	10.0	DG-1008
		0.33	OK	OK	6.320	2.155	2.0				4.3	G-59-14
		3.44	OK	OK	6.436	1.965	13.0				4.1	G-60-14
Ucon DLB 144E	5% Didodecyl Selenide	0	-	-	30.11	6.881	-			174	10.0	3341-22-12
		0.32	OK	OK	29.64	6.777	1.4				9.7	G-59-9
		2.42	OK	OK	32.16	7.156	6.6				10.5	G-60-9
10-C Insulating Oil	5% Didodecyl Selenide	0	-	-	10.26	2.711	-	382	1.00	102	10.0	3341-16-10
		0.33	OK	OK	8.786	2.309	1.4		0.87		8.5	G-59-15
		3.44	OK	OK	10.16	2.514	14.6		0.93		9.8	G-60-15
0-1.5 A[c]	-	0	-	-	25.83	4.42	-			148	10.0	2594-42
		0.32	OK	OK	23.74	4.115	1.0				9.4	G-59-7
		2.42	OK	OK	18.21	3.319	2.0				7.3	G-60-7
C_{18-18} Biphenyl	5% Didodecyl Selenide	0	-	-	34.98	5.384	-			163	10.0	3341-22-1
		0.32	OK	OK	34.88	5.353	1.4				10.0	G-59-8
		2.42	OK	-	36.69	5.556	2.1				10.6	G-60-8
Octylbiphenyl	5% Didodecyl Selenide	0	-	-	17.30	3.100	-			126	10.0	3341-24-3
		0.25	OK	OK	16.86	3.023	0.7				9.7	G-59-19
		3.26	OK	OK	17.16	3.073	1.1				9.9	G-60-19
	5% Didodecyl Selenide + 5% Low Resin V-9[d]	0	-	-	19.43	3.261		383	1.00	131	10.0	3341-24-5
		0.20	OK	OK	19.29	3.245	0.7		0.99		9.9	G-59-22
		2.85	OK	OK	19.38	3.262	1.4		1.00		10.0	G-60-22
	5% Didodecyl Selenide + 10% Acryloid AP-855	0	-	-	48.35	8.666	-			197	10.0	3341-24-6
		0.20	OK	OK	31.50	5.645	0.7				6.6	G-59-23
		2.85	OK	OK	21.64	3.881	-				4.5	G-60-23
	5% Didodecyl Selenide + 5% Polybutene 128	0	-	-	26.29	4.375	-			148	10.0	3341-24-7
		0.20	OK	OK	25.07	4.175	0.7				9.5	G-59-24
		2.85	OK	OK	23.20	3.912	1.4				8.8	G-60-24
Tetralin	5% Didodecyl Selenide	0	-	-	1.840	0.8567	-	182	1.00			3341-24-4
		0.25	OK	OK	1.795	0.8315	0.3		0.98			G-59-20
		3.26	OK	OK	1.835	0.8385	2.5		0.99			G-60-20
Decalin	5% Didodecyl Selenide	0	-	-	2.247	1.016	-	212	1.00			3341-24-8
		0.25	OK	OK	2.224	0.935	1.8		0.93			G-59-21
		3.26	OK	OK	2.400	1.049	11		1.03			G-60-21

a. MTR canal gamma source at 80°F in 410 stainless steel capsules sealed under helium.

b. η_1 (η_{10}) is the viscosity in centistokes of an irradiated fluid at that temperature T_1 (T_{10}) in degrees F at which the original fluid is one centistoke.

c. 0-1.5A Composition [developed on AEC Contract AT(11-1)-174]:

66.2	Alkylbenzene (M.W. 250)
21.8	Poly(alpha-methylstyrene)
7.0	Polybutene 128
4.95	Didodecyl Selenide
0.05	Quinizarin

d. Poly(alpha-methylstyrene).

(See Tables LX and LXI)

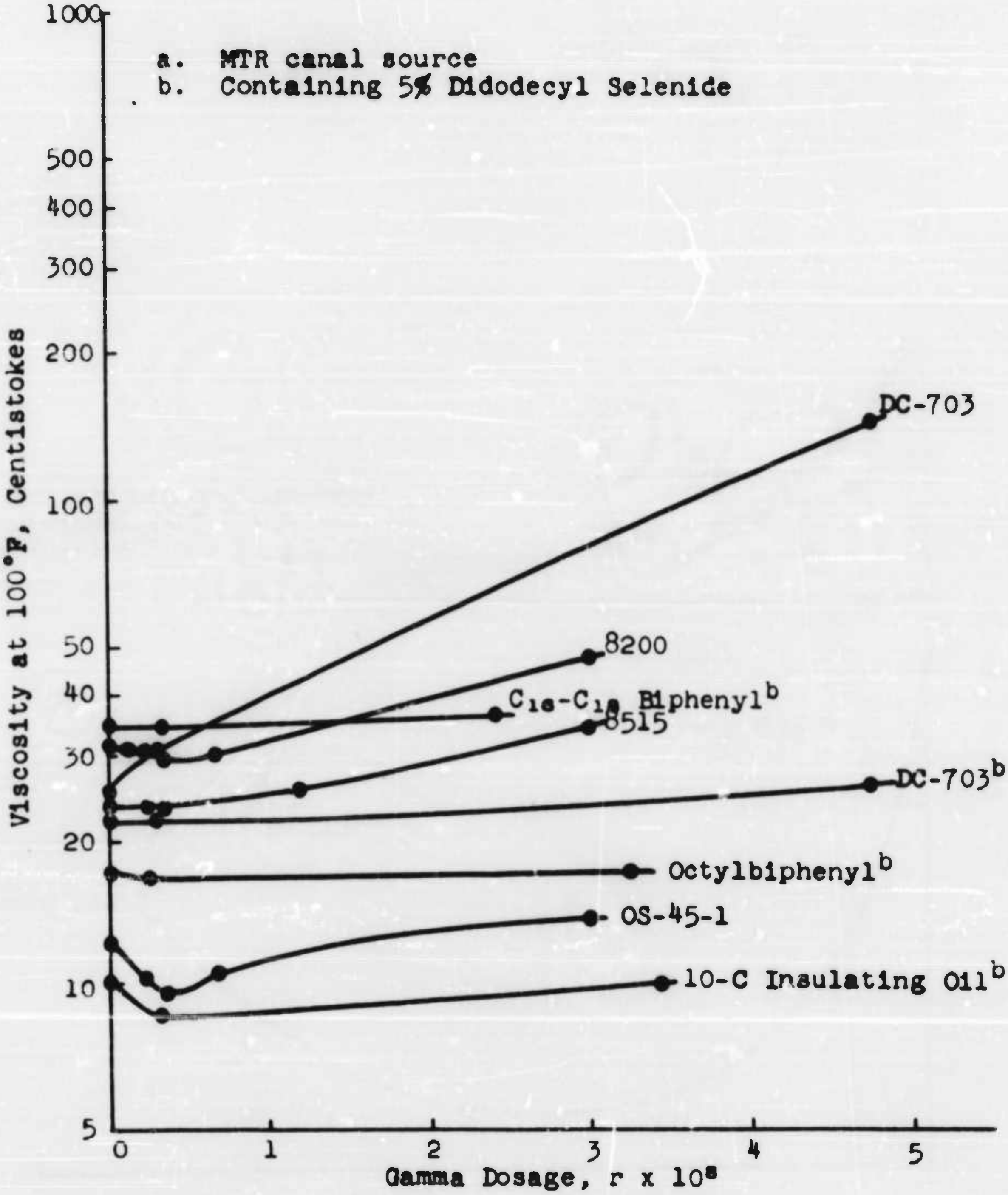


FIG. 20 - VISCOSITY CHANGE OF HYDRAULIC FLUIDS ON IRRADIATION[a]

(See Tables XL and XLI, pages 101 and 102)

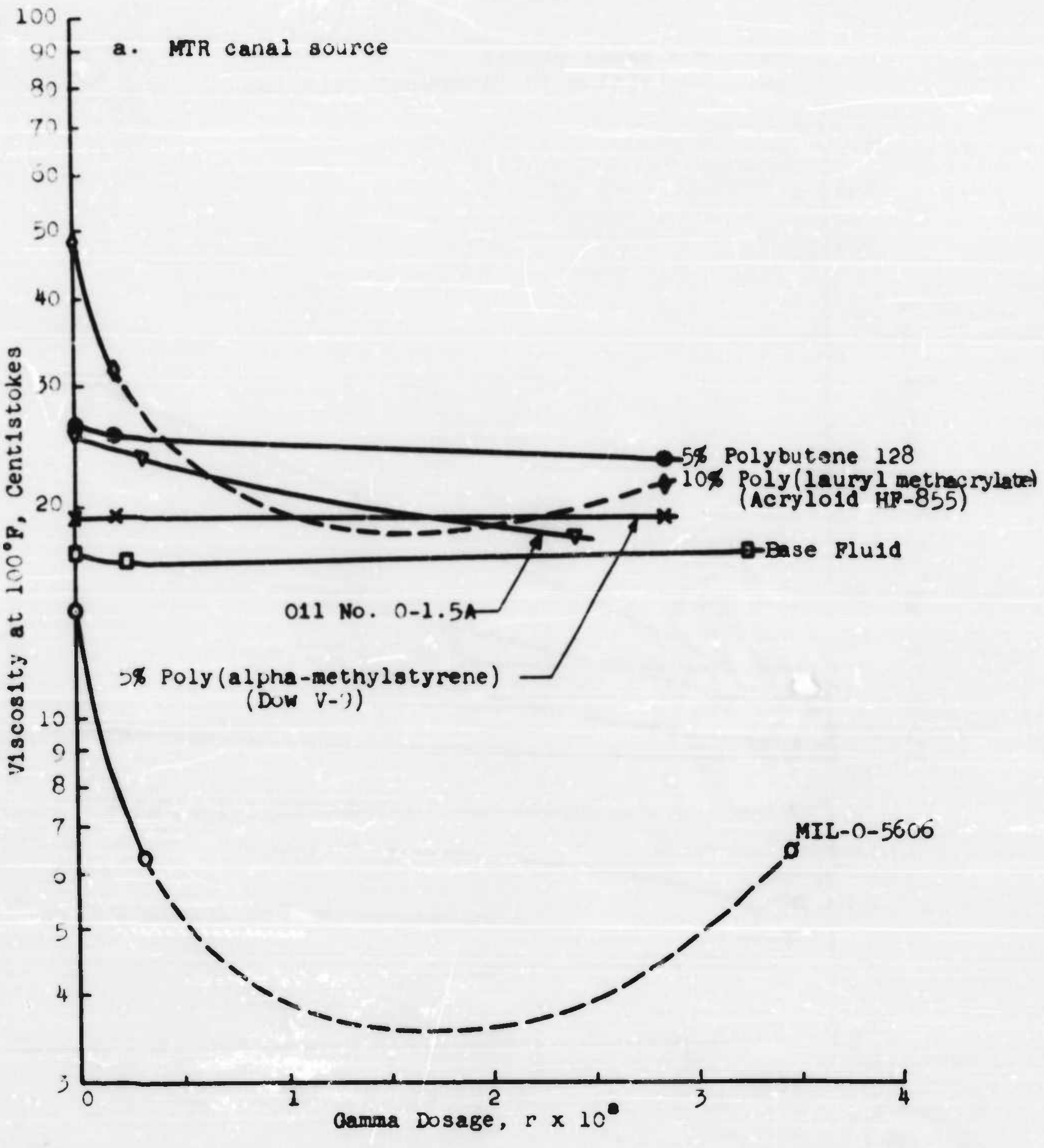


FIG.21 - EFFECTS OF IRRADIATION[a] ON VISCOSITY INDEX IMPROVERS IN OCTYLBIPHENYL

(See Tables XL and XLI, pages 101 and 102)

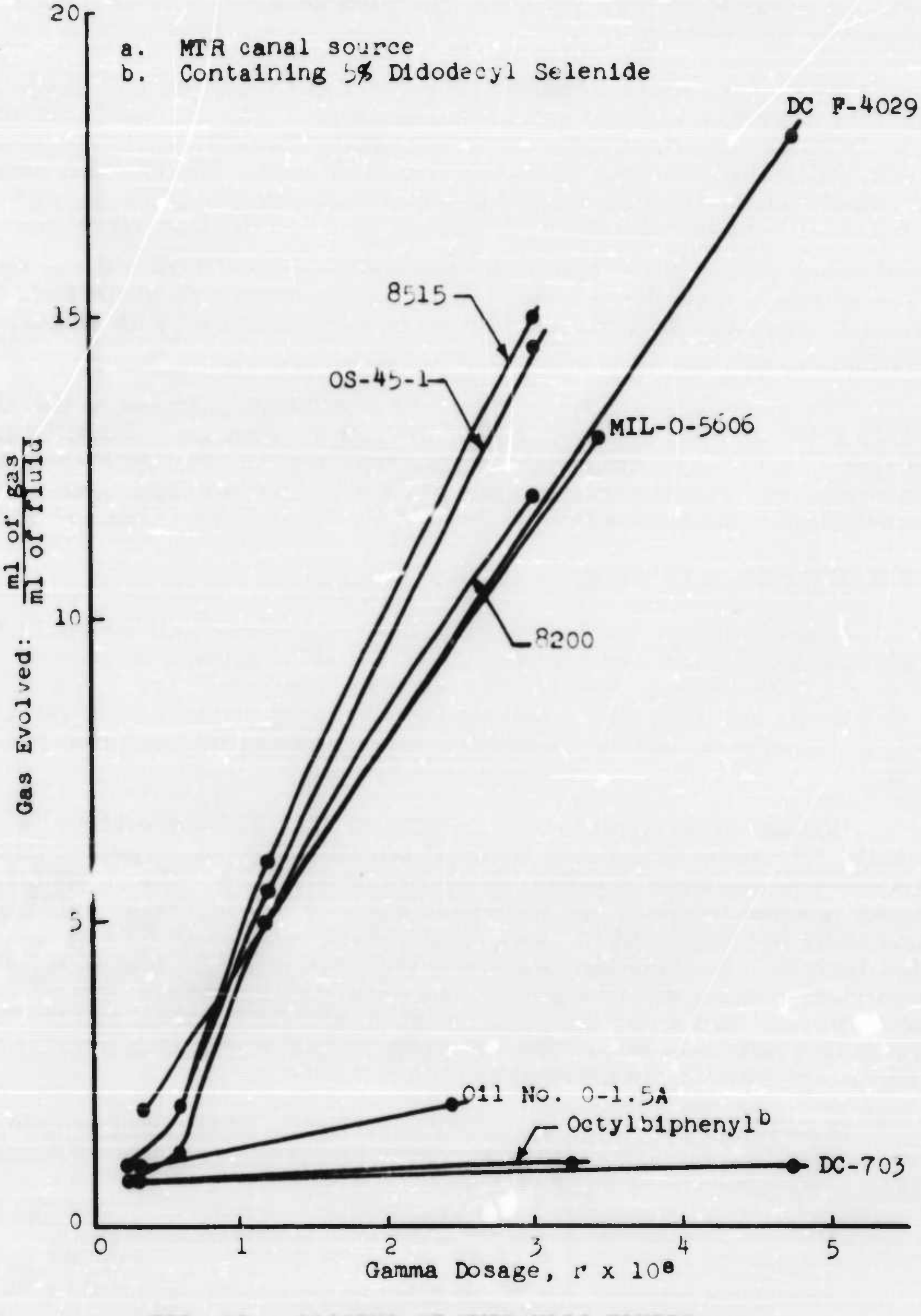


FIG. 22 - GASSING OF HYDRAULIC FLUIDS ON IRRADIATION[a]

of about + 0.5 ml of gas/ml of fluid. Both the petroleum and silicate base hydraulic fluids had about the same rate of gas evolution, about 1 ml gas/ml fluid/ 2×10^7 r. The 8200, 8515, and OS-45-1 Fluids were approximately equivalent. For these three fluids, at four different radiation dosages, gas evolution increased almost linearly with dosage.

Most of the other aliphatic fluids of Tables LX and LXI (page 101 and page 102) were in a similar gas evolution range. Thus, hexa(2-ethylbutoxy)-disiloxane (with or without inhibitors), Dow Corning F-4209, 10-C Insulating Oil and decalin evolved gas at approximately the same rate. On the other hand, the aromatic materials showed less gassing than the aliphatics. The 0-1.5A Fluid, C_{16-18} biphenyl, and tetralin all evolved less than one-fifth as much gas. Thus, molecules composed of about 40% aromatic carbons reduced gas evolution by a factor of five. A further increase in aromatic content to about 60%, as in octylbiphenyl, produced a further reduction in gas evolution by an additional factor of two.

The gases evolved from six of the irradiated samples at the highest dosage ($3\text{-}5 \times 10^8$ r) were analyzed by the mass spectrometer. Results are shown in Table LXII. After subtraction of the helium charge of the capsules and the oxygen and nitrogen which were probably air contamination, hydrogen was the major constituent. Methane was significant only for 0-1.5A (13%) and F-4209 (69%).

5.3.2 Changes in Other Specification Properties

In preparation for hydraulic pump runs, three gallons each of 8200 Fluid and 0-1A Fluid were irradiated in the MTR gamma facility at ambient temperature (about 80°F). The dosages received were 7.8×10^8 r (Series G-61) and about 5×10^8 r (Series G-61A), respectively. No attempt was made to exclude air during these irradiations and some oxidation probably occurred.

Results of the tests on the irradiated 8200 Fluid are given in Table LXIII. The most noticeable physical effects were the large reduction in flash point and increase in vapor pressure and viscosity. Surprisingly, the spontaneous ignition temperature increased also. The hydrolytic stability decreased as measured by the "coke bottle" test, particularly with regard to the insolubles formed. In oxidation and corrosion tests at 347°F and 400°F the most prominant results were large viscosity decreases, copper corrosion at both temperatures, and a coating on magnesium at 347°F. Although the percentage decrease in viscosity was large, the viscosity at 210°F was still greater than that of the unirradiated fluid prior to the test.

In order to check the viscosity equilibrium of irradiated 8200 Fluid, viscosity determinations were repeated on the sample described in Table LXIII. Results are in Table LXIV.

TABLE LXII

MASS SPECTROMETRIC ANALYSES OF GAS EVOLVED FROM IRRADIATED SAMPLES

	MLO-8200	MIL-O-5606	0-1.5A	Dow Corning F-4290	Ucon DLB 144E [a]	C_{16-18} Biphenyl [a]
Fluid Analysis, % by Vol.						
Nitrogen	41.9	6.8	70.7	1.2	8.2	15.9
Oxygen	10.5	1.1	18.1	0.1	0.1	0.1
Helium	7.8	9.2	3.5	8.7	14.0	37.2
Hydrogen	33.3	75.6	5.6	21.7	64.7	44.9
Methane	1.1	-	1.0	62.2	4.4	0.7
Carbon Monoxide	3.3	3.1	0.5	-	-	-
Carbon Dioxide	0.1	1.1	0.1	0.1	0.2	0.2
Ethane	1.6	0.4	0.2	5.9	-	0.4
Ethene	-	0.1	-	-	-	0.3
Propane	-	-	0.2	-	0.6	-
Propene	-	0.1	0.1	-	0.4	0.1
Butane	0.2	0.1	-	0.2	0.2	0.1
Butene	-	-	-	-	-	0.1
Pentane	0.2	-	-	-	-	-
Gas as % of Air- and Helium-Free Fraction						
Hydrogen	83.6	91.2	72.7	24.1	83.4	96.0
Methane	2.8	-	13.0	69.1	5.7	1.5

a. Contains 5% didodecyl selenide.

TABLE LXIII

PROPERTIES OF ORIGINAL AND IRRADIATED[a] 8200 FLUID

Property	Original		After 7.8×10^8 2	
1. Flash, COC, °F	415		115	
2. Fire, COC, °F	455		295	
3. Viscosity, cs				
At -65°F	2234		47,363	
At -40°F	-		9,680	
At 100°F	33.29		131.6	
At 210°F	11.59		37.15	
4. Neutralization Number	0.01		0.08	
5. Pour Point, °F	Below -80		Below -80	
6. Bromine Number	1		5.6	
7. Temperature for Vapor Pressure of 1 mm, °F	400		150	
8. Spontaneous Ignition Temp., ASTM D 286, °F	720		840	
9. Hydrolytic Stability, 200°F				
Copper Weight Change, mg/cm^2	-0.03		0, +0.06	
Viscosity Change at 100°F, %	+2.1		+26.1, +30,1	
Viscosity Change at 210°F, %	+1.0		-8.9, -15.4	
Insolubles, %	0.05		0.36, 1.33	
Neutralization Number	0.10		0.02, 0.30	
10. Rubber Swell, Rubber R,			-	
70 hours at 250°F, %	+7.7		+6.0	
11. Oxidation and Corrosion, 72 hours at °F	347	400	347	400
Metal Weight Change, mg/cm^2				
Aluminum	0	-0.02	+0.10	-0.08
Magnesium	0.03	-	+1.52	-
Steel	0	-0.05	+0.06	+0.04
Copper Strip	+0.5	+0.04	-2.06	-0.88
Silver	0	-0.04	+0.06	-0.14
Neutralization No.	0.47	0.50	2.7	1.2
Viscosity at 100°F, cs	-	-	72.22	81.10
Viscosity Change, %	+8.0	-20.0	-45.1	-38.4
Viscosity at 210°F, cs	-	-	12.05	14.18
Viscosity Change, %	+6.5	-28.0	-67.7	-61.18

a. MTR Canal Gamma Source.

Table LXIV

Viscosity Change With Time For Irradiated 8200 Fluid

Viscosity Measured	Viscosity, cs, at 100°F	210°F
July 18, 1956	131.6	37.15
September 6, 1956	146.8	37.29
Per Cent Change	+11.6	+0.4

The observed change at 100°F is significant. This effect has been noted in some previous experiments and pertinent data are given in Appendix X. In general this past work showed the more effective the oxidation inhibitor used, the smaller the viscosity increase after irradiation.

. Properties of the sample of 0-1A Fluid irradiated under conditions similar to those for the 8200 Fluid are given in Table LXV.

Table LXV

Properties of Original and Irradiated[a] 0-1A Fluid

Property	Original	After 5 x 10^8 r
Flash, COC, °F	260	150
Fire, COC, °F	280	175
Viscosity, cs		
At 100°F	16.94	13.16
At 210°F	3.46	2.76
Viscosity Index	83	34
Pour Point, °F	+20	-35
Neutralization Number	0.01	0.02
Evaporation, D 972, 22 Hours at 210°F	32	32
Vapor Pressure, mm at 400°F	88	115
Spontaneous Ignition Temp., °F	1000	930

[a] MTR Canal Gamma Source.

Considerable volatile material was also formed with this fluid, as shown by the reduction in flash point and increase in volatility. The V.I. improver apparently broke down faster than the relatively stable base stock polymerized. As a result the viscosity did not change markedly. However, there was a considerable decrease in V.I. As is typical of blends containing large amounts of didodecyl selenide, a large reduction in pour point occurred following irradiation.

5.4 Pump Tests (S. R. Calish)

5.4.1 Procedures

Figure 23 shows the principal features of the hydraulic pump test stand used for evaluation of potential hydraulic fluids. It was constructed to accommodate either the Vickers PF-3911 type pump or the New York Air Brake Model 66WA300. The work to date has been with the latter type because delivery was earlier with this model.

Tests on original and irradiated fluids were performed following a calibration run with MIL-O-5606 type oil. The Model 66WA300 pumps will be run at constant delivery with the bypasses blocked by a socket screw. Tests were generally for 150 hours at 160°F, followed by 100 hours at 275°F. Parts were inspected and weighed at the start, at 150 hours, and at 250 hours. If anything unusual occurred, interim inspections were also made.

5.4.2 Unirradiated 8200 Fluid

This fluid was selected for initial tests because of the background of experience available with it and because it complies with most of the specified requirements before irradiation. The properties of original and irradiated 8200 fluid are in Table LXIII (page 108).

The Model 66WA300 pump was run on unirradiated 8200 fluid for 150 hours at 160°F, followed by an additional 90 hours at 275°F. At this point, a piece of rubber lined, fabric covered hose, employed as the pump suction, split causing the fluid to leak from the system. The low pressure cut-off failed to function, and some of the pistons seized due to loss of oil. The spline drive sheared, and the run terminated. Up to this point all operation was normal. The pressure and flow rate were readily maintained. Pump efficiency was essentially constant. As nothing abnormal occurred prior to the failure, no photographs were taken of this run.

Following the loss of oil, the pump was inspected. Seizure of three pistons was noted; but, other than scuffing of the pistons and some deposition of metal, no abnormal wear was apparent. The change in viscosity with time during the entire 240 hours of pump operation on 8200 fluid is shown in Figure 24. Viscosity at 210°F decreased from about 11 cs to 6.3 cs. The change was appreciable during the first 75 hours of operation and proceeded at a considerably reduced rate from there on.

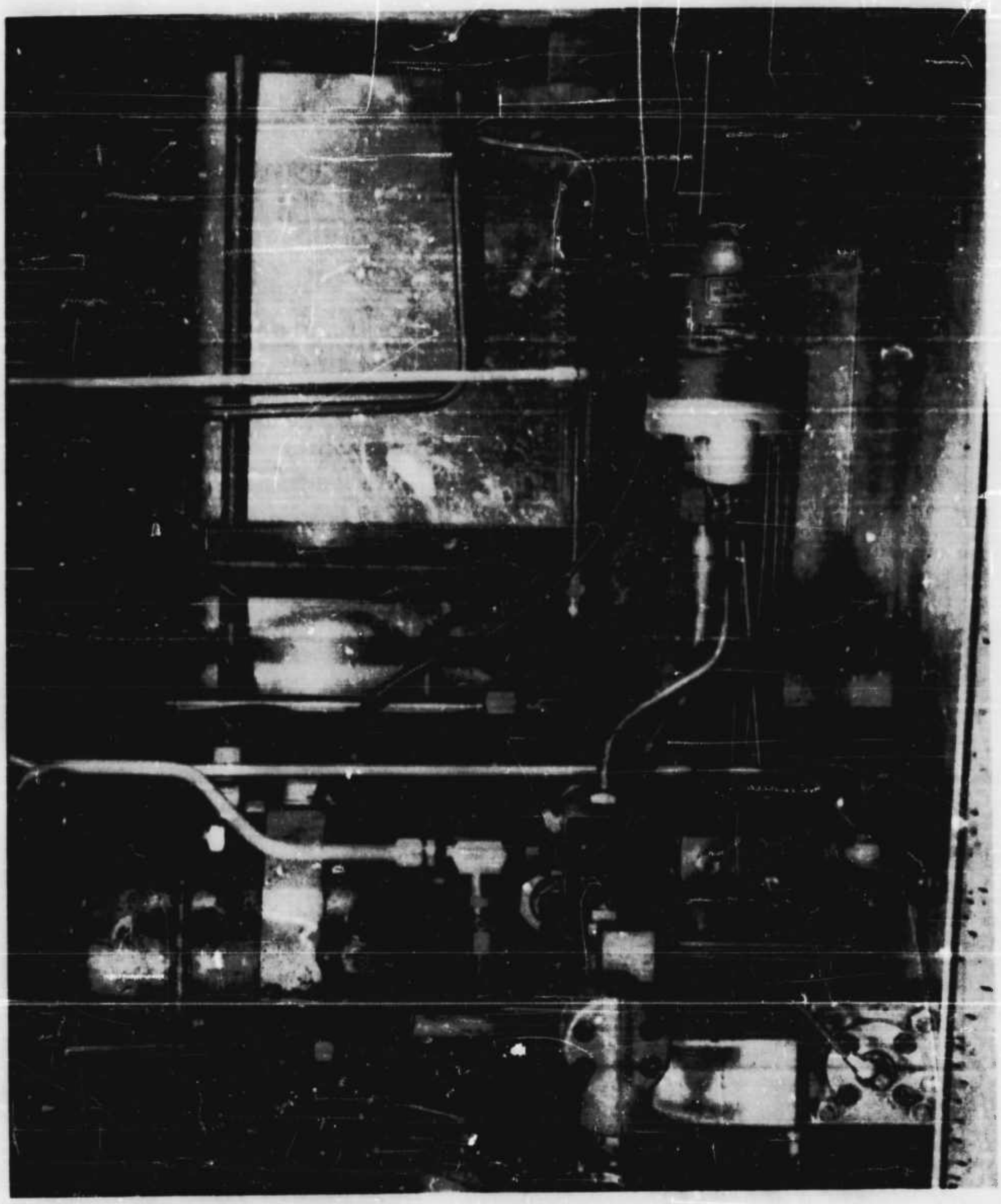


FIG. 23 - HYDRAULIC PUMP TEST STAND NEW YORK AIR BRAKE 66WA300 PUMP

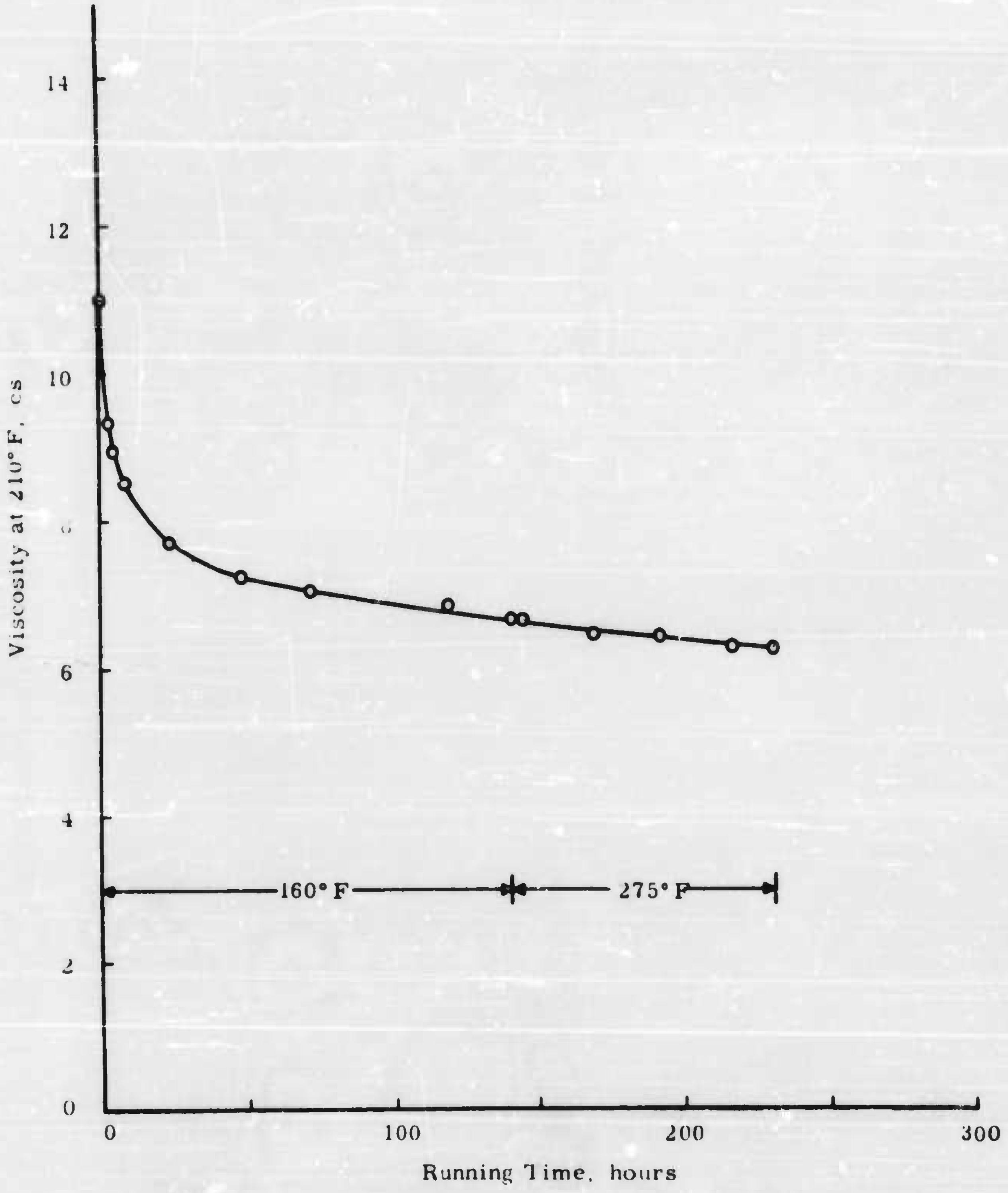


FIG. 24 - VISCOSITY CHANGE OF 8200 FLUID IN NEW YORK AIR BRAKE 66WA300 PUMP TEST NY-7 SPEED 3450 RPM, PRESSURE 3000 PSI

5.4.3 Irradiated 8200 Fluid

The run with irradiated 8200 Fluid was completed without a pump failure. Inspection of the pump after 150 hours operation at 160°F revealed considerable transfer of bronze onto steel rubbinb surfaces. This is shown in Figures 25, 26, and 27, photographs after 67.5 hours at 275°F. In addition to this "bronzing" of the steel, a number of fatigued areas were noticed in the bronze plate.

The pump was reassembled and 100 hours at 275°F was successfully completed. Inspection of the pump after this portion of the test showed that "bronzing" had progressed still further, and some bronze particles were found in areas of the pump not subjected to high oil velocities. From this, it was deduced that pump wear and subsequent smearing of bronze on steel surfaces was responsible for the metal transfer observed.

Despite the wear on the bronze creep plate. pump wear was consistently less with irradiated 8200 Fluid than with fresh 8200 Fluid. This is attributable in part to the increased viscosity of the irradiated fluid. The wear of critical pump parts is compared in Table LXVI for 160°F and Table LXVII for 275°F. Figure 28 shows the change in viscosity at 210°F for the irradiated 8200 Fluid during the course of the run. The change was less regular than with the fresh oil. The reason for the reversal of the curve is not evident. Figure 29 shows pump parts following the run.

5.5 Present Status and Conclusions

The status of the hydraulic fluid development and the conclusions which can be drawn at this time are as follows:

1. Evaluation of the ability of the silicate base fluids, particularly the 8200 Fluid, to withstand radiation is almost completed. Data obtained thus far are in Table LXVIII. The maximum permissible dosage appears to be about 10^8 r. At this level there is negligible viscosity change. Gas, predominantly hydrogen, is evolved at the rate of about 1 ml gas/ml fluid/2 x 10^7 r. While irradiation of 8200 Fluid to 7.85 x 10^8 r triples the viscosity, the fluid may be used in hydraulic systems employing New York Air Brake pumps and some reduction in wear may be expected. Operation of pumps at temperatures much below 0°F would be impaired.

2. Alkyl aromatics and alkyl diphenyl ethers offer the best chance for base materials of outstanding radiation and thermal stability. The physical properties are much inferior to those of the silicate fluids, but viscosity change and gas evolution are reduced by at least a factor of five with even larger improvements probable. The higher the aromatic content, the greater the improvement in radiation stability.

3. Of the new materials synthesized, the alkyl diphenyl ethers have better physical properties and equivalent radiation stability (based on aromatic content) as compared with the corresponding biphenyls. Dodecyl diphenyl ether was chosen as the base stock for a non-V.I. improved fluid, aiming at Phase I viscosity requirements and a dosage of 10^9 r. Data on this fluid are summarized in Table LXIX.

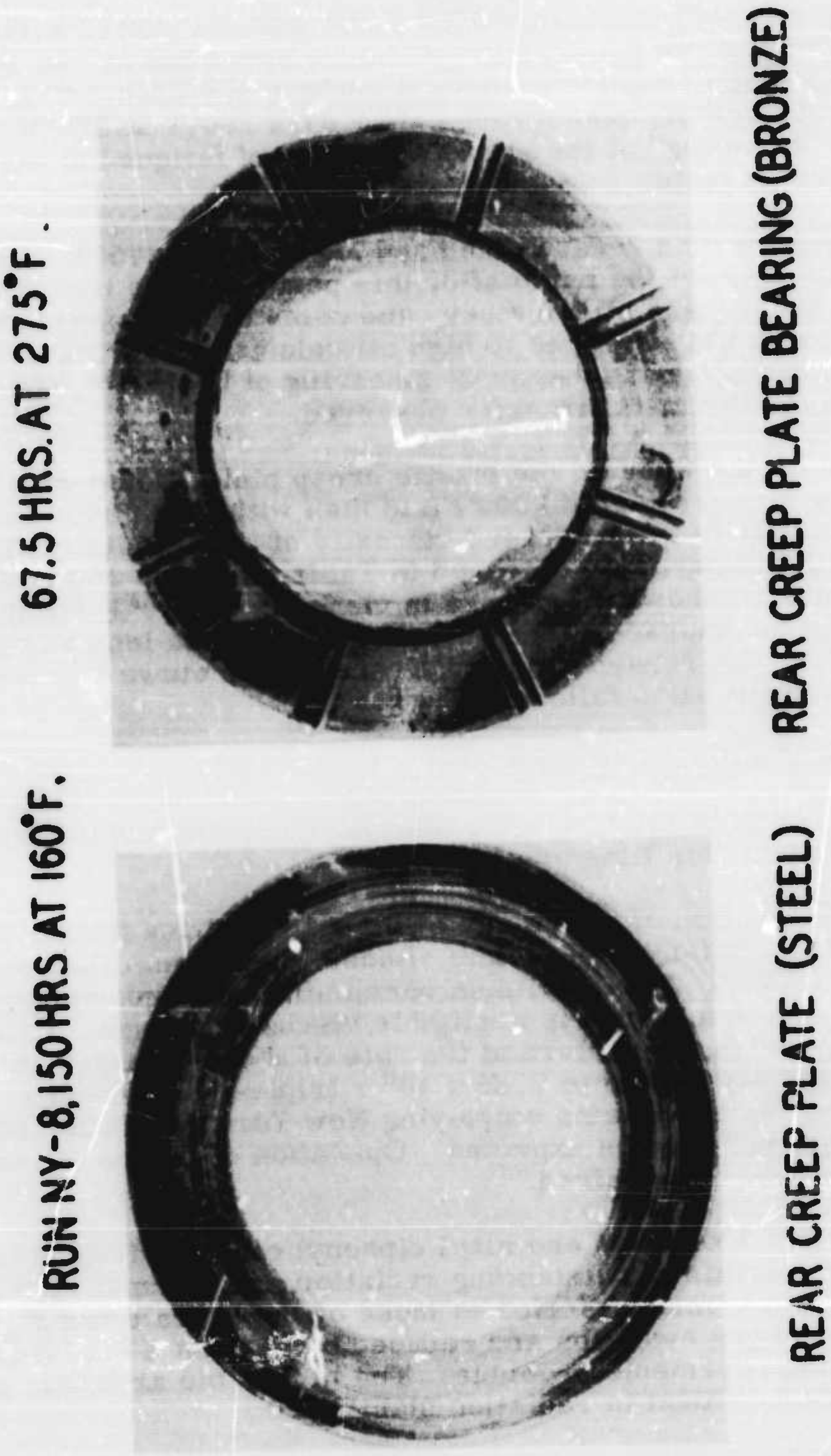
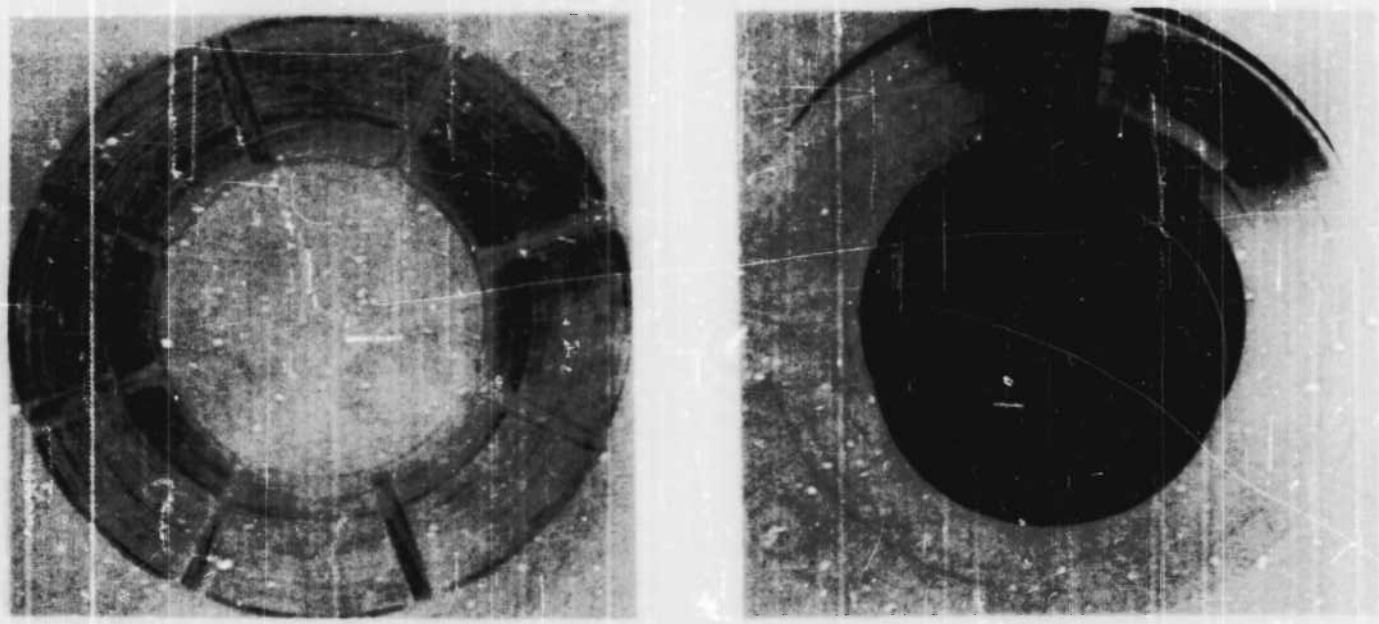


FIG. 25 - CREEP PLATES FROM PUMP TEST ON IRRADIATED 8200 FLUID

RUN NY-8, 150 HRS. AT 160°F, 67.5 HRS. AT 275°F

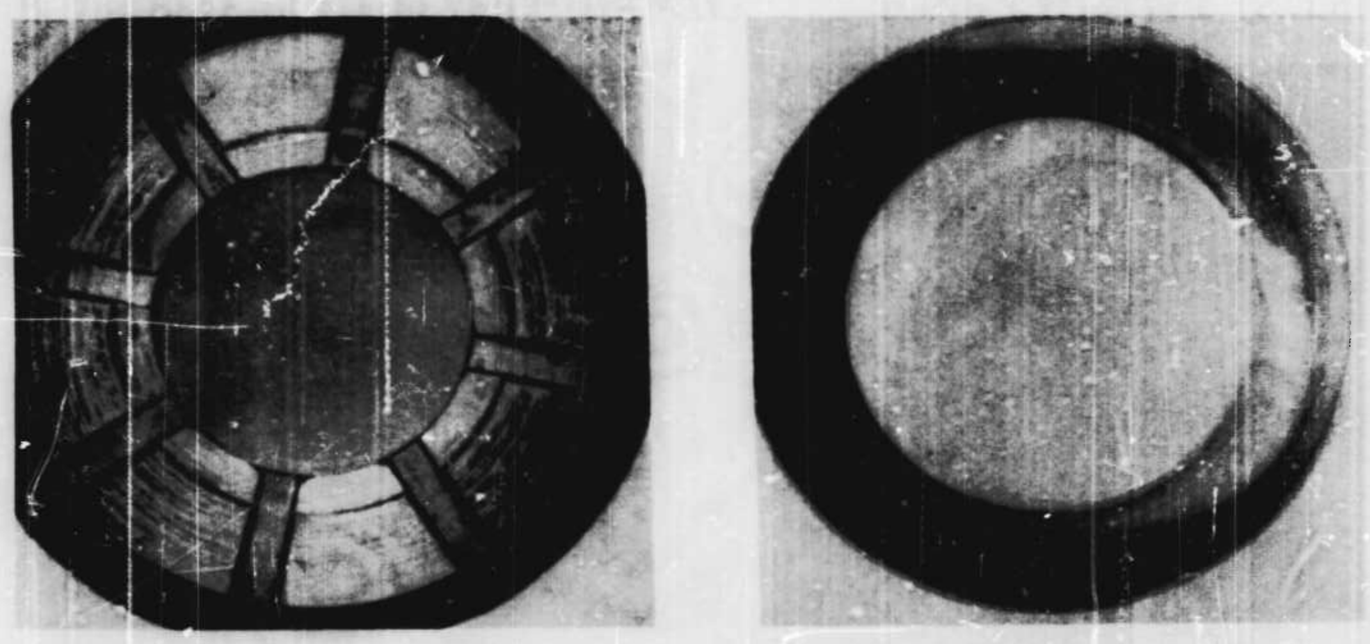


REAR CREEP PLATE BEARING (BRONZE)

PUMP CAMSHAFT (STEEL)

FIG. 26 - CREEP PLATE AND CAMSHAFT FROM PUMP TEST ON IRRADIATED 8200 FLUID

RUN NY 8, 150 HRS. AT 160°F, 67.5 HRS. AT 275°F



THRUST BEARING (BRONZE)

(REAR CREEP PLATE STEEL)

FIG. 27 - CREEP PLATE AND THRUST BEARING FROM PUMP TEST ON IRRADIATED 8200 FLUID

TABLE LXVI

EFFECT OF FLUID IRRADIATION ON PUMP WEAR
NEW YORK AIR BRAKE 66WA300 PUMP OPERATED 150 HOURS AT 160°F

Pump Part[a] - Wt. Loss, mg		8200 Fluid Before Irradiation	8200 Fluid After Irradiation
Piston No.:	1	6.9	4.5
	2	9.6	2.4
	3	5.7	4.6
	4	8.8	3.7
	5	11.6	3.7
	6	8.9	3.6
	7	8.0	3.9
	8	9.7	4.2
	9	5.5	3.4
	Avg.	8.3	3.8
Check Valve No.:	1	1.2	0.4
	2	0.8	0.0
	3	1.2	0.4
	4	1.4	0.4
	5	1.5	0.2
	6	1.3	0.6
	7	1.4	0.3
	8	1.0	0.5
	9	1.3	0.0
	Avg.	1.2	0.3
Piston Sleeve No.:	1	1.0	1.7
	2	0.9	0.7
	3	0.8	0.4[b]
	4	0.9	0.2[b]
	5	0.7	0.5[b]
	6	1.0	0.1[b]
	7	1.6	0.6[b]
	8	0.9	0.1[b]
	9	1.1	0.3[b]
	Avg.	0.8	0.0
Piston Return Collar No.:	1	0.8	0.0
	2	1.6	1.4
	3	1.1	1.4
	4	1.1	0.6
	5	1.7	1.0
	6	2.2	2.6
	7	1.4	1.7
	8	1.8	1.5
	9	1.3	1.2
	Avg.	1.4	1.3

a. All parts are steel.
b. Weight gain.

TABLE LXVII

EFFECT OF FLUID IRRADIATION ON PUMP WEAR (CONT'D)
NEW YORK AIR BRAKE PUMPS FROM TABLE LXVI OPERATED AN ADDITIONAL PERIOD OF 100 HOURS AT 275°F

Pump Part[a] - Wt. Loss mg		8200 Fluid	
		Before Irradiation[b]	After Irradiation
Piston No.	1	6.3[c]	10.1
	2	0.4	8.1
	3	12.1	5.0
	4	11.4	6.4
	5	19.9	2.1
	6	10.9	1.8
	7	15.2	7.8
	8	2.4	12.9
	9	4.6	8.9
	Avg.	9.2	7.0
Check Valve No.:	1	1.0	0.8
	2	1.0	1.2
	3	0.5	1.0
	4	0.6	0.7
	5	0.6	1.9
	6	0.7	0.5
	7	0.0	0.9
	8	0.8	1.4
	9	0.4	0.7
	Avg.	0.6	1.0
Piston Sleeve No.:	1	2.4	1.6
	2	0.3	0.1
	3	0.2[c]	0.5
	4	0.0	0.3
	5	0.1	1.2
	6	0.6[c]	0.6
	7	0.3	0.7
	8	0.9	0.6
	9	0.0	0.2
	Avg.	0.4	0.6
Piston Return Collar No.:	1	0.6	0.5
	2	0.5	0.8
	3	0.1	1.1
	4	0.1	0.7
	5	0.1[c]	0.6
	6	0.2	0.5
	7	0.2	0.9
	8	0.3	0.8
	9	3.6	0.0
	Avg.	0.6	0.7

a. All parts are steel.
b. Test stopped at 90 hours caused by leak in suction line.
c. Weight gain.

Pressure	3000 psi
Speed	3450 rpm
Dosage of Fluid	7.8×10^8 r (See Table LXIII, page 108)

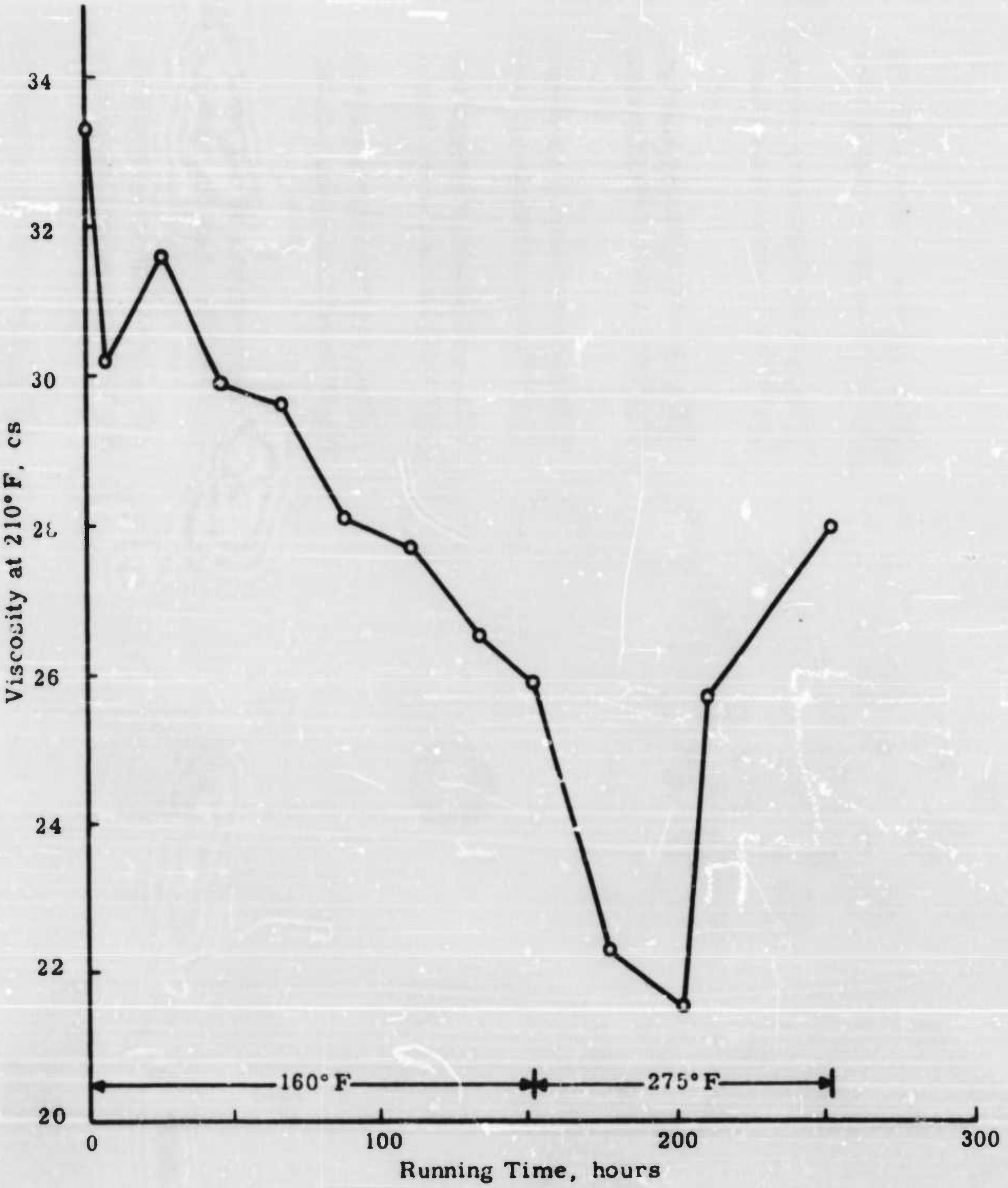


FIG. 28 - VISCOSITY CHANGE OF IRRADIATED 8200 FLUID IN NEW YORK AIR BRAKE 66WA300 PUMP TEST NY-8

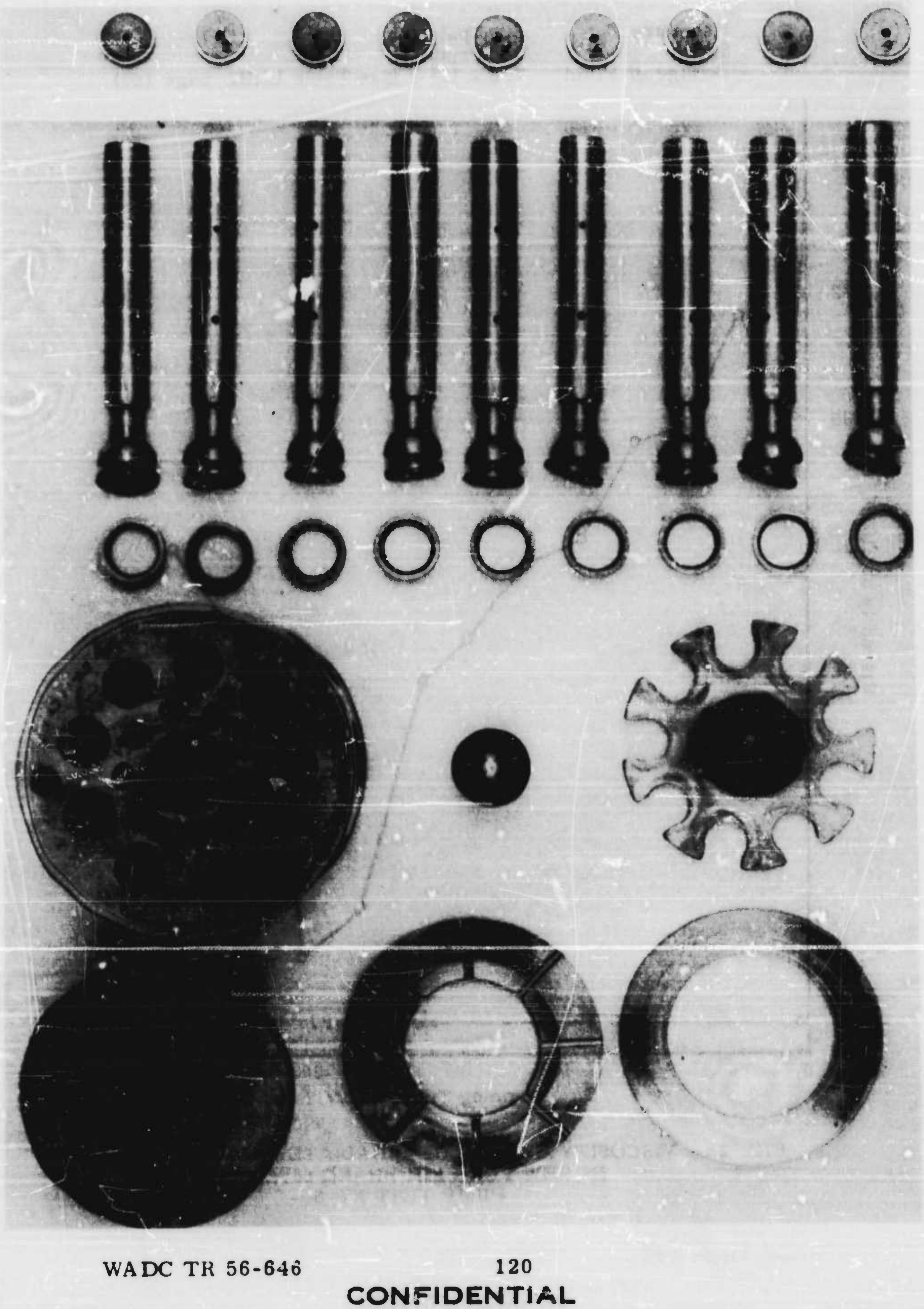


FIG. 29 - PUMP PARTS AFTER TEST ON IRRADIATED 8200 FLUID

TABLE LXVIII

SUMMARY OF DATA ON MLO 8200 FLUID

1. Radiation Dosage, 10^8 r	0*		0.22*[a]	0.34*[a]	1.18*[a]	3.00*[a]	7.85**[b]	
2. Viscosity, cs								
At 400°F	3.82							
210°F	11.59		10.62	10.14	9.95	14.68	37.15	
100°F	33.29		30.79	29.86	30.24	48.09	131.6	
-40°F							9,660	
-65°F	2234						47,363	
Viscosity Index	-							
3. Viscosity, cs								
At 100°F - July 18, 1956							131.6	
Sept. 6, 1956							146.8	
% Change							+11.6	
At 210°F - July 18, 1956							37.15	
Sept. 6, 1956							37.29	
% Change							+0.4	
4. Pour Point, °F	<-100						<-80	
5. Flash Point, COC, °F	415						115	
6. Fire Point, COC, °F	455						295	
7. SIT, °F	720						840	
8. Neut. Number	0.1						0.08	
9. Bromine No.	1						5.6	
10. Vapor Pressure at 400°F, mm Hg	1.0							
11. Temperature for Vapor Pressure of 1 mm Hg, °F	400						150	
12. Oxidation Corrosion								
Temperature, °F	347	400					347	400
Time, hours	72	72					72	72
Wt. Change, mg/cm², Al	0	-0.02					+0.10	-0.08
Mg	-0.03	-					+1.52	-
St	0	-0.05					+0.06	+0.04
Cu	+0.5	+0.04					-2.06	-0.88
Ag	0	-0.04					+0.06	-0.14
Neut. Number	0.47	0.50					2.7	1.2
Viscosity Change, 210°F, %	+6.5							
100°F, %	+8.0	-28						
13. Hydrolytic Stability, 200°F								
Copper Wt. Change, mg/cm²		-0.03					0	+0.06
Viscosity Change, 210°F, %		+1.0					-8.9	-15.4
100°F, %		+2.1					+26.1	+30.1
Insolubles		0.05					0.36	1.33
Neutralization No.		0.10					0.02	0.30
14. Gas Evolved on Irradiation at 80°F	-		1.0	2.0	5.9	12.0		
Composition of Gas, % Wt.								
Hydrogen						83.5		
Methane						2.8		
CO						8.4		
CO_2						0.3		
Ethane						4.0		
Butane						0.5		
Pentane						0.5		
						100.0		
15. Rubber Swell, %, 72 hours at 250°F, Rubber R	+7.7						+6.0	
16. Pump Performance: 3000 psi; (NYA 66WA300 pump)								
150 hours at 160°F	OK						OK	
100 hours at 275°F	OK						OK	

* Batch No. G-14496
** Batch No. G-14275

a. In 10-ml quantities in capsules of 410 stainless steel sealed under helium; MTR Canal Source.
b. In 3.5-gallon quantity in vented aluminum tank; MTR Canal Source.

TABLE LXIX

SUMMARY OF DATA ON DODECYL DIPHENYL ETHER

Additives, % By Wt.	None	2% Parabar 441
1. Radiation Dosage, 10^8 r	0	0
2. Viscosity, cs		
At 400°F	1.09	
210°F	3.57	
100°F	18.47	
-30°F	-	
-40°F	11,608	
Viscosity Index	70	
3. Pour Point, °F	-75	
4. Flash Point, °F		
5. SIT, °F	830	
6. Vapor Pressure, mm Hg at 400°F	25	
7. Oxidation Corrosion		
Temperature, °F		400
Time, hours		72
Wt. Change, mg/cm^2,		
Al		+0.09
Mg		-
St		+0.12
Cu		-4.54
Ag		+0.15
Neutralization No.		-
Viscosity Change, %,		
210°F		-
100°F		-
8. Gas Evolved during Irradiation, ml gas/ml oil	-	-

4. The performance of available polymeric V.I. improvers is unsatisfactory both at high temperature and in the presence of radiation. The polybutenes represent the best compromise of properties of available materials. Alkyl aromatics, having only fair viscosity-temperature properties, require better V.I. improvers of improved stability if their full potential is to be realized. Polymers containing phenyl groups will probably be needed for stability. Lower viscosity base stocks will be required if suitable V.I. improvers can be found. These will probably contain only one aromatic ring per molecule. For the thickened alkylbenzene fluids, data are summarized in Table LXX.

5. When inhibited with selenides, the polyglycol diethers show less radiation damage than the other aliphatics tested. (Data on Ucon DLB 144E are summarized in Table L , page 85.) Similarly, inhibited methyl phenyl silicone shows relatively good stability. (See Table LXXI for a summary of data.)

5.6 Future Work

Work on the study of the capability of 8200 Fluid should be completed. The evaluation of the dodecyl diphenyl ether should also be completed in an attempt to obtain a Phase I fluid for 10×10^8 r.

To guard against an unexpected weakness in the preferred alkyl aromatics, a limited amount of work should be done on several other base stocks. A fluid meeting Phase II viscosities should be formulated from the Ucon DLB series lubricants to obtain a 5×10^8 r fluid. Further samples of methyl phenyl silicones should be tested to determine the capability of this type of fluid. Inadequate lubricity may make the use of silicones doubtful except under favorable conditions. A light petroleum oil should also be evaluated as V.I. improvers become available.

New materials of two types should be synthesized for evaluation as base stocks: alkylbenzenes and diphenylalkanes of improved low temperature properties. The former are expected to be of interest primarily for use in V.I. improved fluids and the latter for more stable materials of improved viscosity-temperature properties.

A greatly expanded program of screening radiation damage inhibitors is required. Compounds as effective as the dialkyl selenides are desired without their deleterious effect on certain metals.

The development of aromatic base fluids meeting Phase II and III viscosity requirements depends on the use of viscosity index improvers. The capability of polybutenes as to temperature and radiation dosage should be determined. For high dosages, new materials must be synthesized. Past experience indicates that the inclusion of phenyl groups in the polymer is necessary. However, the aliphatic/aromatic ratio must exceed a minimum value if adequate V.I. improvement is to be obtained. For this purpose, hydrocarbon condensation polymers with benzene rings in the main chain should be synthesized. In addition, vinyl polymers or copolymers may be of interest for this purpose.

Additional testing of original and irradiated fluids in pumps should be undertaken. Alkyl aromatic - and alkyl diphenyl ether - based fluids should be run and their properties compared with those of more conventional fluids, as well as any future formulations which appear promising. Both New York Air Brake and Vickers pumps should be used and temperatures above 275°F employed, if feasible.

TABLE LXX

SUMMARY OF DATA ON ALKYLBENZENE FLUIDS

	Fluid 0-1A[a]		Fluid 0-1.5A[b]		
1. Radiation Dosage, 10^8 r	0	5	0	0.32[c]	2.42[c]
2. Viscosity, cs					
At 400°F	1.06[d]				
210°F	3.46	2.76	4.42	4.12	3.32
100°F	16.94	13.16	25.83	23.74	13.21
Viscosity Index	83	34			
3. Pour Point, °F	+20	-35			
4. Flash Point, °F	260	150			
5. Fire Point, °F	280	175			
6. SIT, °F	1000				
7. Neutralization No.	0.01	0.02			
8. Evaporation, % 22 hours at 400°F	32	32			
9. Vapor Pressure at 400°F, mm Hg	88				
10. Gas Evolved During Irradiation at 80°F	-	-	-	1.0	2.0

a. Developed on AEC Contract AT(11-1)-174 as General Purpose Lubricants -

Composition	0-1A, %	0-1.5A, %
Mixed Alkylbenzenes (m. w.~250)	74.45	66.2
Poly(alpha-methylstyrene) (Dow V-9 Resin)	15.00	21.8
Polybutene 128	5.50	7.0
Didodecyl Selenide	5.00	4.95
Quinizarin	0.05	0.05

b. In 200-ml quantity in tin-lined vented can; MTR Canal Source.

c. In 10-ml quantity in capsules of 410 SS sealed under helium; MTR Canal Source.

d. Extrapolated.

TABLE LXXI

SUMMARY OF DATA ON DOW CORNING 703

Additive, % By Wt.	1 PAN[a]				5 DDS[a]		
1. Radiation Dosage, 10^8 r		0	0.30[b]	4.75[b]	0	0.30[b]	4.75[b]
2. Viscosity, cs							
At 400°F		1.6*					
210°F		5.47	6.40	24.54	3.06	6.03	5.54
100°F		25.63	31.02	145	22.52	22.48	26.03
-30°F		45,249					
-40°F		-					
Viscosity Index		156					
3. Pour Point, °F		-40					
4. Flash Point, °F							
5. SIT, °F		840					
6. Vapor Pressure, mm Hg at 400°F		0.9					
7. Oxidation Corrosion							
Temperature, °F	400				400		
Time, hours	72				72		
Wt. Change, mg/cm², Al	-0.03				-0.22		
Mg	-				0.08		
St	-0.03				-0.02		
Cu	-0.02				-		
Ag	+0.02				-		
Neutralization No.	-				1.9		
Viscosity Change, %, 210°F					13.9		
100°F					25.8		
8. Gas Evolved during irradiation, ml gas/ml oil			0.7	1.0		0.3	1.4

a. Additives: PAN = phenyl-alpha-naphthylamine
DDS = didodecyl selenide

b. In 10-ml quantities in capsules of 410 stainless steel sealed under helium; MTR Canal Source.

* Extrapolated.

6. GEAR LUBRICANTS

(S. R. Calish)

6.1 Requirements

The target requirements for a radiation resistant aircraft gear lubricant are given in Table LXXII. A comparison of these requirements with those of the aircraft gas turbine lubricant will show them to be closely allied except for low temperature properties, film strength, and radiation dosage. It is likely that a turbine oil based on an aromatic compound would meet the gear oil specification but for the stringent film strength requirement. Thus, the principal effort on gear oils has been the investigation of extreme pressure (EP) compounds and their effects on metals and load carrying capacity. As with the gas turbine and hydraulic fluid development work, various phases were set up for intermediate goals which represented relaxation of some of the gear oil requirements. These will be apparent as the discussion proceeds.

Table LXXII

Target Specification For Gear Lubricant

	Original	Irradiated
1. Radiation Dosage, 10^8 r	-	50
2. Viscosity, cs		
At 210°F, min	5.5	3.0
At -40°F, max	3500(7000)[a]	-
3. Viscosity Index	163(147)	-
4. ASTM Pour Point, °F, max	-75(-30)	-65(-10)
5. Radiation Stability, at °F	-	350
Acid No., max	-	2
Wt. Change, mg/cm^2		
Steel	-	
Aluminum	-	± 0.4 (± 0.6)
Magnesium	-	
Sludge	-	None on container wall
6. Mean Hertz Load, min	40	40(30)
7. Evaporation, % in 6.5 hr at 400°F	20(40)	-
8. Ryder Gear Test	Level to be determined	

a. ( ) Alternate minima.

6.2 Selection of Extreme Pressure Additives

Table LXXIII shows several base materials which were considered as potential carriers for the EP agents used. In addition to those shown, a mineral oil was also employed. For preliminary screening, sixteen extreme pressure additives were evaluated in both a polyglycol and a mineral oil. The screening procedures included a form of the Mean Hertz Load Test[1] in which only 79, 100, 126, and 158 kg loads were used, and the scar on a single ball was measured in only one direction in each test. In addition, Falex Extreme Pressure Tests[2] were performed on the same unirradiated oil-additive combinations. Preliminary correlation using MIL-O-6086, Grade L, as a reference appeared to be good between these abbreviated screening tests and the full-scale evaluation.

The data obtained are given in Table LXXIV. From the extreme pressure screening tests, the additives in Table LXXV were found to be satisfactory in the two base oils as indicated.

Table LXXV

Effective Extreme Pressure Additives

Additive	Active Element	Effective In	
		Mineral Oil	Polyglycol
Wax Disulfide	Sulfur	X	X
Zinc Dialkyl Dithiophosphate	Phosphorus, Sulfur		X
Sulfurized Olefin	Sulfur	X	X
Santopoid S	Sulfur, Chlorine	X	X
Santopoid 22	Sulfur, Chlorine, Phosphorus, Zinc	X	X
Anglamol 88	Sulfur, Phosphorus, Chlorine		X
Complus 77	Sulfur, Phosphorus	X	X
Alkyl Acid Phosphate Amine Salts	Phosphorus		X

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[1] Federal Test Method Standard No. 791, Method 6503 (Dec. 5, 1956).

[2] Bulletin Nos. 3, 12, 121, 122, Faville-LeValley Corporation, 105 West Adams Street, Chicago, Illinois, February 3, 1948.

TABLE LXXIII

SOME PROPERTIES OF POTENTIAL BASE STOCKS FOR GEAR LUBRICANTS

	Requirements - Unirradiated			Ucon DLB 144E	Tridecyl Azelate	Hercoflex 600	Diisodecyl Phthalate	Diisooctyl Terephthalate	C_{18}-C_{18} Biphenyl
	Phase I	Phase II	Phase III[1]						
Viscosity at 100°F, cs[2]	-	-	-	32.4	34.7	24.3	42.0	29.7	37.8
Viscosity at 210°F, cs	5.5 min.	5.5 min.	5.5 min.	7.16	6.37	4.775	5.47	4.85	5.54
Viscosity at -40°F, cs	40,000 max.	40,000 max.	3500(7000)max.	-	18,404	7791	39,000	-	-
Viscosity Index[2]	103	103	164 (147)	167	139	132	59	90	89
Pour Point, °F	-40 max.	-40 max.	-75 (-30)	-65	-80	Below -80	-45	-65	-40
Evaporation, %	40 max.	40 max.	20 (40) max.	-	3.1	7.2	-	11.7	8.6
Gravity, °API[2]				12.7	24.2	-	-	-	-
ASTM Flash Point, °F[2]				455	480	470	440	-	-
ASTM Fire Point, °F[2]					565	530	470	-	-

1. ( ) indicate alternate minima.
2. Not specification requirement.

TABLE LXXIV

RESULTS OF FILM STRENGTH SCREENING TESTS ON POTENTIAL GEAR LUBRICANTS

Sample No.	Base Oil	Additive[a]	Mean Hertz Load Screen[b]				Falex EP,[c]
			79 kg	100 kg	120 kg	150 kg	Load at Failure, lb
MIL-C-6086A (L)	Mineral Oil	Santopoid S	P, P	P, P	P, P	PX, PX	2300, 2250[f]
MIL-C-6086A (M)	Mineral Oil	Santopoid S	P, P	P, P	X, X		3400, 3400[g]
3311-3-1	Polyglycol Diether[d]	Sulfurized Diparaffin Sulfide	P	P, P	X, X		4500+, 4500+
-2		P_2S_5-Pinene Product	P, P	P, P	X, X		3550, 3700
-3		Sulfochlorinated Lard Oil	P	X			2250, 2200
-4		Sulfurized Olefin	P	P, P	X, X		3000, 2950
-5		Tricresyl Phosphate		X			2100, 1800, 1900
-6		Dibenzyl Disulfide (1%)	P	X			2200, 2200
-7		Anglamol 77X	P	P, X	X		2250, 2500, 2500
-8		Anglamol 82	P	P, X	X		3500, 3800, 3700
-9		Anglamol 88	P	P	X		3650, 4500+, 4500+
-10		Anglamol 40	P	X			1800, 1800
-11		Santapoid S	P	P, P	X, X		3400, 3900
-12		Santapoid 33	P	P, P	X		2450, 3200, 3250
-13		Santapoid 22	P	P	X		4100, 4200
-14		Monsanto PC 1354	P	P	X		4300, 4450
-15		Complus 77	P	P	X		3950, 3900
-16		Elco SCL Concentrate	P	X			4500+, 4500+
3311-4-1	Mineral Oil[e]	Sulfurized Diparaffin Sulfide	P	X			3650, 3350, 3250
-2		P_2S_5-Pinene Product	P	X			2000, 2000
-3		Sulfochlorinated Lard Oil	P, X	P, X	X		2350, 2250
-4		Sulfurized Olefin	X				4500, 4500
-5		Tricresyl Phosphate	X				1900, 1900
-6		Dibenzyl Disulfide (1%)	X				4500+, 1700, 4500+
-7		Anglamol 77X	P	P, P	X, X		2500, 2300
-8		Anglamol 82	P	X			2400, 2550
-9		Anglamol 88	P	X			2700, 2800
-10		Anglamol 40	X				4500+, 4500+
-11		Santapoid S	P, P	P, X	X		4500+, 4500+
-12		Santapoid 33	P, P	P, X	X		2900, 2900
-13		Santapoid 22	P, P	P, X	X		4500+, 3750, 4100
-14		Monsanto PC 1354	P	X			1800, 1950
-15		Complus 77	P	X			3350, 3200
-16		Elco SCL Concentrate	P	X			1500, 1550

a. 5% by weight unless noted.
b. P = pass
X = fail by seizure
c. Standard Steel/Steel EP test.
d. Dow PG-18
e. Solvent Treated Naphthenic Base
f. Mean Hertz Load 57,64
g. Mean Hertz Load, 59

In previous tests, chlorine-containing materials became corrosive on irradiation[1]. For this reason, work was concentrated on those five additives containing only phosphorus and/or sulfur. Further phosphorus-sulfur olefin condensation products were investigated, as well as other combinations of sulfur and phosphorus compounds. Corrosion tests on the combinations of each extreme pressure additive and base oil noted in Table LXXV were performed. Results are shown in Table LXXVI.

In the corrosion test, the fluid was heated in a beaker at 250°F for 168 hours. One-inch square specimens of aluminum, magnesium, and 1020 steel were immersed in 100 ml of liquid. Specimens were weighed before and after the test, and the oil was observed visually for insolubles. Under these conditions, little corrosion was noted and only magnesium showed a significant weight loss in two instances. However, several additives gave heavy precipitation, suggesting that these extreme pressure additives were borderline in stability at 250°F. In the presence of ionizing radiation, the stability was expected to be further reduced, particularly with air present.

6.3 Evaluation of Irradiated Fluids

From the described work in Section 6.2, six additives were selected for further evaluation. These additives were incorporated into three different base oils, although not all additives were used with each oil as shown in Table LXXVII. Sufficient sample was prepared to determine complete Mean Hertz Loads on the original oils and oils irradiated to 10×10^8 r. In addition, the base oils without additives are being checked. All these samples were sent to WADC in August 1956 for the full Mean Hertz Load runs.

A comparison of the viscosities of the experimental gear oil blends before and after irradiation is in Table LXXVII. (The base oils are compared in the gas turbine lubricant section (pages 67-70). The most significant fact is that most of the EP additives adversely affected radiation stability. In some cases, the effect of the additive was paramount, as the blend was worse than the base oil alone. Viscosity increases ranged from about 30% to 300%. Only the sulfurized olefin appeared to be neutral in its effect on radiation stability and it may actually have enhanced the stabilizing effect of the selenide.

6.4 Status of Gear Oil

In view of the requirement for radiation stability at 50×10^8 r, alkyl aromatic base oils are the most logical for consideration. Distilled C_{16-18} biphenyl meets the viscosity at 210°F requirement, but if a maximum limiting viscosity of 3500 cs is assumed, the low temperature limit of operability will be about -10°F. Because gear sets are rarely power limited, it can also be assumed that somewhat higher viscosities than 3500 cs can be tolerated.

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[1] Carroll, J. G. and Calish, S. R., "Some Effects of Gamma Radiation on Commercial Lubricants," ASLE Preprint No. 57AM 1B-1, submitted for publication in Lubrication Engineering.

TABLE LXXVI

RESULTS OF CORROSION TESTS[a] ON POTENTIAL GEAR OILS

Oil No. and Description		Weight Loss, mg			Appearance at 168 Hours			
		Al	Mg	Steel	Al	Mg	Steel	Oil
3296-38-1	Spray Oil 99%	0.7	0.7	0.5	Bright	Bright	Bright	Clear
3296-38-3	Spray Oil 94% Wax disulfide 5%	0.1	4.8	0.5	Bright	Heavy Brown Lacquer	Slightly Dulled	Clear
3296-38-4	Spray Oil 94% Sulfurized olefins 5%	0.0	0.1	0.3	Dull - Slightly Darkened	Dull - Darkened	Purple "Peacock" Lacquer	Sediment on Bottom
3296-38-5	Spray Oil 94% Anglamol 77X 5%	0.3	0.1	0.2	Light Brown Dull	Light Brown Dull	Brown - "Peacock"	Slightly Opaque Light Sediment on Bottom
3296-38-6	Spray Oil 94% Santopoid S 5%	0.1	0.1	0.1	Light Purple Peacock	Light Purple	Dark Peacock	Opaque Light Sediment on Bottom
3296-38-7	Spray Oil 94% Santopoid 33 5%	0.4	0.1	0.5	Dull Light Brown Lacquer	Dull Light Brown Lacquer	Dull Brown	Opaque - Floc Heavy Sediment on Bottom
3296-38-8	Spray Oil 94% Santopoid 22 5%	0.5	3.6	0.5	Dull - Very Light Peacock	Dull Gray	Dull Dark Brown	Opaque - Floc Heavy Sediment on Bottom
3296-38-9	Spray Oil 94% Complus 77 5%	0.3	0.2	0.4	Light Peacock	Very Light Peacock	Dark Brown Lacquer Peacock	Very Opaque Very Heavy Sludge on Bottom
3296-38-12	Polyglycol 98%	0.6	0.5	1.0	Bright	Bright	Bright	Clear
3296-38-14	Polyglycol 93% Zinc dialkyl-dithio phosphate 5%	0.5	0.0	0.3	Dull Gray	Dull Gray Light Peacock	Light Peacock	Opaque Semisolid Lumps in Oil
3296-38-15	Polyglycol 93% Anglamol 88 5%	0.8	0.5	0.6	Very Light	Slightly Dulled	Very Light Peacock	Clear - Dark Light Sludge on Bottom

a. 168 hours at 250°F.
b. All oils contained 1% didodecyl selenide except 3296-38-12, 14, and 15 which contained 2%.

TABLE LXXVII

VISCOSITY CHANGE OF IRRADIATED[a] GEAR LUBRICANTS

Base Stock	Additives	Sample Number	Viscosity, cs		T_{10}	η_{10}
			100°F	210°F		
Ucon DLB 144E	5% Diparaffin Sulfide	4535-31-1 C-1	32.01 19.48	7.27 4.45	179 -	- 6.25
	5% Zinc Dialkyldithiophosphate + 2% Dibenzyl Selenide	4535-31-2 A-2	30.31 91.56	6.89 12.84	174 -	- 21.0
	5% Sulfurized Olefin + 2% Dibenzyl Selenide	4535-31-3 A-3	29.12 56.79	6.76 11.40	173 -	- 18.5
	0.1% Alkylamine Salt of Alkylphosphoric Acid + 2% Dibenzyl Selenide	4535-31-5 A-5	30.09 115.1	7.01 17.52	177 -	- 27.5
	5% Santolube 395X + 2% Dibenzyl Selenide	4535-31-6 A-6	53.71 101.5	6.72 5.48	184 -	- 22.1
C_{16}-C_{18} Biphenyl	2% Dibenzyl Selenide	4535-29-2 C-2	51.78 76.81	6.81 8.87	181 -	- 13.6
	5% Sulfurized Olefin + 2% Dibenzyl Selenide	4535-31-7 B-7	49.45 71.89	6.59 8.49	179 -	- 14.0
	0.1% Alkylamine Salt of Alkylphosphoric Acid + 2% Dibenzyl Selenide	4535-31-8 B-8	51.78 77.75	6.834 8.956	181 -	- 13.8
	5% Santolube 395X + 2% Dibenzyl Selenide	4535-31-9 B-9	57.83 84.96	7.58 9.66	189 -	- 13.1
	5% Santolube 395X + 2% Dibenzyl Selenide[b]	4535-31-12 C-12	58.09 80.80	7.57 9.99	191 -	- 13.0
Diisooctyl Terephthalate	5% Sulfurized Olefin + 5% Dibenzyl Selenide	4535-31-10 B-10	29.43 42.28	4.85 6.04	155 -	- 13.2
	0.1% Alkylamine salt of Alkylphosphoric Acid + 2% Dibenzyl Selenide	4535-31-12 C-11	29.96 72.24	4.98 8.56	156 -	- 20.0

a. 7.5 x 10^8r at 80°F in MTR Canal Gamma Source.
b. Blend repeated due to blending error.

The pour point of C_{16-18} biphenyl is slightly higher than that specified (-55° F vs -75° F), but this is still substantially lower than the viscosity target limitation. The evaporation characteristics of the distilled C_{16-18} biphenyl are satisfactory for gear oil use. With suitable inhibitors of the selenide type, this material will probably pass the irradiation stability requirements with irradiation at 350° F for 50 x 10^8 r.

The remaining specification test is a Mean Hertz Load of 40 and subsequent gear test. While no experience with finished gear oil formulations from alkyl aromatic bases is at hand, such oils have been submitted to WADC for test, both before and after irradiation. It is believed the film strength requirement can be met by the incorporation of EP agents, such as sulfur compounds, in the oil.

In summary, it appears that the combination of distilled C_{16-18} biphenyl plus selenide inhibitor and a sulfur-containig EP agent will meet all but the -40° F viscosity requirement. If the temperature is raised to -10° F, the oil should comply. All available data on the C_{16-18} biphenyl were presented in Table II (page vii).

6.5 Future Work

Two base oils, the C_{16-18} biphenyl and diisooctyl terephthalate, have been sent to Southwest Research Institute for micro-Ryder Gear Tests as part of the gas turbine lubricant evaluation work. These results should be valuable in establishing the performance base line for further compounding of these materials with extreme pressure agents to increase their film strength as gear oils.

As yet, neither the Mean Hertz Load data nor the Ryder Gear Test values are available. No estimate of current status is possible until these data are at hand; however, once the physical property requirements for the engine oil are approached, improvement in film strength should be relatively easy. Consolidation of the engine and gear oil into a single product may be accomplished as in current MIL-L-25336 oils.

Future work on gear oils should be concentrated on evaluation of the effect of extreme pressure agents on thermal and radiation stability of potential base stocks. Materials suitable for engine oils should be used as the base stocks from which gear oil blends can be made. The finished products may well be high film strength engine oils.

7. FUEL SURVEY

7.1 Tests on Irradiated Jet Fuels (J. T. Guerin)

7.1.1 Introduction

Effects of gamma radiation on petroleum jet fuels were studied in this phase of the project. The ultimate objective was to predict the level of radiation at which various jet fuels might provide marginal aircraft engine performance. This prediction was to be based on the observed changes in fuel properties as measured in various laboratory tests. In order to obtain adequate information on irradiated fuels, 3.5-gallon samples were used in the work. Three nominal levels of gamma dosage obtained were used: 1, 5, and 10 x 10^8 r.

Previous work[1] in this field indicated radiation damage to jet fuels to be appreciable within the gamma dosage range of 10^8 r to 10 x 10^8 r. Small (12 cc) samples were used in the earlier work and only limited tests by microanalytical techniques were performed. The results obtained, therefore, were subject to the errors associated with these nonstandard tests. Also, some of the important properties of the irradiated samples could not be determined because of the relatively large sample volume which would have been required.

7.1.2 Test Fuels

Eight production fuels were selected for the program of which five were JP-4 type and three were JP-5 type as described in Table LXXVIII. The fuels were chosen to represent different geographical crude petroleum sources so that the results would have as broad an application as possible.

Table LXXVIII

Jet Fuels in Survey

Calif. Res. Fuel No.	Description
J-813	JP-4 West Texas Crude
J-852	JP-4 Salt Lake (Rangely) Crude
J-728	JP-5 type. A highly refined, aromatic-free kerosene from Eastern U.S. Crude (Pratt and Whitney F-112)
J-782	JP-4 Middle East Crude (RAF-105-55)
J-872	JP-4 Mid-Continent Crude (RAF-106-55)
J-771	JP-5 Los Angeles Basin Crude (RAF-104-55)
J-746	Special JP-5 Eastern U.S. Crude (RAF-99-55)
J-770	JP-4 San Joaquin Crude (RAF-107-55)

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[1] "A Survey of the Radiation Stability of Jet Fuels," California Research-AEC Report No. 9 (TID 5366), June 30, 1956 (SECRET).

Fuel J-728 was a special, heavy acid treated, highly paraffinic stock essentially aromatic and olefin free. It was not representative of current JP-5 production fuels but was included in order to confirm the expected pronounced radiation effects on a highly paraffinic fuel. This would be representative of one of the fuel types that has been suggested as a "supersonic" jet fuel.

7.1.3 Test Program

It was planned to obtain maximum information on chemical and physical changes in jet fuels resulting from exposure to radiation. The 1 to 10 x 10^8 r dosages were chosen to bracket the radiation tolerance of the fuels and the original and irradiated samples were tested to determine changes in color, gravity, volatility, heating value, viscosity, hydrocarbon-type composition, hydrogen content, carbon content, refractive index, and gum content.

True boiling point (TBP) distillations were performed on all fuels in order to obtain 10% volume fractions for further tests. A spinning band column was used. It was operated at 20:1 reflux ratio, giving approximately 12.5 theoretical plates. These distillations were conducted under a vacuum of 10 mm Hg for temperatures above 350°F to prevent cracking. Tests of the fractions were made to determine how changes caused by irradiation were distributed in the fuel.

Thermal stability tests using the CFR Fuel Coker are yet to be conducted on all fuels and their irradiated counterparts. It is planned to test all fuels at the same time to prevent errors due to possible drift in coker severity.

7.1.4 Test Results

The results of the laboratory tests on whole fuels and on 10% volume fractions of these are in Tables LXXIX through LXXXIV. A discussion of the effects of radiation on the particular properties of the fuels follows.

Color. - Radiation had a marked effect on color of the fuels. In general, the greater the dosage the darker the fuel color. This was not like the color change which occurs with aging of jet fuels. Aging results in tan and brown colors and irradiation developed yellow coloration.

Volatility. - Both TBP and ASTM D 86 distillations were made, but this discussion is based mainly on TBP data. The D 86 apparatus which is used in jet fuel specification tests is limited to 600°F maximum and is not as sensitive as the spinning band column. Both distillation methods showed the same trends. All TBP temperatures were corrected to 29.92 in Hg.

Figure 30 compares graphically the effect of irradiation on the TBP initial boiling points, 10% points, 50% points, and 80% points for all fuels. Figures 31, 32, 33, 34, 35, and 36 show the changes in TBP distillation curves for the individual fuels. All irradiated fuels showed marked increases in distillation temperatures over the 60% points; the higher the dosage, the higher the resulting distillation temperatures. The irradiated JP-5 fuels showed a reduction in initial boiling point. The JP-4 fuels showed little change in distillation below the 60% points. If lower boiling materials were formed in

TABLE LXXIX

INSPECTIONS ON IRRADIATED[a] JP-4 FUELS

Fuel	J-313 West Texas JP-4				J-352 Salt Lake (Rangely) JP-4			
Gamma Dosage, 10^8 r	0	1.0	5.1	8.5	0	1.0	5.0	7.7
Inspection or Test								
1. Color, Saybolt	+2	+15	0	+15	+30	+17	+16	-6
2. Gravity, °API	53.7	51.4	48.5	44.8	51.0	50.1	47.1	44.7
3. Density,	0.7640	0.7736	0.7861	.8026	0.7753	.7792	0.7923	0.8031
4. Aniline Point	130	126	131	142	140	140	146	154
Aniline-Gravity Product	6981	6476	6354	6362	7140	7014	6877	6884
5. Distillation, D 86								
% Recovered at °F								
Start	152	170	142	156	123	140	136	133
5	213	220	212	216	174	180	190	178
10	233	242	235	241	211	220	230	212
20	259	265	266	272	271	276	282	272
30	274	280	282	290	310	315	328	318
40	286	292	293	304	337	341	358	354
50	300	300	304	320	350	365	375	383
60	310	313	318	346	377	383	400	410
70	319	325	336	400	393	400	427	446
80	336	339	372	460	413	418	468	498
90	351	366	495	Too Heavy	436	446	Too Heavy	Too Heavy
95	368	440	Too Heavy	Too Heavy	449	476	Too Heavy	Too Heavy
End Point	414	470	Too Heavy	Too Heavy	469	508	Too Heavy	Too Heavy
Recovered	98	97.5	Too Heavy	Too Heavy	97	98	Too Heavy	Too Heavy
Residue	1	1.5	Too Heavy	Too Heavy	1	1	Too Heavy	Too Heavy
Loss	1	1	Too Heavy	Too Heavy	2	1	Too Heavy	Too Heavy
6. True Boiling Point Distillation								
Temp., °F at % Dist.								
Start	87	85	88	88	86	82	89	87
10	193	203	196	224	201	195	190	198
20	236	249	239	262	258	255	256	276
30	256	272	264	291	297	314	316	326
40	274	292	285	311	333	342	350	362
50	289	307	303	330	362	366	380	395
60	304	325	322	355	383	391	411	431
70	317	340	338	430	411	421	443	466
80	332	356	379	651	438	443	468	633
90	367	385	582	777	459	470	-	768
95	390	452	709	-	473	506	-	-
Vol. % in Flask	3.4	4.0	5.0	9.1	4.6	3.7	16.0	7.6
7. Hydrocarbon Analysis, FIA Method								
Aromatics, Vol. %	9	2	9	-	11	9	-	-
Olefins, Vol. %	1	16	19	-	Trace	9	-	-
Saturates, Vol %	90	82	72	-	89	82	-	-
8. Aromatics, By Infrared Absorption, Vol. %	9	8	8	7	11	9	9	9
9. Kinematic Viscosity, cs								
At -40°F	2.35	3.04	4.51	9.40	3.31	4.72	8.33	15.02
0°F	1.70	1.86	2.58	4.44	2.31	2.55	4.06	6.43
100°F	0.78	0.84	1.04	1.51	0.96	1.04	1.38	1.75
10. Carbon, Wt. %	85.64	85.85	86.18	85.85	85.33	85.48	85.93	86.20
11. Hydrogen, Wt. %	14.28	14.24	13.84	13.62	14.20	14.63	13.61	14.02
N_H, 10²² atoms/cc	6.61	6.67	6.59	6.62	6.67	6.91	6.53	6.82
12. Refractive Index	1.4289	1.4295	1.4360	1.4450	1.4340	1.4329	1.4402	1.4463
13. Filter Residue, mg/500 ml	1.5	0.5	0.1	(b)	1.9	2.4	0.2	3.2
14. Adherent Gum, mg	-	2.6	2.1	2.5	0	2.1	2.5	3.3
15. Hydrogen/Carbon Wt. Ratio	0.167	0.156	0.161	0.159	0.167	0.171	0.158	0.163
Hydrogen/Carbon Atom Ratio	2.00	1.99	1.93	1.90	2.00	2.05	1.90	1.95
16. Net Heating Value, Btu/lb (calculated)	18,680	18,630	18,620	18,620	18,700	18,685	18,670	18,570

a. [illegible]-gallon quantities exposed in the MTR Canal Gamma Source.

b. Water in sample.

TABLE LXXX

ANALYSIS OF DISTILLED FRACTIONS OF IRRADIATED[a] JP-4 FUELS

Fuel	J-813 West Texas JP-4				J-[illegible]2 Salt Lake (Rangely) JP-4			
Gamma Dosage, 10^8 r	0	1.0	5.1	8.5	0	1.8	2.9	7.7
0-10%								
Gravity, °API	71.6	67.7	70.4	65.6	79.9	76.2	77.9	75.5
Refractive Index	1.3889	1.3899	1.3864	1.3992	1.3736	1.3780	1.3751	1.3819
Hydrogen, Weight %	15.18	15.44	15.57	14.78	15.55	15.22	15.50	15.63
Carbon, Weight %	84.81	84.00	84.36	83.63	80.80	78.78	81.78	83.51
Aromatics, Volume %	-	-	-	2	-	23	-	-
10-20%								
Gravity, °API	58.4	58.0	59.0	56.7	63.0	62.2	63.0	61.6
Refractive Index	1.4138	1.4130	1.4128	1.4152	[illegible]	1.4070	1.4062	1.4061
Hydrogen, Weight %	14.43	14.10	14.37	14.40	14.42	15.59	15.20	14.92
Carbon, Weight %	85.62	85.66	85.54	85.56	81.47	84.50	82.34	85.10
Aromatics, Volume %	5	4	4	4	-	5	5	5
20-30%								
Gravity, °API	55.5	55.4	55.7	50.9	56.6	55.7	56.3	56.0
Refractive Index	1.4202	1.4211	1.4210	1.4251	1.4194	1.4218	1.4212	1.4215
Hydrogen, Weight %	14.69	14.04	14.54	(13.86)	14.50	14.28	14.98	14.20
Carbon, Weight %	85.38	85.96	85.83	(85.11)	85.36	85.55	85.16	84.40
Aromatics, Volume %	5	7	6	7	12	-	10	9
30-40%								
Gravity, °API	52.0	52.6	52.9	53.1	52.0	51.4	51.7	51.1
Refractive Index	1.4296	1.4130	1.4270	1.4207	1.4300	1.4317	1.4309	1.4322
Hydrogen, Weight %	13.56	13.90	14.12	(13.86)	14.20	14.33	14.31	14.01
Carbon, Weight %	85.01	85.90	85.62	(85.11)	85.86	85.77	85.59	85.66
Aromatics, Volume %	12	10	9	4	19	11	15	11
40-50%								
Gravity, °API	52.2	52.5	53.0	50.2	49.1	48.5	49.4	47.3
Refractive Index	1.4291	1.4275	1.4270	1.4329	1.4359	1.4370	1.4357	1.4392
Hydrogen, Weight %	14.56	14.35	14.28	14.36	14.04	14.22	14.23	14.26
Carbon, Weight %	85.31	85.75	85.70	85.78	85.75	85.85	85.46	85.62
Aromatics, Volume %	7	7	5	9	17	17	11	9
50-60%								
Gravity, °API	50.7	50.4	49.9	48.9	46.6	46.2	46.9	45.8
Refractive Index	1.4318	1.4324	1.4342	1.4309	1.4413	1.4424	1.4409	1.4431
Hydrogen, Weight %	14.42	14.12	13.68	14.06	14.22	13.98	14.06	13.76
Carbon, Weight %	85.68	85.83	86.33	86.00	85.78	85.82	85.68	86.07
Aromatics, Volume %	11	11	11	7	15	12	9	7
60-70%								
Gravity, °API	48.5	48.2	48.8	46.3	43.5	44.8	45.1	44.1
Refractive Index	1.4388	1.4385	1.4271	1.4419	1.4488	1.4458	1.4448	1.4470
Hydrogen, Weight %	13.76	13.92	14.04	13.04	14.23	13.66	14.18	14.30
Carbon, Weight %	86.24	85.88	86.09	85.94	85.94	86.40	86.08	85.63
Aromatics, Volume %	7	14	9	6	12	10	7	4
70-80%								
Gravity, °API	47.7	47.3	45.4	34.6	45.0	45.5	43.1	39.7
Refractive Index	1.4394	1.4399	1.4412	1.4735	1.4452	1.4485	1.4408	1.4589
Hydrogen, Weight %	13.88	14.06	13.72	13.04	14.05	13.82	13.79	13.95
Carbon, Weight %	86.24	86.00	85.89	86.44	86.10	85.66	86.30	85.90
Aromatics, Volume %	11	9	13	10	10	-	5	5
80-90%								
Gravity, °API	46.6	46.1	40.8	27.6	41.9	42.0	41.2	30.7
Refractive Index	1.4413	1.4429	1.4562	1.4950	1.4530	1.4522	1.4552	1.4873
Hydrogen, Weight %	13.89	14.04	13.62	11.95	13.74	13.91	14.02	12.91
Carbon, Weight %	86.08	86.02	86.06	86.90	85.77	85.88	85.96	86.87
Aromatics, Volume %	10	10	8	11	9	7	8	20
90-								
Gravity, °API	43.5	44.5	29.8		41.3	40.7		26.2
Refractive Index	1.4486	1.4469	1.4901		1.4548	1.4579		1.4983
Hydrogen, Weight %	14.27	13.90	12.56		13.84	12.56		12.47
Carbon, Weight %	85.76	85.74	87.22		85.42	87.21		87.20
Aromatics, Volume %	14	7	15		8	10		24

a. 3.5-gallon quantities exposed in the MTR canal gamma source

TABLE LXXXI

INSPECTIONS ON AN IRRADIATED[a] JP-4 AND A JP-5 FUEL

Fuel	J-728 Heavy Acid Treated JP-5 Type				J-782 Middle East JP-4			
Gamma Dosage, 10^8 r	0	0.87	5.29	8.90	0	1.66	5.20	9.52
Inspection or Test								
1. **Color**	+28	+15	B-16	B-16	+13	+2	B-16	B-16
2. **Gravity**, °API	48.2	47.5	44.2	41.6	50.4	49.7	46.6	43.6
3. **Density**	0.7874	0.7905	0.8054	0.8174	0.7779	0.7809	0.7945	0.8081
4. **Aniline Point**	178	179	193	205	138	138	143	149
5. **Distillation**, D 86								
% Recovered at °F								
Start	398	391	272	210	120	126	130	133
5	409	410	403	270	169	163	165	182
10	416	416	410	325	203	198	205	216
20	423	423	423	423	258	258	268	282
30	429	431	430	438	309	302	313	332
40	434	436	449	451	339	336	348	371
50	439	442	460	472	364	364	378	395
60	444	449	476	509	384	385	406	436
70	449	457	506	559	404	407	434	483
80	457	466	564	77% at 600	430	432	473	547
90	468	489	86% at 600		466	477	501	89% at 600
95	477	531			503	523		
End Point	491	553			527	567		
Recovered	98	98			97.5	98		
Residue	1.5	1			1.5	1		
Loss	0.5	1			1	1		
6. **TBP Distillation**								
Temp. °F at % Dist.								
Start	366	175	159	136	94	83	87	87
10	409	397	390	396	194	194	207	194
20	425	421	418	430	256	257	273	265
30	439	439	433	449	319	315	312	327
40	446	455	448	468	349	338	342	369
50	459	462	460	483	377	377	373	407
60	466	465	477	515	402	401	398	441
70	476	480	495	700	433	426	428	508
80	488	493	690	776	457	457	496	653
90	500	513	729	-	502	517	652	783
95	512	756	-	-	517	569	-	-
Volume % in Flask	4.2	4.6	5.6	14.6	5.0	4.8	5.0	8.6
7. **Hydrocarbon Analysis**								
FIA Method								
Aromatics, Volume %	0	4	0	too hvy	12	12	too hvy	too hvy
Olefins, Volume %	0	3	16	too hvy	3	8	too hvy	too hvy
Saturates, Volume %	100	93	84	too hvy	85	80	too hvy	too hvy
8. **Aromatics**, by Infrared Absorption, Volume %	nil	nil	nil	nil	-	6	5	6
9. **Kinematic Viscosity, Centistokes**								
At -40°F	Fr at -28°F	at -25°F 14.1[b]	freezes	180	4.25	4.83	8.36	16.7
At 0°F	0.94	7.93	17.7	40.6	2.38	2.60	4.08	7.02
At 100°F	1.86	1.95	3.28	5.39	1.02	1.06	1.41	2.00
10. **Carbon**, Weight %	85.1	85.1	85.9	85.7	85.6	85.4	85.9	86.3
11. **Hydrogen**, Weight %	14.9	14.9	14.1	14.3	14.4	14.6	14.1	13.7
n_H, 10^{22} atoms/cc	7.11	7.14	6.89	7.04	6.79	6.91	6.79	7.13
12. **Refractive Index**	1.4360	1.4379	1.4462	1.4530	1.4367	1.4345	1.4429	1.4508
13. **Filter Residue**, mg/500 ml	0.8	1.4	0.2	2.3	0.9	2.1	3.2	2.3
14. **Adherent Gum**, mg	-	10.6	0.8	7.6	-	10.3	0.3	11.8
15. **Aniline-Gravity Constant**	8580	8502	8531	8528	6955	6859	6664	6496
16. **Net Heating Value, Btu/Pound (calculated)**	18,840	18,830	18,835	18,835	18,715	18,705	18,680	18,660

a. 3.5-gallon quantities exposed in the MTR Canal Gamma Source.
b. Frozen at -40°F.

TABLE LXXXII

ANALYSIS OF DISTILLED FRACTIONS OF AN IRRADIATED[a] JP-4 AND A JP-5 FUEL

Fuel	J-728 Heavy Acid Treated JP-5 Type				J-782 Middle East JP-4			
Gamma Dosage, 10^8 r	0	0.87	5.20	8.90	0	1.06	5.20	9.52
0-10%								
Gravity, °API	52.0	54.5	55.4	56.4	81.8	78.9	71.4	77.8
Refractive Index	1.4272	1.4235	1.4198	1.4152	1.3730	1.3781	1.3890	1.3778
Hydrogen, Weight %	14.9	14.7	15.8	15.8	17.1	17.2	15.6	14.8
Carbon, Weight %	85.1	85.3	84.2	84.2	82.9	82.8	84.4	85.2
Aromatics, Volume %	nil	nil	nil	nil	nil	nil	1	nil
10-20%								
Gravity, °API	50.2	51.7	50.5	51.9	63.1	63.3	60.0	63.2
Refractive Index	1.4323	1.4300	1.4319	1.4303	1.4068	1.4062	1.4135	1.4075
Hydrogen, Weight %	14.7	14.6	14.5	15.0	15.6	15.1	15.5	15.4
Carbon, Weight %	85.3	85.4	85.5	85.0	84.4	84.9	84.5	84.6
Aromatics, Volume %	nil	nil	nil	nil	6	11	6	5
20-30%								
Gravity, °API	42.9[b]	50.5	49.7	50.3	56.3	55.8	54.0	55.7
Refractive Index	1.4344	1.4325	1.4343	1.4337	1.4220	1.4235	1.4270	1.4239
Hydrogen, Weight %	10.7[b]	14.5	14.8	15.9	15.1	14.7	14.7	14.9
Carbon, Weight %	89.3[b]	85.5	85.2	84.1	84.9	85.3	85.3	85.1
Aromatics, Volume %	nil	nil	nil	nil	10	6	10	8
30-40%								
Gravity, °API	49.0	49.4	49.0	49.3	51.9	52.1	51.3	51.3
Refractive Index	1.4352	1.4350	1.4359	1.4360	1.4331	1.4320	1.4330	1.4327
Hydrogen, Weight %	14.9	15.4	14.8	15.2	14.7	14.7	14.4	14.8
Carbon, Weight %	85.1	84.6	85.2	84.8	85.3	85.3	85.6	85.2
Aromatics, Volume %	nil	nil	nil	nil	13	12	8	8
40-50%								
Gravity, °API	48.2	48.9	48.5	48.0	50.2	49.5	47.3	48.2
Refractive Index	1.4365	1.4365	1.4370	1.4389	1.4363	1.4372	1.4413	1.4392
Hydrogen, Weight %	14.5	14.4	14.6	15.1	14.5	14.5	14.5	22.8•
Carbon, Weight %	85.5	85.6	85.4	84.9	85.5	85.5	85.5	77.2•
Aromatics, Volume %	nil	nil	nil	nil	11	8	6	5
50-60%								
Gravity, °API	48.1	47.4	47.8	45.8	47.4	46.3	45.8	45.8
Refractive Index	1.4375	1.4390	1.4385	1.4433	1.4412	1.4434	1.4441	1.4440
Hydrogen, Weight %	14.8	14.5	14.7	15.0	14.4	14.0	14.7	14.7
Carbon, Weight %	85.2	85.5	85.3	85.0	85.6	86.0	85.3	85.3
Aromatics, Volume %	nil	nil	nil	nil	4	7	2	3
60-70%								
Gravity, °API	47.9	45.4	42.2	41.4	45.1	45.2	43.5	40.9
Refractive Index	1.4378	1.4424	1.4399	1.4539	1.4400	1.4459	1.4483	1.4540
Hydrogen, Weight %	14.7	14.7	14.7	20.1[b]	14.4	14.3	14.6	12.1
Carbon, Weight %	85.3	85.3	85.3	79.9[b]	85.6	85.7	85.4	87.9
Aromatics, Volume %	nil	nil	nil	<1	6	6	3	11
70-80%								
Gravity, °API	47.2	46.4	41.7	35.2	41.1	43.4	37.0	34.2
Refractive Index	1.4389	1.4411	1.4532	1.4704	1.4541	1.4490	1.4631	1.4736
Hydrogen, Weight %	14.4	14.1	13.9	13.6	13.7	14.5	13.7	13.3
Carbon, Weight %	85.6	85.9	86.1	85.4	86.3	85.5	86.3	86.7
Aromatics, Volume %	nil	nil	nil	nil	5	4	4	5
80-90%								
Gravity, °API	47.1	47.1	35.9	33.9	38.3	38.5	29.0	27.8
Refractive Index	1.4378	1.4403	1.4686	1.4756	1.4610	1.4598	1.4913	1.4962
Hydrogen, Weight %	14.4	14.3	13.1	13.3	13.9	13.6	12.5	12.2
Carbon, Weight %	85.6	85.7	86.9	86.7	86.1	86.4	87.5	87.8
Aromatics, Volume %	nil	nil	2	2	5	4	11	3
90-								
Gravity, °API	47.1	41.1	33.4	solid ↓	34.4	solid ↓	solid ↓	solid ↓
Refractive Index	1.4400	1.4543	1.4750		1.4591			
Hydrogen, Weight %	14.5	14.5	13.2		13.1			
Carbon, Weight %	85.5	85.5	86.8		86.9			
Aromatics, Volume %	nil	<1	nil					

a. 3.5-gallon quantities exposed in the MTR Canal Gamma Source.
b. Being rechecked.

TABLE LXXXIII

INSPECTIONS ON IRRADIATED[a] JET FUELS (J-872, J-771)

Fuel	J-872 Mid-Continent JP-4				J-771 Los Angeles JP-5			
Gamma Dosage, 10^8 r	0	1.08	5.32	7.57	0	0.90	4.91	8.31
Inspection or Test								
1. Color, Saybolt	+18	-1	B-16	B-16	+4	-7	B-16	B-16
2. Gravity, °API	53.8	52.8	48.8	45.9	37.5	37.2	35.4	33.6
3. Density,	0.7636	0.7678	0.7848	0.7976	0.8375	0.8388	0.8478	0.8571
4. Aniline Point	132	131	139	149	134	134	137	146
Aniline-Gravity Product	7102	6917	6783	6839	5025	4985	4850	4906
5. Distillation, D 86								
% Recovered at °F								
Start	148	150	157	131	360	357	336	285
5	198	184	212	157	382	371	377	359
10	232	232	256	236	390	388	384	389
20	276	275	278	278	402	400	401	406
30	290	296	283	296	414	414	418	421
40	298	302	292	307	424	424	431	438
50	308	308	305	321	434	434	449	455
60	312	316	322	344	446	444	462	480
70	318	325	346	423	460	460	484	518
80	330	341	436	544	478	478	518	574
90	368	410	572	604	498	506	606	84% At 600°F
95	432	506	93% At 600°F	Too Heavy	522	535	Too Heavy	
End Point	475	520			540	549		
Recovered	98	98	93		98	98		
Residue	1	1	3		1	1		
Loss	1	1	2		1	1		
6. True Boiling Point Distillation								
Temp., °F at % Dist.								
Start	86	89	91	91	238	257	243	174
10	160	172	210	194	360	355	358	357
20	276	277	288	287	387	378	384	388
30	292	294	299	300	407	400	415	418
40	296	301	306	308	425	422	431	442
50	306	308	316	322	442	441	452	466
60	317	317	329	341	457	459	475	493
70	329	329	348	454	482	478	502	536
80	341	343	474	632	502	501	544	686
90	398	424	681	794	530	535	709	778
95	454	478	93.7% At 771°F		554	571	784	91.3% At 784°F
Vol. % in Flask	5.0	4.8	6.3	8.3	5.2	4.6	5.0	8.6
7. Hydrocarbon Analysis, FIA Method								
Aromatics, Vol. %	8	8	(76)	Too Heavy To Run	22	23	Too Heavy To Run	Too Heavy To Run
Olefins, Vol. %	1	6	(0)		Trace	0		
Saturates, Vol. %	91	86	(24)		78	77		
8. Aromatics, by Infrared Absorption, Vol. %								
9. Kinematic Viscosity, cs								
At -40°F	2.732	3.140	5.475	11.10	18.18	23.00	47.00	117.9
0°F	1.668	1.888	3.001	5.004	7.011	7.991	13.66	29.37
100°F	0.7850	0.8445	1.162	1.714	1.900	1.973	2.703	4.259
10. Carbon, Wt. %	85.5	84.6	85.8	86.2	86.5	85.9	86.7	86.8
11. Hydrogen, Wt. %	14.4	15.3	14.1	13.7	13.2	13.8	13.0	12.9
N_H, 10^{22} Atoms/cc	6.67	7.12	6.71	6.63	6.70	7.02	6.68	6.70
12. Refractive Index	1.4267	1.4267	1.4373	1.4451	1.4619	1.4629	1.4682	1.4743
13. Filter Residue, mg/500 ml	2.4	3.7	9.2	0	4.0	2.7	3.0	0.4
14. Adherent Gum, mg	-	8.5	27.1	26.0	-	4.9	13.5	58.9
15. Aniline-Gravity Constant	7102	6917	6783	6839	5020	4985	4850	4906
16. Net Heating Value, Btu/lb (calculated)	18,720	18,700	18,690	18,695	18,445	18,440	18,425	18,430

a. 3.5-gallon quantities exposed in the MTR Canal Gamma Source.

TABLE LXXXIV

ANALYSIS OF DISTILLED FRACTIONS OF IRRADIATED[a] JET FUELS (J-782, J-771)

Fuel	J-872 Mid-Continent JP-4				J-771 Los Angeles JP-5			
Gamma Dosage, 10^8 r	0	1.08	5.32	7.57	0	0.90	4.91	8.31
0-10%								
Gravity, °API	76.0	80.6	73.4	76.0	42.6	47.1	47.5	49.5
Refractive Index	1.3705	1.3750	1.3864	1.3781	1.4432	1.4384	1.4371	1.4322
Hydrogen, Wt. %	16.3	15.4	17.2	15.5	12.5	14.2	13.8	14.6
Carbon, Wt. %	83.6	84.5	82.7	84.4	87.2	85.5	85.9	85.1
10-20%								
Gravity, °API	54.3	60.6	57.7	59.4	39.3	42.0	41.8	42.5
Refractive Index	1.4107	1.4098	1.4174	1.4130	1.4509	1.4490	1.4496	1.4489
Hydrogen, Wt. %	(11.4)	15.2	16.0	14.8	12.0	14.0	13.7	13.6
Carbon, Wt. %	(88.5)	84.7	83.9	85.1	87.7	85.7	86.0	86.1
20-30%								
Gravity, °API	54.5	54.3	55.3	55.5	39.5	40.0	39.9	40.2
Refractive Index	1.4235	1.4244	1.4219	1.4215	1.4564	1.4548	1.4550	1.4547
Hydrogen, Wt. %	14.9	14.9	14.9	15.1	13.6	13.9	13.6	12.9
Carbon, Wt. %	85.1	85.0	85.0	84.8	86.1	85.8	86.1	86.9
30-40%								
Gravity, °API	55.0	54.9	55.0	55.3	38.4	38.4	39.1	39.6
Refractive Index	1.4229	1.4232	1.4227	1.4228	1.4598	1.4587	1.4571	1.4560
Hydrogen, Wt. %	15.4	15.1	15.0	15.2	13.2	13.1	13.3	13.4
Carbon, Wt. %	84.5	84.8	84.9	84.7	86.5	86.5	86.4	86.3
40-50%								
Gravity, °API	54.4	54.3	53.6	52.9	38.1	38.6	38.6	38.8
Refractive Index	1.4229	1.4240	1.4263	1.4279	1.4600	1.4590	1.4589	1.4583
Hydrogen, Wt. %	14.9	15.2	15.5	15.1	13.4	13.4	13.2	13.5
Carbon, Wt. %	85.0	84.7	84.4	84.8	86.3	86.3	86.5	86.2
50-60%								
Gravity, °API	52.3	52.3	53.6	50.8	37.0	37.3	38.3	37.9
Refractive Index	1.4291	1.4283	1.4323	1.4326	1.4643	1.4630	1.4615	1.4622
Hydrogen, Wt. %	14.8	14.8	16.2	14.5	13.6	13.7	13.6	14.0
Carbon, Wt. %	85.1	85.1	83.7	85.4	86.1	86.0	86.1	85.7
60-70%								
Gravity, °API	50.0	49.1	50.4	47.6	37.1	36.0	36.9	36.7
Refractive Index	1.4349	1.4343	1.4334	1.4396	1.4652	1.4642	1.4655	1.4657
Hydrogen, Wt. %	14.5	14.2	13.4	14.2	13.4	12.9	13.1	13.6
Carbon, Wt. %	85.4	85.7	86.5	85.7	86.3	86.8	86.6	86.1
70-80%								
Gravity, °API	49.2	49.2	46.0	37.8	35.3	36.1	35.7	32.2
Refractive Index	1.4372	1.4364	1.4430	1.4654	1.4706	1.4683	1.4686	1.4804
Hydrogen, Wt. %	14.7	14.2	14.0	13.7	13.2	13.2	14.3	12.7
Carbon, Wt. %	85.2	85.7	85.9	86.2	86.5	86.5	85.4	87.0
80-90%								
Gravity, °API	49.4	47.8	35.9	29.0	34.7	35.5	30.2	23.9
Refractive Index	1.4359	1.4402	1.4710	1.4928	1.4720	1.4702	1.4870	1.5091
Hydrogen, Wt. %	14.1	14.5	(8.1)	12.4	12.8	13.1	12.3	11.2
Carbon, Wt. %	85.8	85.4	91.8	87.5	86.9	86.6	87.4	88.5
90- %								
Gravity, °API	44.1	42.9	25.6	-	33.4	34.4	21.4	-
Refractive Index	1.4483	1.4537	1.5000	-	1.4758	1.4731	1.5196	-
Hydrogen, Wt. %	13.9	14.0	11.8	-	12.6	13.4	13.8	-
Carbon, Wt. %	86.0	85.9	88.1	-	87.1	86.3	85.9	-

a. 5.5-gallon quantities exposed in the MTR Canal Gamma Source.

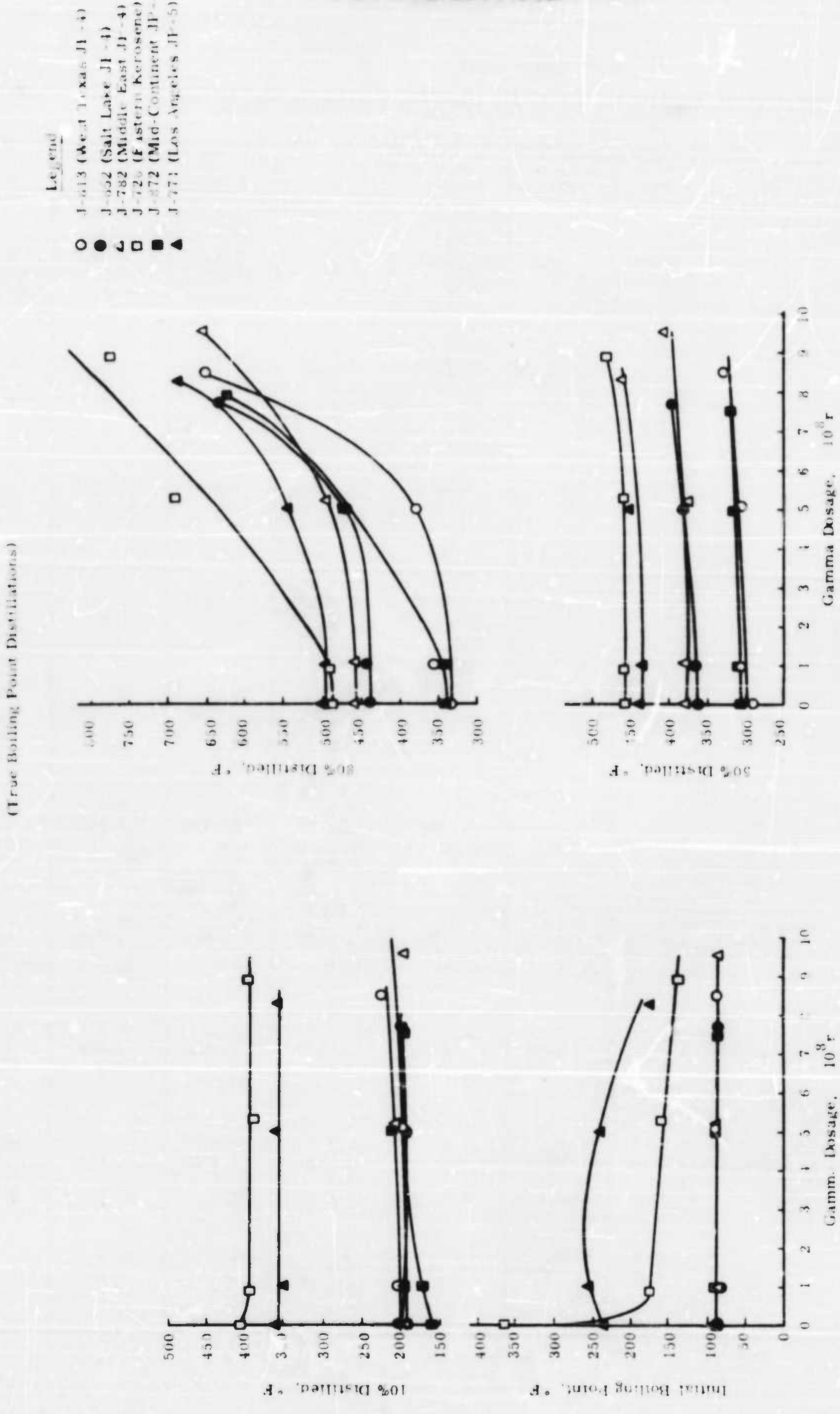


FIG. 30 - EFFECT OF RADIATION ON VOLATILITY OF JET FUELS (FOUR JP-4, ONE JP-5, AND ONE KEROSENE TYPE)

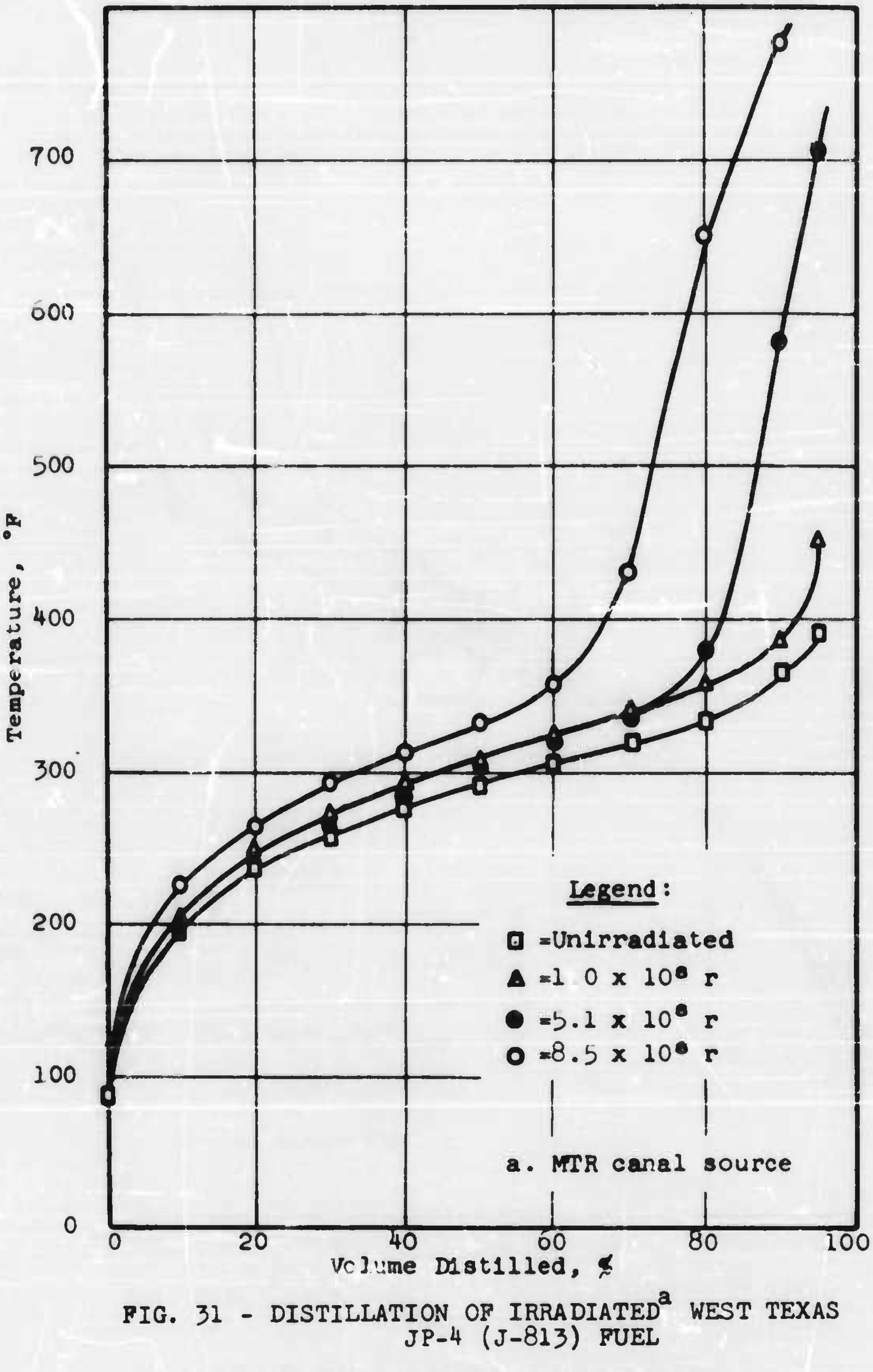


FIG. 31 - DISTILLATION OF IRRADIATED[a] WEST TEXAS JP-4 (J-813) FUEL

(True Boiling Point Method

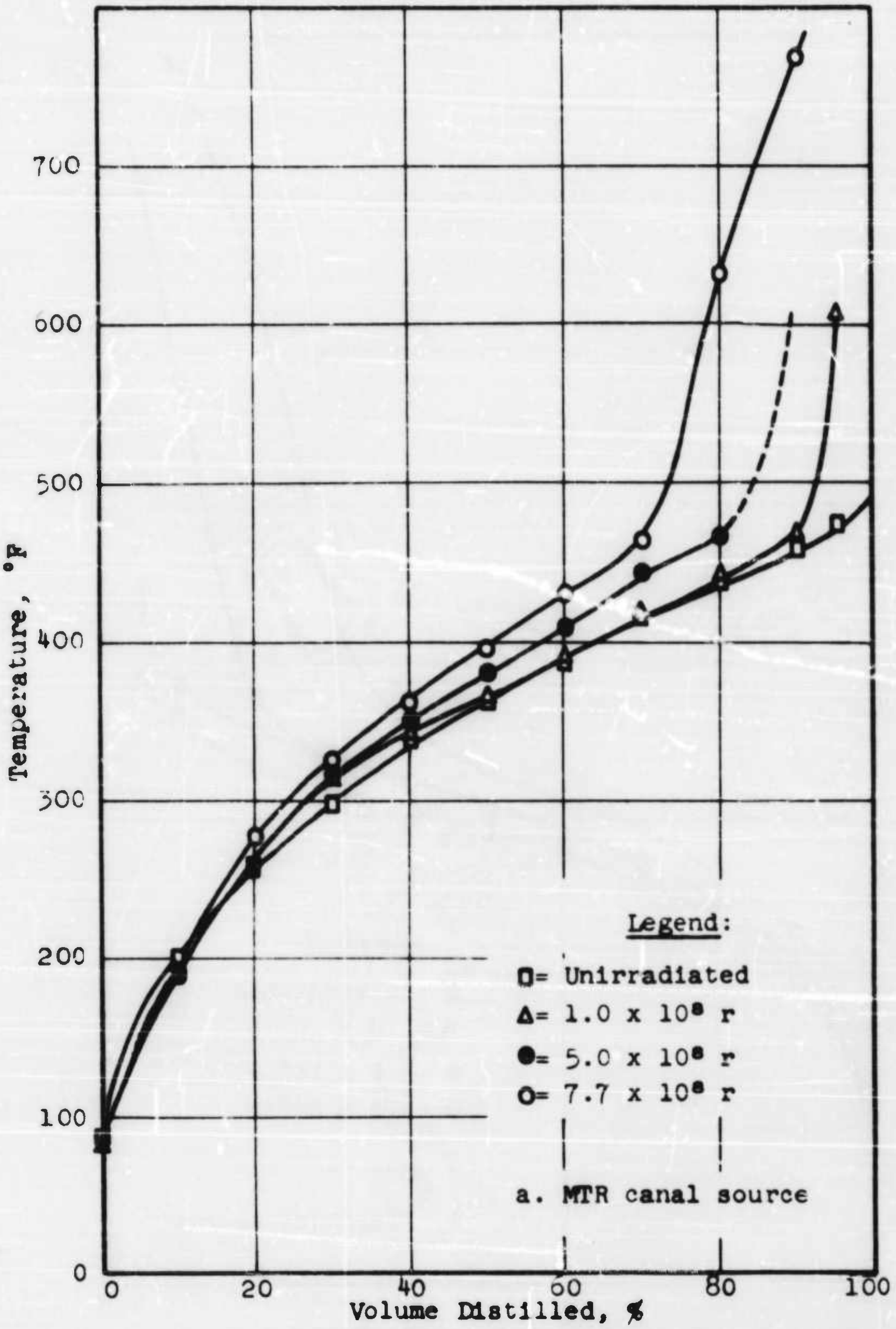


FIG. 32 - DISTILLATION OF IRRADIATED[a] SALT LAKE JP-4 (J-852) FUEL

(True Boiling Point Method)

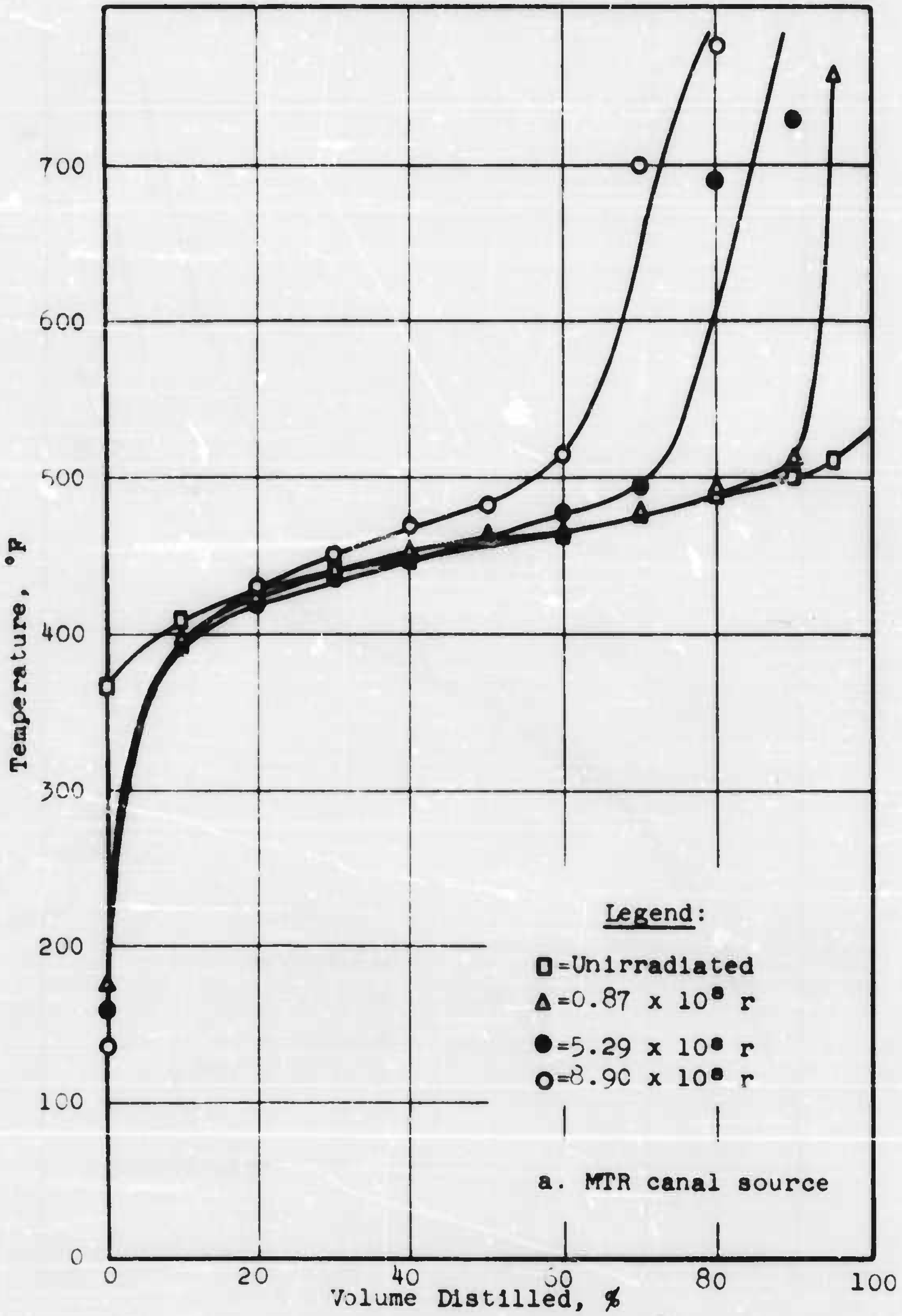
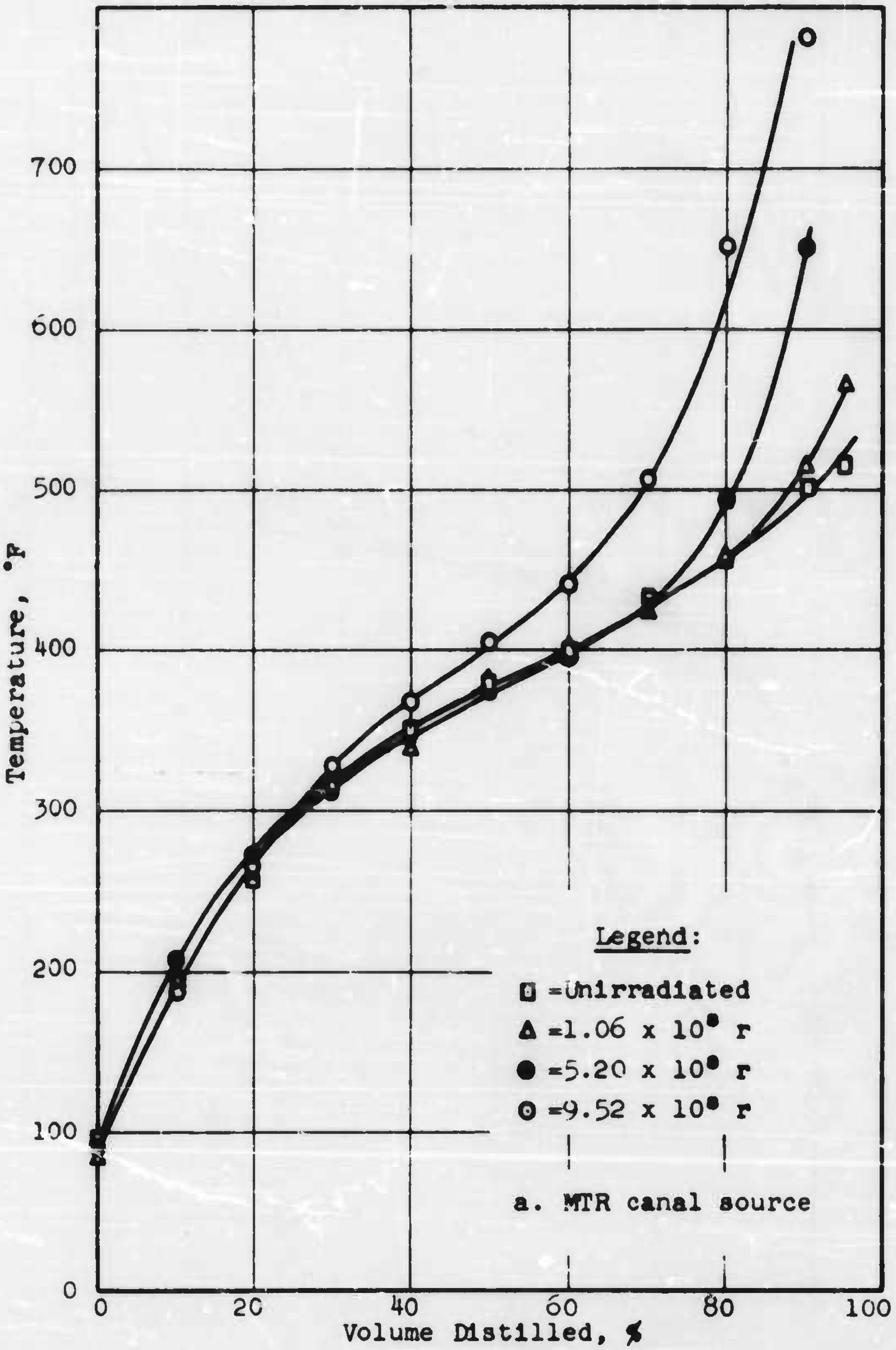


FIG. 33 - DISTILLATION OF IRRADIATED[a] KEROSENE-TYPE FUEL (J-728)

(True Boiling Point Method



a. MTR canal source

FIG. 34 - DISTILLATION OF IRRADIATED[a] MIDDLE EAST JP-4 (J-782) FUEL

(True Boiling Point Method

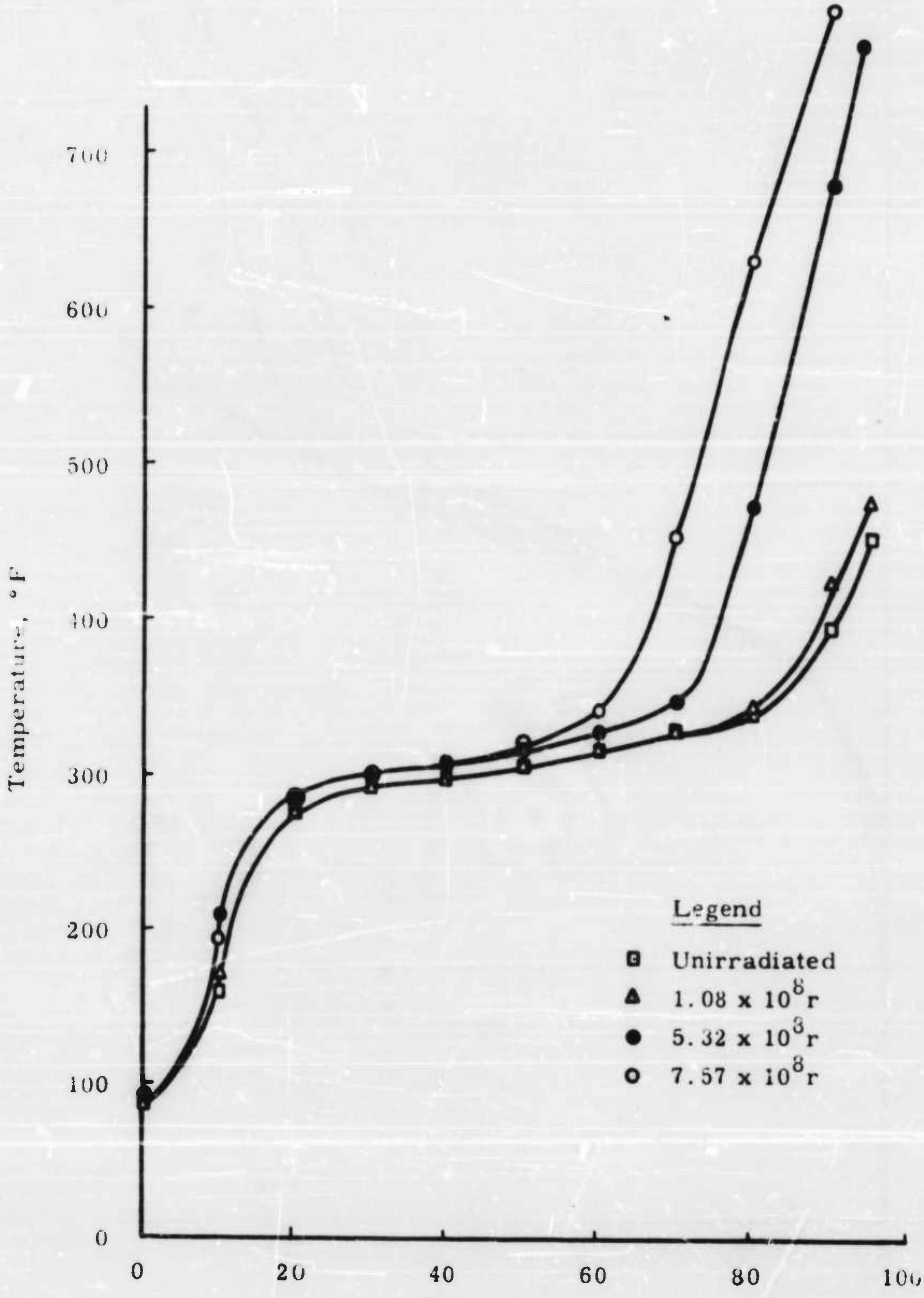


FIG. 35 - DISTILLATION OF IRRADIATED MID-CONTINENT JP-4 (J-872) FUEL
(TRUE BOILING POINT METHOD)

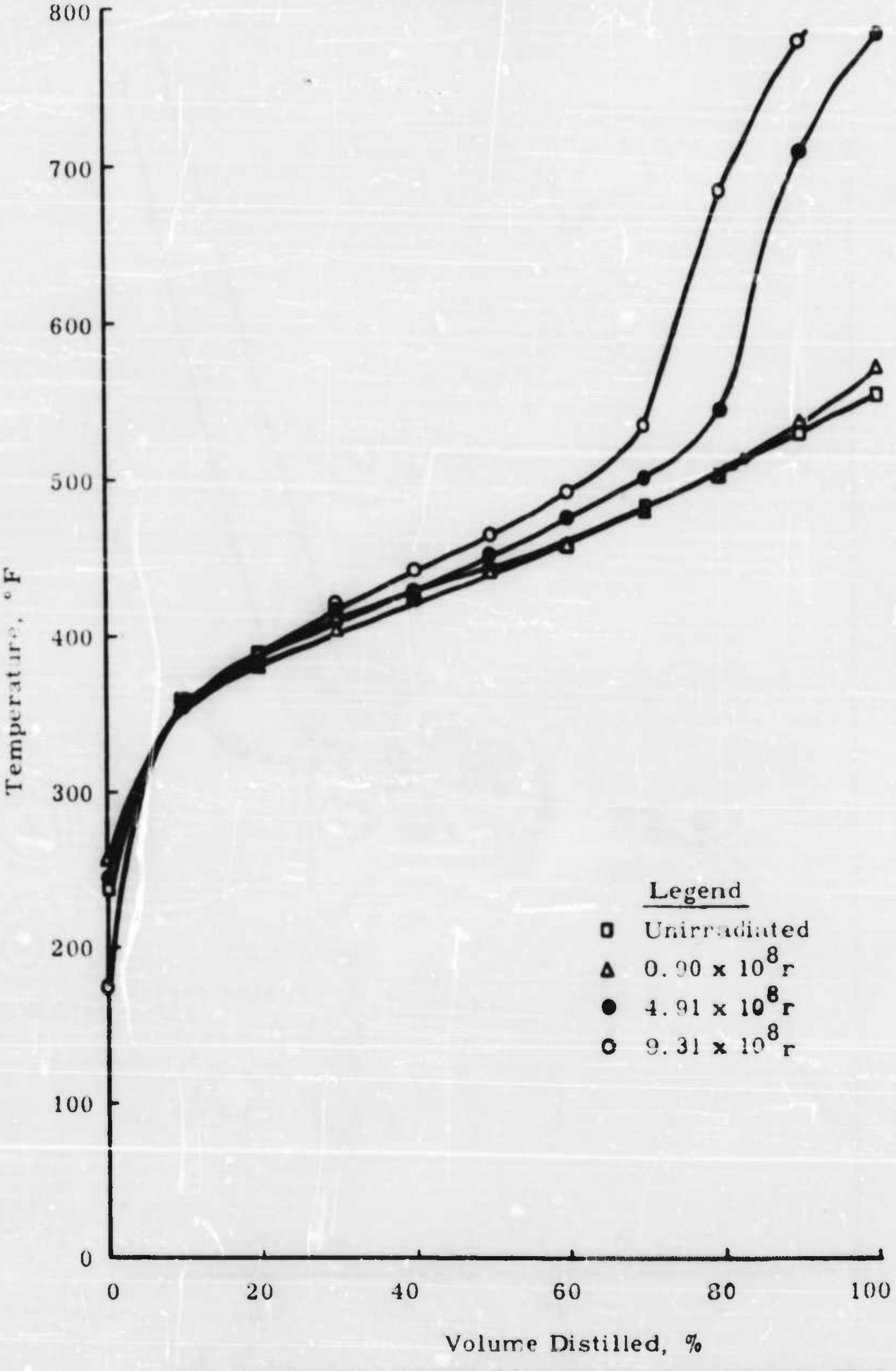


FIG. 36 DISTILLATION OF IRRADIATED JP-5 (J-771) TYPE FUEL (TRUE BOILING POINT METHOD)

the JP-4 fuels, as is believed to be the case, all products boiling below the canal temperature would be lost through the vent on the irradiation container (see later section entitled "Fuel Loss From Irradiation").

Figure 37 shows the effect of aromatics on volatility caused by irradiation. Changes in D 86 distillation temperatures for the zero aromatic J-728 and the 22% aromatic J-771 at about 10^8 r are given. The aromatics reduced the formation of higher boiling materials, i.e., enhanced radiation stability.

Heating Value. - Values for the fuels were calculated by the aniline point-gravity product correlation. No great changes were anticipated and the bomb calorimeter method was not considered precise enough to show these. Figure 38 gives plots of API gravity, aniline point, aniline-gravity product and calculated net heating value for the six fuels at all radiation levels. It may be noted that gravity fell off uniformly with increasing dosage while aniline point increased with irradiation. Because of the compensation in these two values, calculated heating value changed very little. The maximum loss in heating value was only 0.3% observed with J-813.

Hydrogen and Carbon Content. - Two methods of analysis for hydrogen were used. The one employed on fuels J-813 and J-852 was a combustion method which was found to be unsuitable for the volatile distilled fractions. Equipment for a beta-ray method of hydrogen analysis was installed for use on fuels J-728, J-782, J-872, and J-771. (See Appendix XII for a description of this method.) J-813 after a dosage of 1.0×10^8 r was analyzed for hydrogen by both methods so that a comparison was available. Table LXXXV gives the hydrogen content determined by both methods.

Table LXXXV

Hydrogen Analyses of J-813 and Its Fractions (Dosage = 1.0×10^8 r)

Fraction	Hydrogen, Wt. Per Cent		Difference
	Lamp Method	Beta-Ray Method	
Whole Fuel	14.24	14.82	+0.58
0-10%	15.44	16.38	+1.06
10-20%	14.10	14.83	+0.73
20-30%	14.04	13.53	-0.51
30-40%	13.90	14.79	+0.89
40-50%	14.35	14.93	+0.58
50-60%	14.12	14.99	+0.87
60-70%	13.92	14.02	+0.10
70-80%	14.06	14.14	-0.08
80-90%	14.04	21.74	+7.70
90-	13.90	22.27	+8.37

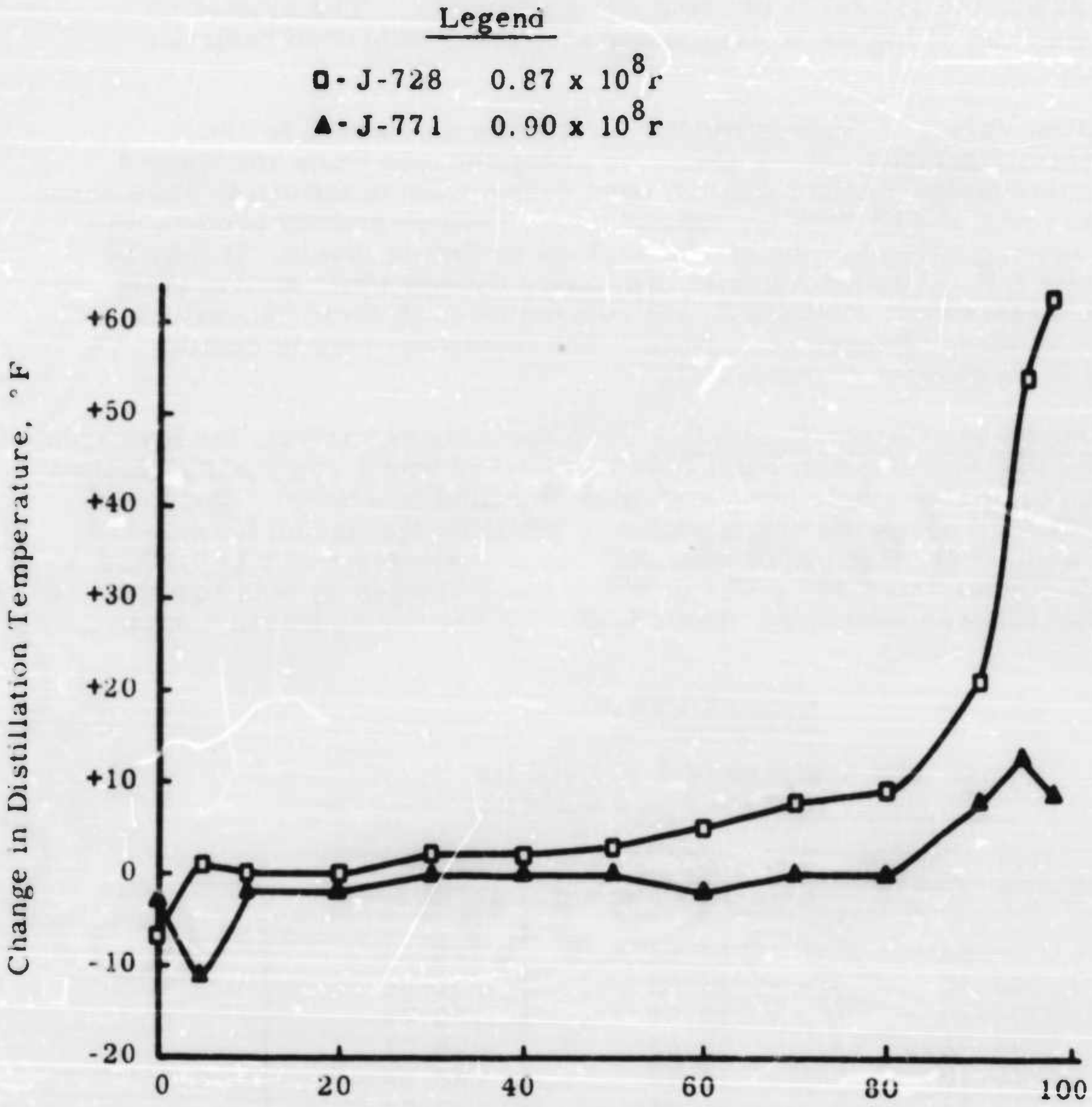


FIG. 37 - CHANGE IN ASTM D 86 DISTILLATION TEMPERATURES CAUSED BY GAMMA IRRADIATION [SHOWING MORE PRONOUNCED CHANGE IN A ZERO AROMATIC FUEL (J-728) AS COMPARED TO A 22% AROMATIC FUEL (J-771)]

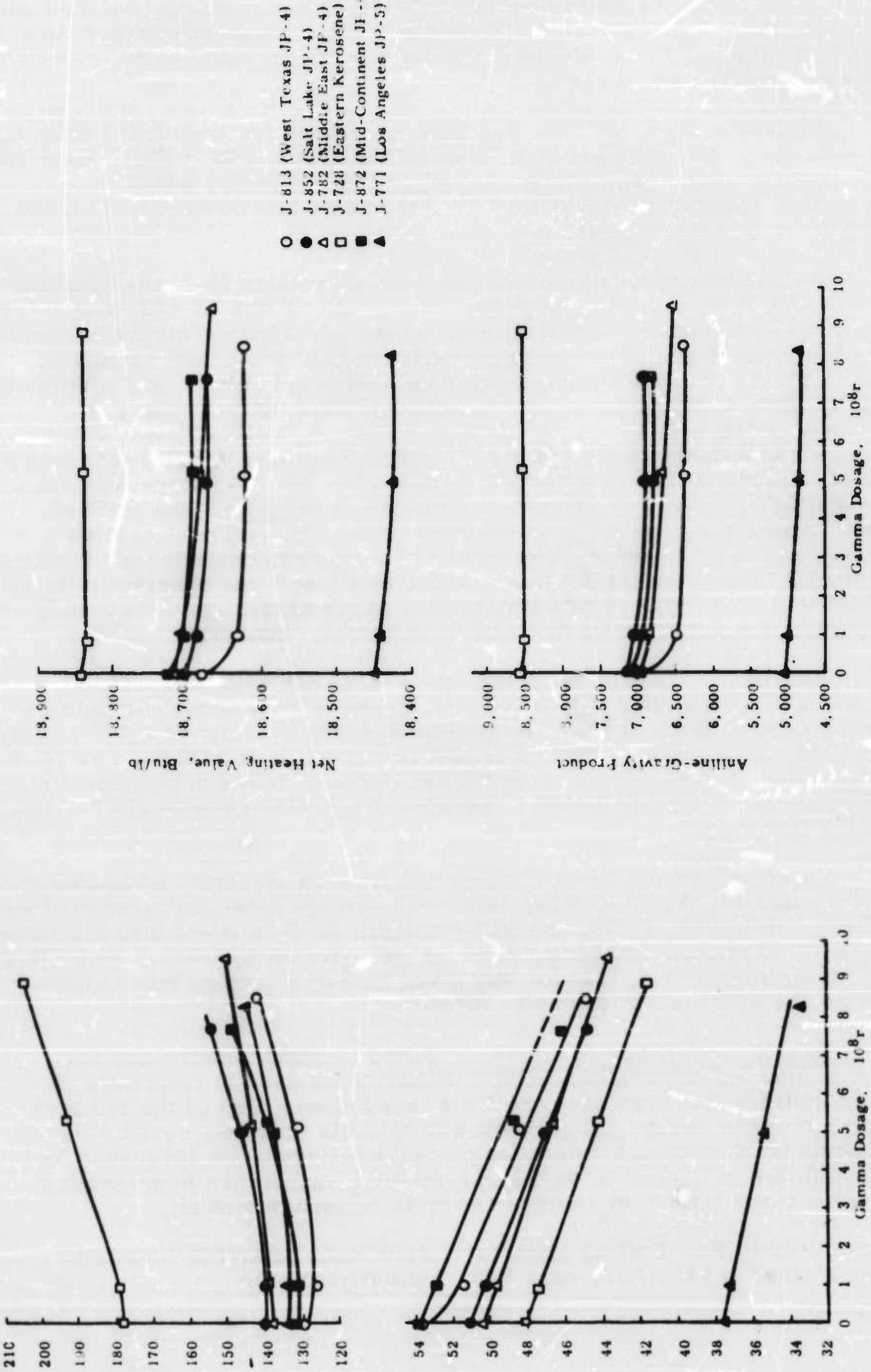


FIG. 38 - EFFECT OF IRRADIATION ON API GRAVITY, ANILINE POINT, ANILINE-GRAVITY PRODUCT, AND NET HEATING VALUE OF JET FUELS (FOUR JP-4, ONE KEROSENE, AND ONE JP-5 TYPE JET FUELS)

Poor agreement between the two methods is shown particularly with the high boiling fractions. The beta-ray method values are consistently higher than the lamp method values. The extremely high values for the last two fractions may result from a calibration error.

Hydrogen atom content, N_H, was calculated for each fuel before and after irradiation. The data are in Tables LXXIX (page 136), LXXXI (page 138), and LXXXIII (page 140). Only small changes in this property, which is proportional to neutron shielding ability, were noted and no consistent trend resulting from irradiation was apparent.

Hydrogen/carbon atomic ratios were calculated from the hydrogen and carbon analyses on J-813 and J-852. On J-728, J-782, J-872, and J-771 the carbon was determined by difference, taking into consideration the sulfur content of the base fuel. The hydrogen/carbon ratios were then calculated by dividing weight per cent hydrogen by weight per cent carbon and multiplying by 12.

Figure 39 shows the hydrogen/carbon atomic ratio for J-813 as a function of average boiling point of the distilled fractions from the original fuel and the three irradiated samples. Changes in ratio were not marked within the boiling range of the original unirradiated fuel. The data show a downward trend in hydrogen/carbon ratio which continues into the high boiling point material formed by irradiation. This same trend was observed with all six of the fuels. The lower hydrogen/carbon ratios of the fractions boiling over 500° F indicate the composition of these to be largely unsaturates.

Viscosity. - All fuels increased in viscosity with increased gamma dosage. A fuel viscosity of 10 centistokes is considered a maximum for starting a turbojet engine. After gamma dosages of about 10×10^8 r, only one of the four JP-4 fuels, J-813, met this requirement at -40° F. The JP-5 types, J-723 and J-771, did not meet the requirement in the unirradiated state at -40° F. All JP-4 type fuels were satisfactory in this respect after a dosage of about 5×10^8 r.

Figure 40 shows the effect of irradiation on viscosity measured at -40° F, 0° F, and 100° F, A similar, viscosity-dosage relationship existed for all six fuels. However, J-771, the 22% aromatic JP-5, showed less viscosity increase with increasing dosage than did the zero aromatic J-728. From this it was concluded tentatively that for any given radiation dosage less change in viscosity should result in aromatic fuels.

Hydrocarbon-Type Analysis. - Infrared spectrometry and the fluorescent indicator adsorption method (FIAM) were used to determine if changes in hydrocarbon type resulted from irradiation. Use of the FIAM is limited to petroleum fuels boiling below 600° F[1]. Actually the real limitation of the method is viscosity, not distillation range. Irradiation increased fuel viscosity and this is thought to be the reason for large errors in aromatics determinations and failure of some of the fuels to separate at all.

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[1] American Society For Testing Materials, 1955 Book of ASTM Standards, Part 5, Method D 1319-55T, page 748, Philadelphia 1955.

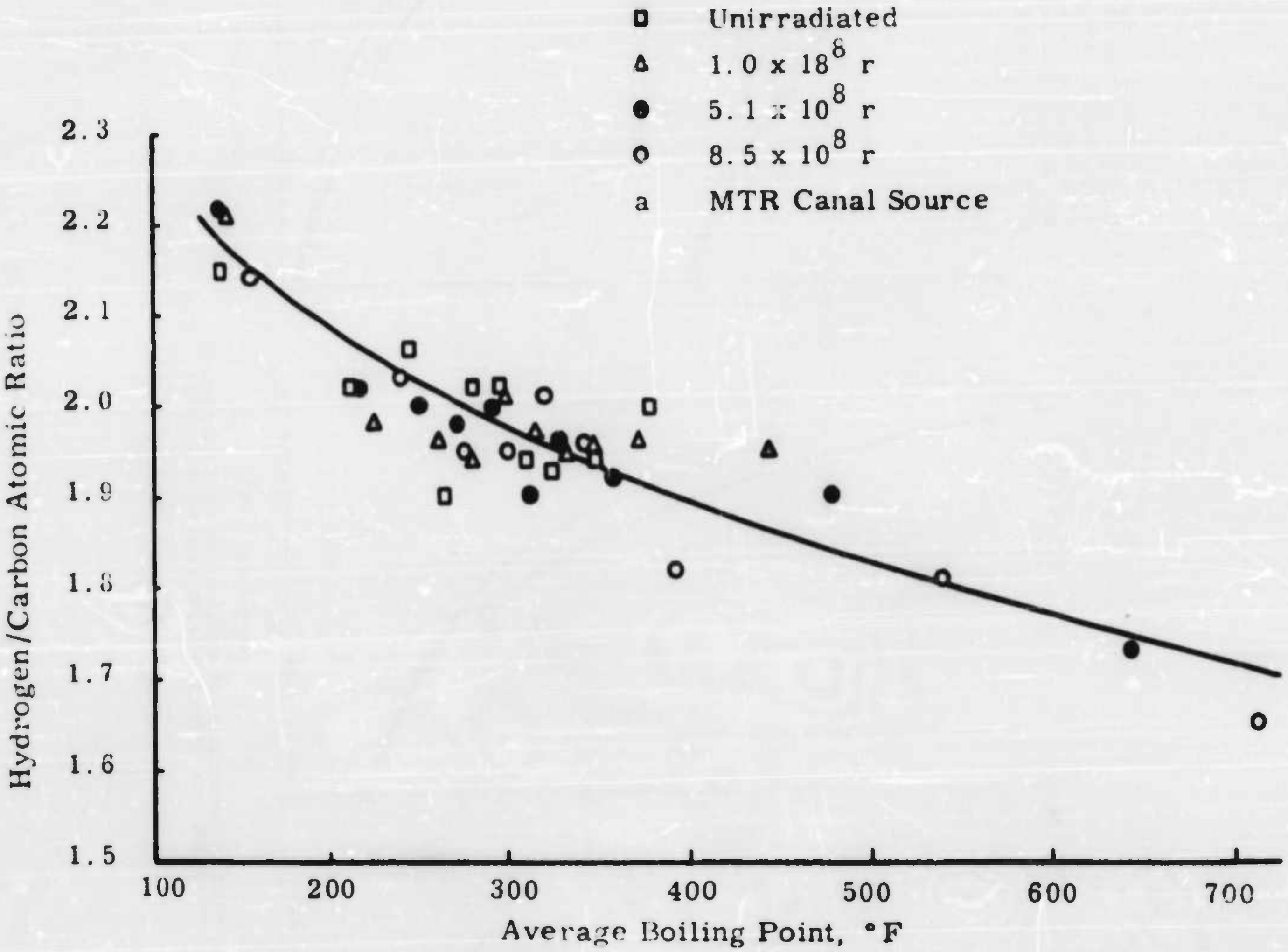
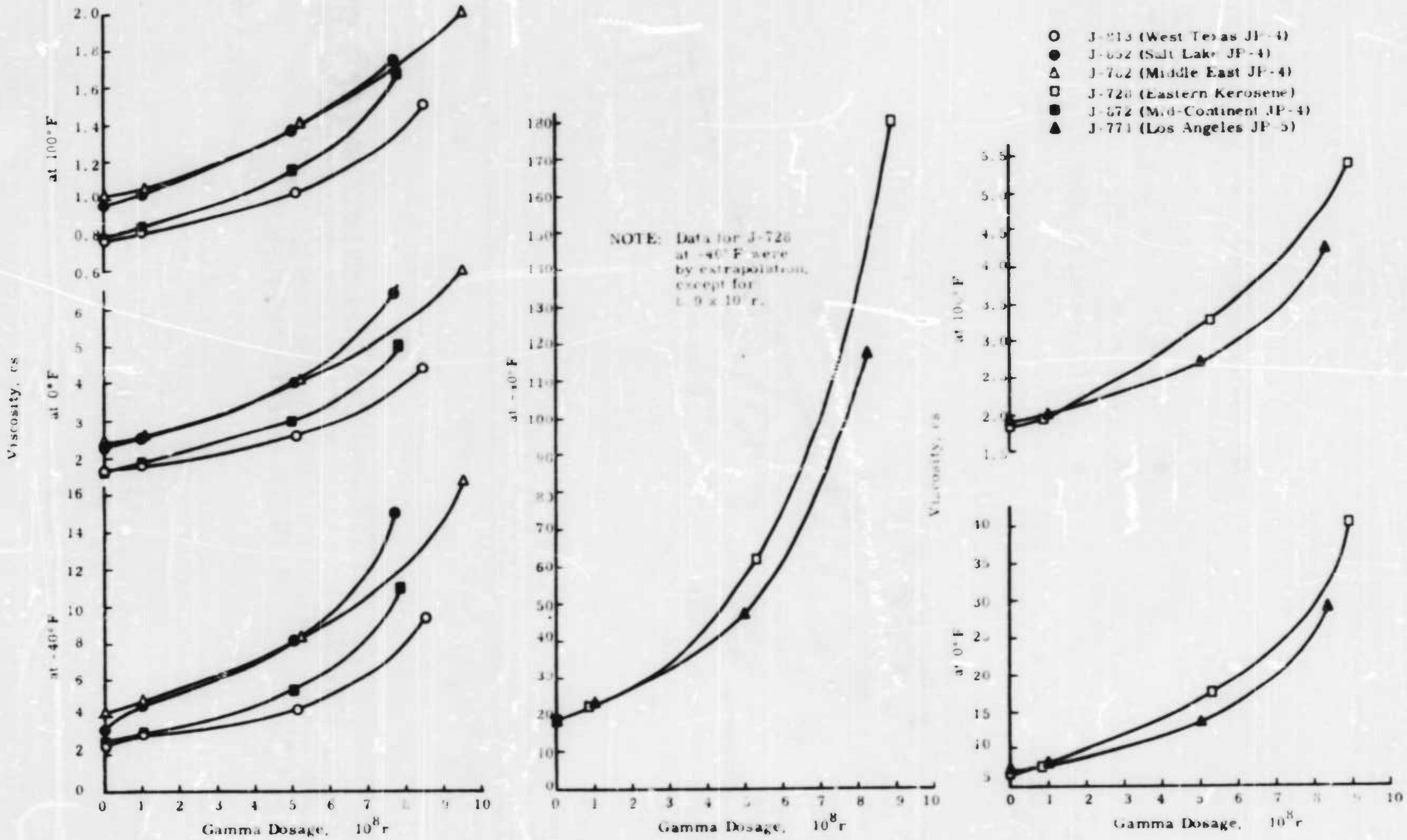


FIG. 39 - EFFECT OF IRRADIATION[a] ON HYDROGEN/CARBON ATOMIC RATIO OF A JP-4 FUEL (J-813 FROM WEST TEXAS CRUDE) (BASED ON ANALYSIS OF DISTILLED FRACTIONS)



NOTE: Data for J-728 at -40°F were by extrapolation, except for 1.9 x 10^8 r.

FIG. 40 - EFFECT OF IRRADIATION ON VISCOSITY OF JET FUELS (FOUR JP-4 TYPE, ONE KEROSENE TYPE, AND ONE JP-5 TYPE)

Previous experience with a method using the 6-1/4 micron band of the infrared spectra in conjunction with FIAM had given good results for determining aromatics in gas oil fractions[1]. The same technique was applied to this program and results were not as successful. For example, fuels J-872 and J-771 showed no aromatic absorption in the 6-1/4 micron band for the whole fuels or the distilled fractions. The FIAM showed 8% aromatics present in the unirradiated J-872 and 22% in J-771. No reason for failure of the infrared method was apparent.

With fuels J-813, J-852, J-728, and J-782 estimates of the aromatic distribution were possible and they are given in Tables LXXX (page 137) and LXXXII (page 139). Aromatics appeared to be present in the fractions of the irradiated fuels boiling above the final boiling points of the original unirradiated fuels. The amount was small for J-728; only 2% was present in the 80-90% fractions for dosages of 5.29 and 8.90 x 10^8 r. Of the JP-4 fuels (excepting J-872), all appeared to have aromatics present in the fractions of the irradiated samples boiling higher than the final boiling points of the original fuels.

Refractive index measurements on all fuels and distilled fractions were obtained in order to assist in identifying hydrocarbon types. Little change was found in refractive index through the boiling range of the original unirradiated fuel for the irradiated samples. The higher boiling fractions formed by radiation showed higher indexes, which would result from the presence of either olefins or aromatics.

Deposition Tendency. - Two tests were used to indicate the deposition tendency of the fuels: the filter residue test and the adherent gum test. Details of these tests are given in Appendix XI. Results of both gum determinations are given in Tables LXXIX (page 136), LXXXI (page 138), and LXXXIII (page 140).

The filter residue test, which is a measure of suspended gum, gave very low values not influenced by irradiation level. Adherent gum, that is, gum which adhered to the interior surface of the aluminum fuel containers was very low except in the cases of J-872 and J-771. In these two cases there appeared to be an upward trend in gum value with increasing dosage. Without more data it could not be stated that this was an irradiation effect. The lack of gum in the other fuels pointed to contamination as the cause of gum with J-872 and J-771.

Fuel Loss From Irradiation. - Attempts to obtain the fuel loss volumes resulting from irradiation have not yet been successful. On the samples which were weighed accurately, loss of undetermined volumes occurred at the MTR during pressure testing on all but two samples, J-872 and J-771 both at dosages of 1 x 10^8 r. The loss with J-872, a JP-4, was 0.34% by volume, while for J-771, a JP-5, the loss was only 0.065%. At a dosage of 10^9 r fuel losses were estimated at 1.5% for JP-4 type fuels and 0.5% for JP-5 fuels. This was based on measurements that included undetermined fuel handling losses and would constitute an upper limit for loss by irradiation.

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[1] "A Survey of the Radiation Stability of Jet Fuels," California Research-AEC Report No. 9 (TID 5366), June 30, 1956 (SECRET).

7.1.5 Concluding Discussion

Irradiation of JP-4 fuels at a dosage of 10^8 r has little effect on properties influencing engine performance. A dosage of 5×10^8 r forms appreciable quantities of high boiling material. However, a viscosity under 10 centistokes at -40°F was maintained by all JP-4 fuels. This indicates that in-flight engine starting should be no problem with JP-4 fuels at fuel temperatures of -40°F or higher where dosage has not exceeded 5×10^8 r. The high boiling material would not be expected to affect combustion efficiency measurably. However, this material may increase engine deposits and critical thermal stability of the irradiated fuels. The latter has not been evaluated.

JP-5 fuels do not appear to be satisfactory, not because of less resistance to radiation effects, but because some of their properties are inherently close to the borderline due to their higher boiling range. For this reason, no margin exists for the changes that take place through irradiation. The advantage of having aromatics present in a fuel was well illustrated by a comparison of radiation effects on zero aromatic J-728 and 22% aromatic J-771. Fuel loss by irradiation is not great even at the highest radiation dosage investigated, 10^9 r.

7.2 High Energy Fuels (K. L. Hall)

7.2.1 Introduction and Objectives

Due to the current interest in the so-called "high energy" fuels, the radiation stability of one such fuel, ethyldecaborane (HEF-3), was studied. It was desirable to determine the threshold radiation levels which were required to appreciably damage this material. The toxicity and generally hazardous nature of these compounds dictated that work proceed slowly and with caution. Thus the initial objectives were to obtain qualitative information on the radiolysis of HEF-3 at low dosages and to perfect handling techniques for this potent material.

7.2.2 HEF-3 Starting Material

Two 25-ml samples of HEF-3 were received from Olin Mathieson Chemical Corporation (OMCC). The first (Sample Z-236) was shipped in a stainless steel cylinder under 30 psig of nitrogen. This container leaked. The liquid had a cloudy appearance and its infrared spectrum showed evidence of hydrolysis. The second (Sample Z-279) was shipped in a stainless steel cylinder under 40 psig of nitrogen and was received in good condition. As reported by OMCC, this sample consisted of 96-98% ethyldecaborane, the major contaminant being diethyldecaborane. The liquid was clear and its infrared spectrum showed its purity to be greater than that of the first sample.

The unirradiated Z-279 was examined spectrometrically from time to time and evidence was found for its decomposition. The material was stored in a room maintained at about -30°F. About three months after receipt, mass spectra up to mass number 260 were obtained. A group of peaks at 220-235 and another beginning at 250 were recorded. The most intense single peak in these groups was about 2500 times smaller than the 133-152 group from ethyl decaborane. Three months later the mass spectrum was obtained extending to mass 400.

This time three groups of peaks showed up above the 133-152 group as indicated by the bar graph of Figure 41. The new groups were now about eight times more intense than before. Thus, at least one other component of high molecular weight was appearing in the unirradiated Z-279.

Without samples of this unknown with which to calibrate the high mass-mass spectrometer, the following interpretation is only speculation. It appeared that ethyldecaborane ($B_{10}H_{13}Et$) dimerized on standing to produce the group of peaks at 275-300 in Figure 41. The loss of one or two ethyl groups from the dimer ($B_{20}H_{26}Et_2$) might account for the groups at 240-265 and 210-235, respectively. There are probably less than 26 hydrogen atoms in the boron hydride dimer unit.

Infrared spectra similarly taken of the unirradiated ethyl decaborane gave further evidence that the sample was changed on standing. An unidentified band at 8.38 microns was not present in spectra taken on receipt of Sample Z-279. As with the mass spectra, positive identification would require pure samples of the unknown with which to calibrate the spectrometer.

7.2.3 Results of Irradiations

Work was conducted on small portions of HEF-3 to explore major radiolytic changes with a minimum of hazard and handling problems. The irradiations were conducted in the California Research cobalt-60 source in a gamma flux of about 0.3×10^6 r/hr. Table LXXXVI summarizes these irradiations.

Table LXXXVI

Irradiations of HEF-3

Sample No.	Irradiation Containers	Irradiation Atmosphere	Volume Irradiated ml	Dosage, 10^8 r	Gas Evolution ml Gas (STP)/ ml Fluid
Z-236-1	Stainless Steel	Helium	5	0.6	6
Z-279-1	Pyrex Gage Glass	Vacuum	0.5	1.0	8
Z-279-2	Pyrex Gage Glass	Vacuum	0.5	2.5	11
Z-279-3	Pyrex Gage Glass	Vacuum	0.5	4.8	19
Z-279-4	Pyrex Gage Glass	Vacuum	0.5	12.0	44

The gas evolution was approximately a linear function of the dosage. It is notable that the material was still liquid at 12×10^8 r, near a limiting value for typical aliphatic hydrocarbons.

A small amount of a gelatinous solid was first observed in Sample Z-279-3. Visual examination of the samples indicated that little more solid had formed in Sample Z-279-4 but that the viscosity had increased.

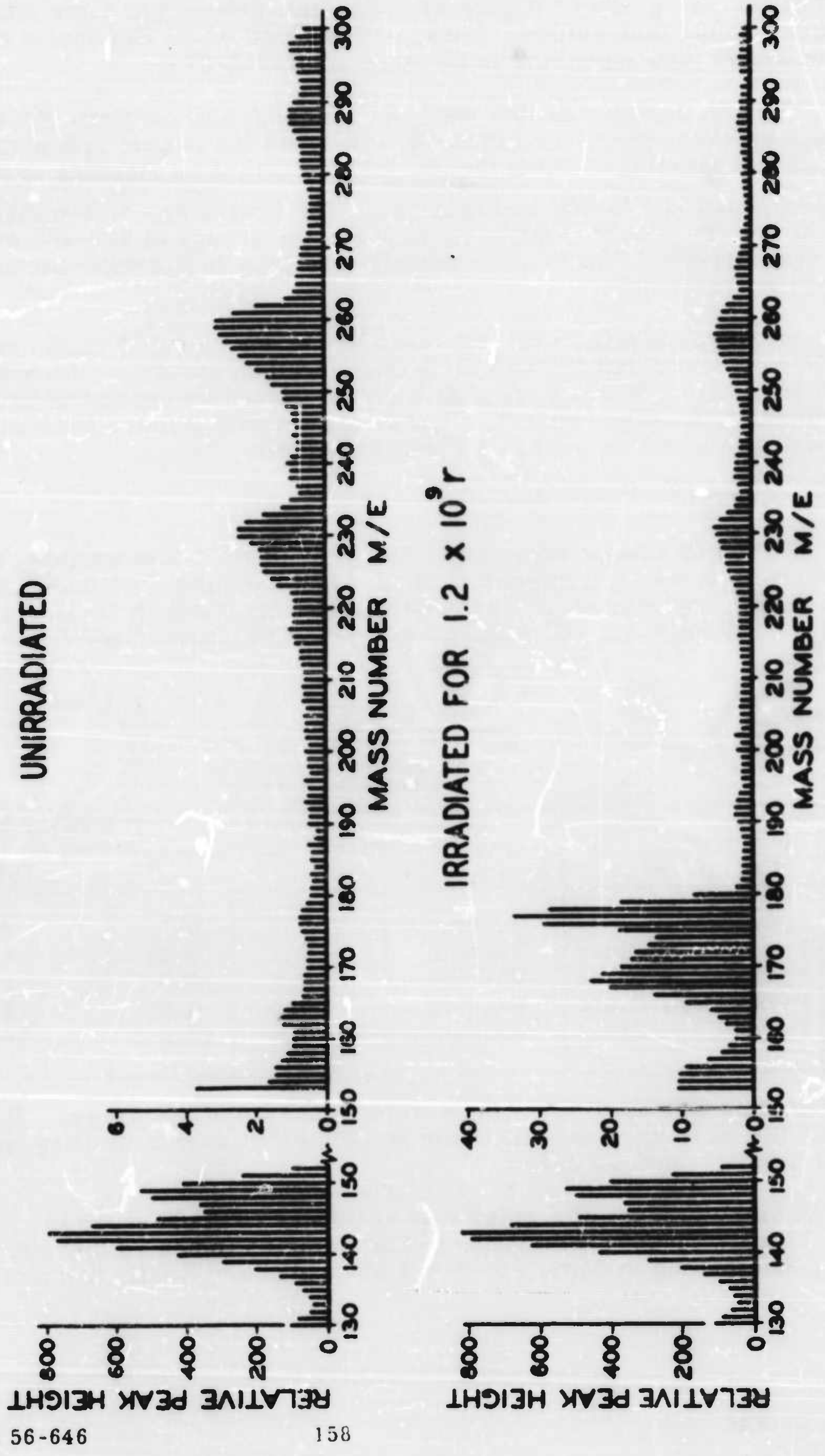


FIG. 41- HIGH MASS SPECTRA OF ETHYLDECABORANE

Observations were made on both the liquid and gas phases using a high-mass and a normal-mass mass spectrometer, respectively. The latter was used to obtain analyses on the evolved gases by isothermally distilling successive fractions directly into the spectrometer. The helium present in Sample Z-236-1 interfered with the analysis. Figure 41 (page 158) depicts the high mass spectra of Sample Z-279-4 irradiated to 1.2 x 10^9 r and of unirradiated Z-279 taken at the same time for comparison. The irradiated sample had several groups of peaks of higher molecular weights than the starting material. The group around 177 is in about the right range for diethyldecaborane. On the basis of these and other mass spectra in the low molecular weight range, the following fragments were qualitatively identified: diethyldecaborane, decaborane, octaborane, ethylpentaborane, pentaborane, propane, ethane, methane, and hydrogen.

The irradiated fluids were diluted with carbon disulfide and cyclohexane for infrared work. No major changes in the over-all purity were detected by this means although several unidentified bands appeared in the 7-9 micron region. The ultraviolet spectrum of Sample Z-279-4 permitted a value of 16% to be assigned to the lower limit of the total ethyldecaborane decomposed.

7.2.3 Conclusions and Future Work

Compared with typical aliphatic hydrocarbons HEF-3 appears to be exceptionally stable with respect to radiolytic solidification. The decomposition products consist of lower boron hydrides and low molecular weight hydrocarbons. As yet, no MS, IR, or UV evidence has been found for polymer formation although polymers surely result in irradiations. Gas is evolved in roughly the same amount as expected for aliphatic hydrocarbons. Since the decomposition products are flammable and toxic, precautions must be taken in handling irradiated HEF-3.

Higher flux sources such as the MTR Canal Source should be used in the continuation of this program. Duplicate exposures covering the dosage range 2.5 to 75 x 10^8 r are suggested. Steel capsules sealed in a helium atmosphere should be used. The extension of the dosages to high values will permit the determination of the threshold dosage, i.e., the point on the damage-dosage curve above which the material very rapidly solidifies. The low dosages will confirm previous gas evolution results carried out in vacuum in glass containers.

An additional 200 ml of HEF-3 has been received from Olin-Mathieson. Arrangements have been made with Olin-Mathieson to ship the unopened irradiated capsules to Reaction Motors, Incorporated, a subsidiary of OMCC. Gas evolution, viscosity, heat of combustion, spontaneous ignition temperature, vapor pressure, etc. can be determined. No other analytical work is anticipated due to the difficulties in handling and repurifying compounds for use as spectrometer standards.

APPENDIX 1

PREPARATION OF DIISOOCTYL TEREPHTHALATE

(M. J. Schlatter)

Exploratory Laboratory Studies

Experiments were carried out to test procedures suitable for barrel-scale preparation of diisooctyl terephthalate. A previous barrel-scale preparation from dimethyl terephthalate and isooctyl alcohol using sodium methylate as catalyst gave the trouble cited in Section 2.2, page 9. This prompted additional laboratory-scale work.

Three runs were made. In each case dimethyl terephthalate (Hercules, 194.2 g, 1.00 mole), "Isooctyl" alcohol (Enjay, 390.7 g, 3.00 moles) and benzene (100 g) were charged to a 1-liter 3-neck flask with thermometer, stirrer, distillation head, and condenser. About 50 ml of benzene was distilled off to remove traces of water, the mixture was cooled to 158°F and the ester interchange catalyst added.

Litharge as Catalyst

This material (0.097 g, 0.05% based on dimethyl terephthalate) was used in two experiments. In the first (4524-2), the temperature was raised gradually from 266°F to 417°F in 3 hours. Ester interchange occurred readily at 212°F to 302°F and benzene, methanol, and some isooctyl alcohol distilled off. Nitrogen was then admitted through a fine capillary, the pressure gradually reduced to 20 mm, and the temperature raised to 428°F to remove excess isooctyl alcohol. The product was cooled and then filtered through Celite. The second experiment (4524-3) was similar to the first except that the product was stirred for 30 minutes with Norite A (20 g) before filtering through Celite. The products were 0.5 g and 3.0 g, respectively, under the theoretical weight. Both were colorless (though they yellowed slightly on standing); neutral equivalents were nil. Spectrographic lead analyses showed the untreated product to contain 110 ppm of lead and the Norite treated sample to contain less than 1 ppm of lead. Norite treatment of the product from 4524-2 gave the following results:

Norite Treat, g/100 ml	Lead Analysis, ppm
None	110
1	9
2	0.95
10	0.95

All of the product from 4524-2 was treated with Norite A at a 5 g/100 ml level, and the products from runs 4524-2 and 4524-3 were combined. Analyses and physical properties of this sample are shown in Table VII, page 10.

Sodium Methylate as Catalyst

This agent (2.5 g, 1.28% based on dimethyl terephthalate) was used as ester interchange catalyst (4524-4). The procedure was essentially the same as that just described. Reaction occurred at a somewhat lower temperature than in the runs using small amounts of litharge, and the temperature was kept below 338° F. Before reducing the pressure, the mixture was cooled and half of the batch removed. This was shaken with 100 ml of 0.6 N hydrochloric acid. A solid precipitate was formed in the mixture which made separation difficult. Isooctyl alcohol was removed from the remainder of the batch as described for the previous runs. This product had a faint yellow color and contained a gelatinous precipitate. As the litharge catalyst appeared satisfactory and a simple method for removing the lead had been found, the experiments with sodium methylate were abandoned.

Large-Scale Preparation

Transesterification

Dimethyl terephthalate (Hercules, 194 lb, 1.00 lb mole), "isooctyl" alcohol (Enjay, 379 lb, 2.01 lb moles), and benzene (100 lb) were charged to a 300-gallon stainless steel jacketed kettle equipped with stirrer, spray tower, condenser, and receiver. Benzene (51.5 lb) was distilled off to remove traces of water, and 44 g of litharge was added as ester interchange catalyst. After heating for 6 hours at 300° F, a total of 185.5 pounds of distillate consisting of benzene, methanol, and some isooctyl alcohol was collected. Theory for methanol formed in the reaction and added benzene is 164 pounds.

Stripping and Decatalyzing Operations

To strip off the excess of isooctyl alcohol, the mixture was heated gradually to about 400° F while stirring (27 hours). The stirrer was stopped, and the mixture stripped by passing in oil-pumped nitrogen while slowly reducing the pressure to about 22 inches of vacuum. Two cylinders of nitrogen were used in a period of 7.5 hours, and the temperature in this period was raised gradually to 550° F. The nitrogen rate was decreased, and the temperature raised slowly to 580° F (10 hours). Cracking became apparent, and octenes were found in the distillate.

The mixture was cooled to 190° F (8 hours), stirred with 10 pounds of Norite A for 2 hours, and filtered through a Sparkler filter which was precoated with Celite 545. This gave 329 pounds (84% theory) of crude diisooctyl terephthalate. On cooling, the product set to a soft, brown paste having a neutralization number of 31.5 mg KOH/g of sample. This corresponds to diisooctyl terephthalate product containing 16% monoisooctyl terephthalate.

APPENDIX II

ALKYLATION OF BIPHENYLS

(M. J. Schlatter)

Exploratory Laboratory Studies

In this laboratory-scale work use of phosphoric acid-boron trifluoride catalyst gave lighter colored products, having higher pour points, than were obtained using aluminum chloride modified with chloroform. Aluminum chloride-nitrobenzene complex gave products more nearly like those obtained under similar conditions with the phosphoric acid-boron trifluoride catalyst. Increasing the biphenyl to olefin ratio decreased the pour point and viscosity somewhat with phosphoric acid-boron trifluoride, but had little effect with aluminum chloride modified with chloroform.

The aromatic compound to be alkylated was placed in a 3-neck flask equipped with efficient stirrer, thermometer, dropping funnel, and reflux condenser with outlet tube. (Some large-scale laboratory alkylations were carried out successfully in an open, 12-quart enameled pail and in open stainless steel beakers.) When solvent was used, it was also added at this point. The mixture was heated until liquid or until the desired reaction temperature was reached. The catalyst was added and alkylating agent introduced at a rate which permitted the temperature to be kept between the initial reaction temperature and a point 27° F higher.

Stirring was ordinarily continued for at least one hour after the addition was complete or until bromine numbers indicated that most of the added olefin had reacted. When aluminum chloride was used as catalyst, the reaction mixture was washed with dilute hydrochloric acid and then with water. With other catalysts water alone was used. Hot washes were employed with products which were viscous or solid at room temperature. Solvents and excess starting materials were removed by distillation from a Claisen flask under reduced pressure. Further distillation of some products was carried out through a short Vigreaux column at about 2 mm.

In runs using chloroform modified aluminum chloride catalyst, the chloroform was added to the reaction mixture followed by the aluminum chloride. The aluminum chloride-nitrobenzene catalyst was preformed by shaking these materials until homogeneous. The phosphoric acid-boron trifluoride catalyst used in some experiments was obtained by saturating 100% phosphoric acid with boron trifluoride at about 175° F. The mixture was then heated with stirring at 212° F to remove excess boron trifluoride.

Purification

Laboratory experiments showed that a solution of the crude product in two volumes of mixed hexanes gave a stable emulsion when shaken with 10% sodium bicarbonate solution. Extraction with 10% sodium hydroxide gave less trouble with emulsions and also removed part of the product color. Shortly after separating, the aqueous phase became turbid and thickened as sodium terephthalate precipitated. This resulted from rapid saponification of the sodium salt of the monoisooctyl terephthalate extracted from the crude product. As isooctyl alcohol was also formed in this reaction, it was important to separate the aqueous phase quickly in order to prevent collection of this material with the diisooctyl terephthalate product.

The monoester was removed from the crude product as follows: Product prepared as just described (309 lb) and product from a previous batch which also contained monoisooctyl terephthalate (75 lb) was charged to a 300-gallon, stainless steel kettle and stirred with 80 gallons of mixed hexanes. This mixture was then extracted with two 50-gallon portions of 10% sodium hydroxide solution and two 50-gallon portions of 10% sodium bicarbonate solution. As the quality of the product was more important than the recovery, the base extractions were carried out as rapidly as possible, discarding any emulsion layers in order to minimize contamination of the product with isooctyl alcohol.

About 30 minutes was required for the two caustic extractions and addition of the first bicarbonate wash. Two hours was used to carry out bicarbonate extractions and to allow complete settling of the aqueous layer. The hexane solution was then dried by stirring with 10 pounds of anhydrous sodium sulfate for two hours. The mixture was filtered through paper in a Sparkler filter. The hexanes were stripped from the product by pumping the mixture slowly into a 30-gallon, steam-heated, glass-lined kettle arranged for distillation. When most of the hexanes were removed and the bottoms temperature reached 200° F, the mixture was stripped further by passing in a slow stream of pure, dry nitrogen and reducing the pressure gradually to 22 inches of vacuum. The bottoms temperature rose slowly to 280° F over a period of 7 hours. The mixture was then cooled to 110° F and clarified by filtering through a small "Ful-flo" cotton filter. A total of 175 pounds of product was obtained. This corresponds to 46% of the crude product charged to the purification process. Parallel experiments in the laboratory gave recoveries of 70%. The principal losses were probably incurred in the rapid separations during the base extractions.

In Table VII, page 10 analysis and properties of this product are compared with those of a laboratory-scale product and literature values. The last product was reportedly obtained by reaction of terephthaloyl chloride with Enjay "isooctyl" alcohol.

APPENDIX III

BARREL-SCALE PREPARATION OF C_{16-18} ALKYLBIPHENYL

(REACTION OF BIPHENYL WITH C_{16-18} ALPHA-OLEFINS)

(M. J. Schlatter)

Alkylation (Exp. 4524-20)

Biphenyl (850 pounds, 5.51 moles) was melted in a 300-gallon, glass-lined, jacketed reaction kettle equipped with stirrer. The temperature was adjusted to 160°F and 8.4 pounds (0.07 moles) of chloroform was added. The mixture was stirred, and 20 pounds (0.15 moles) of anhydrous aluminum chloride was added over a period of 10 minutes. Considerable fuming occurred during this addition. Mixed C_{16-18} alpha-olefins (360 pounds, 1.58 moles, Archer-Daniels-Midland) was next pumped in at a rate of approximately 3 pounds per minute at 155-195°F. This addition required 2.25 hours. Stirring was continued for an additional 2.25 hours at 160-175°F. At this time, the bromine number of the crude reaction mixture was less than one, indicating the alkylation to be essentially complete.

The catalyst was removed by three washing operations, one with a hot solution of 6 pounds of concentrated hydrochloric acid in 50 gallons of water and two with 50-gallon portions of hot water. Water remaining in the product was removed by heating the mixture to 220°F and blowing with nitrogen. The contents of the reactor were then filtered through a "Ful-flo" filter into clean drums. The product weighed 1165 pounds.

Stripping of Alkylate

Excess biphenyl was stripped from 1145 pounds of the crude alkylate in a six-batch operation using a 100 liter, electrically heated, stainless steel still equipped with a short spray column. Stripping was carried to a bottoms temperature of 491-660°F at 15-30 mm. The product was dark red by transmitted light; it had a dark green fluorescence. A total of 475 pounds of bottoms (theory for monoalkylbiphenyl = 604 pounds; yield = 62.5%) was obtained.

Clay Treatment of Alkylate

Part of the bottoms product (390 pounds) was percolated at room temperature through an 8-inch diameter column containing 40 pounds of dry Floridin clay. A total of four days was required for the stock to pass through the column. This gave 359 pounds of clay treated bottoms. This product was light orange in color with a slight green fluorescence. Additional product (15 pounds) was obtained by eluting the column with 10 gallons of mixed hexanes and evaporating the solvent. Properties of the clay treated alkylate are in Table X, page 14.

Distillation of Alkylate

About 80 pounds of untreated stripped alkylate was distilled at 0.8 mm. This distillation was carried out rapidly at a reflux rate of 1:1 in a 50-liter stainless steel still equipped with a 1-foot Pennsylvania State column. After taking a small precut, approximately 10% cuts were collected. The properties of these are also in Table X, page 14.

Infrared spectra of the distillation cuts showed them to be predominantly meta- and paraalkylbiphenyls containing a small amount of orthoalkylbiphenyl. Distillate Cuts 4524-28-3 to 4524-28-6 contain approximately equal amounts of meta and para isomers. The para isomers increased in Cut 7 and predominated in Cuts 8 and 9. As expected, these findings showed the fractions having high para isomer contents to have high pour points.

Clay Treatment of the Bottoms From The Alkylate Distillation

The polyalkylbiphenyl bottoms from the alkylate distillation (6954 g) and 500 g of dry filtrol clay were heated to 450°F in 40 minutes, while blowing with high purity nitrogen. The mixture was allowed to cool to 250°F while continuing the nitrogen flow and was then filtered. The clear, dark red clay treated product weighed 6620 g. Its properties are in Table X, page 14.

APPENDIX IV

SYNTHESIS OF 1,9-DIPHENYLNONANE

(A. C. Ettling)

Into a 2-liter flash was weighed 282 g (1.5 moles) azeleic acid, 500 g benzene, and 145 g (1.05 moles) phosphorus trichloride. The mixture was warmed on a steam plate to 122°F with occasional agitation. The diacid chloride solution was allowed to cool for 15 minutes and decanted from the orthophosphorus acid into a dropping funnel.

Benzene (about 1200 g) and anhydrous aluminum chloride (400 g, 3 moles) was placed in a 5-liter flask equipped with stirrer, dropping funnel, thermometer, and reflux condenser with gas outlet. The diacid chloride solution from above was added over a period of 90 minutes. Evolution of HCl gas was moderate. The mixture was heated to 167°F and stirred for 2 hours. It was then cooled to room temperature and poured onto iced dilute acid in an enameled pail. The aqueous layer was separated and the benzene solution was washed with dilute acid followed by water. Excess benzene was evaporated on a steam plate. The crude diketone was a white crystalline solid.

The crude diketone, about 2 liters triethylene glycol, 300 g potassium hydroxide, and 250 g 95+% hydrazine (EK No. 902), was placed in a 5-liter stainless steel flask equipped with stirrer, thermometer, water by distillation trap and reflux condenser. The stirrer was started and heat slowly applied to 428°F. Water and lower boiling material was removed through a stopcock on the bottom of the water trap. Stirring was at 428°F for 3 hours. The mix was then cooled and diluted with much water. The aqueous layer was discarded and the hydrocarbon layer was water washed and dried. The product was distilled through a short Vigreaux column and the fraction boiling at 356-374°F at 2 mm pressure was collected. Properties of this fraction are in Table XIII, page 18.

APPENDIX V

REACTION OF BUTADIENE WITH BIPHENYL AND ALKYLBIPHENYL

(M. J. Schlatter)

Reaction With Biphenyl (Exp. 4524-39)

The reactor used consisted of a 500-ml electrically heated, turbo vessel equipped with a dry ice cooled reflux condenser. The condenser exhaust was connected with a "U" tube containing just enough mercury to act as a seal and yet to permit gas to pass in either direction with a slight pressure differential. A gas circulating pump recirculated gas from the top of the reactor through the vigorously stirred reaction mixture. Butadiene was introduced through a connection in the reactor gas inlet line. Biphenyl (231 g, 1.5 moles) was melted in the reactor by heating to 158°F. Chloroform (3.0 g, 0.025 mole), and 6.7 g (0.05 mole) of aluminum chloride were added. Butadiene (23 g, 0.42 mole) was condensed in an ampule and then added over a period of one hour. Cooling was required to maintain the 176-185°F reaction temperature. Stirring was continued for two hours. The catalyst was then decomposed by adding 130 ml of hot 3 N hydrochloric acid. The organic layer was transferred to a Claisen flask and excess biphenyl stripped off up to 428°F at 1.5 mm. Further distillation gave 24 g of fraction boiling largely at 518°F at 1.0 mm which is probably largely the condensation product from two molecules of biphenyl and one of butadiene. The residue boiling above 653°F at 1.0 mm (50.7 g) was a dark, tar-like material which is probably largely polymeric products containing units derived from butadiene and from biphenyl.

Reaction With C_{16-18} Alkylbiphenyl (Exp. 4524-40)

The same apparatus was used for this reaction as was used for the reaction of biphenyl and butadiene. Distilled C_{16-18} alkylbiphenyl (445-509°F at 0.8 mm; 224 g, 0.6 mole), 1.8 g (0.015 mole) of chloroform and 4.0 g (0.03 mole) of aluminum chloride were placed in the reactor and the addition of 16.3 g (0.3 mole) of butadiene was started at 122°F. As no reaction occurred at that temperature, the temperature was raised slowly. At 172°F an exothermic reaction started and cooling was necessary to keep the reaction temperature at 176-185°F. One hour was required after reaction started to complete the butadiene addition; stirring was continued for an additional 2.5 hours at this temperature.

The catalyst was decomposed by adding 130 ml of hot 3 N hydrochloric acid. This gave a thick emulsion. About 2 liters of ether was added, the aqueous layer withdrawn, and the ether stripped off. Residual ether and traces of water were removed by passing high purity nitrogen through the product while heating on a steam plate. The residual product (4571-45-1) weighed 241 g. Properties of the original C_{16-18} alkylbiphenyl and the butadiene treated product are summarized in Table LXXXVII.

Table LXXXVII

Properties of Butadiene "Coupled" C_{16-18} Alkylbiphenyl

Properties	C_{16}-$_{18}$-Alkylbiphenyl	Total Butadiene Treated Product
Boiling Range	229-265°C at 0.8 mm	-
Viscosity, cs		
At 100°F	37.4	124.7
At 210°F	5.36	11.98
At Pour Point	870,000	150,000
Viscosity Index	78	92
Pour Point	-55	-30

APPENDIX VI

SYNTHESIS OF DIBENZYL SELENIDE

(M. J. Schlatter)

Using the following procedure, 2 to 2.5 pounds of dibenzyl selenide can be prepared per run. This is as large a scale as is convenient working in a 12-liter flask. Four similar experiments were carried out. Yields and amounts of products given are averages for the four runs (Experiment 4524-27).

Preparation of Sodium Selenide (Care: Selenium and Some Selenium Compounds Are Toxic)

Selenium metal powder (450 g, 5.70 moles) was added with stirring to a hot solution of 2250 g (56.2 moles) of sodium hydroxide dissolved in 9 liters of water in a 12-liter, three-neck flask. The flask was heated by a steam-heated water bath. The mixture was stirred for one hour at 167-176°F to disperse the selenium, and 1050 g (6.63 moles) of "Rongalite CZ" (General Dyestuffs Corporation trade name for $HCHO \cdot NaHSO_2 \cdot 2H_2O$) was then added in small portions over a two-hour period. The flask was purged with nitrogen during this time. The temperature was maintained at 167-176°F during the "Rongalite" addition, and stirring was continued for four hours at this temperature after the addition was completed. The mixture was then cooled slowly to room temperature. (If cooling is rapid, the sodium selenide precipitates as very fine crystals that are difficult to separate and wash.) After standing for 12 to 48 hours, the mother liquor was decanted. The crystals were washed by decantation with three 2-liter portions of absolute alcohol. A nitrogen stream was maintained in the apparatus during these operations to avoid air oxidation of the sodium selenide.

Reaction of Benzyl Chloride and Sodium Selenide to Give Dibenzyl Selenide

The flask containing the sodium selenide prepared as just described was fitted with a reflux condenser, dropping funnel, and stirrer. Absolute alcohol (7 liters) was added, the mixture heated to reflux temperature, and 1442 g (11.40 moles) of benzyl chloride added over a period of two hours. To insure completion of the reaction, the mixture was refluxed with stirring for 12 hours. On cooling, most of the sodium chloride and product formed in the reaction separated from the lighter alcohol layer. Usually the product crystallized with the sodium chloride, but in one experiment remained as a heavy liquid layer until seeded.

The alcohol layer was drawn off and diluted with an equal volume of water. This was extracted with benzene. The crude product remaining in the flask was extracted with three 2-liter portions of hot water to remove sodium chloride. The heavy product layer was then filtered through a hot Buchner funnel, cooled, and seeded. When it was solid, residual water was drained off, and the product was recrystallized from mixed hexanes. The water extracts of the crude product were extracted with benzene. Additional product was recovered by combining these and the other benzene extracts, removing benzene by distillation, and crystallizing from mixed hexanes. This gave 1140 g (77% of theory) of dibenzyl selenide as colorless to pale yellow needles, m.p. 45.0-46.0°C.

APPENDIX VII

GREASE TEST PROCEDURES

(B. W. Hotten)

Thin Film Heat Stability

A film of grease 1-mm thick is smeared on the bottom of an aluminum dish. The dish is heated in an oven, usually at 300°F or 350°F, and examined periodically. The time required for the grease to become too stiff or brittle for use as a lubricant is taken as a measure of its life. A useful correlation was found between this test and the standard high speed bearing test.

Boiling Water Test

A 5-g globular sample of grease is dropped into boiling water in a beaker. The time required (up to 60 minutes) for the grease to disintegrate or emulsify is taken as a measure of its water resistance.

Oven Evaporation Test

This test is intended to permit the evaluation of the tendency of lubricating fluids to lose the lower boiling fractions under the conditions indicated. It is substituted for specification methods when many samples must be screened.

The test employs a forced air circulation oven capable of temperature control within + 2°F of a desired temperature. Standard glass evaporation dishes (bottom $\overline{5}$ mm of a 50-ml beaker) are used. The dishes are tared and then filled with grease to within 1 mm of the top. The dishes plus sample are weighed. As many samples can be tested simultaneously as can be stored in the oven. Reference lubricants are always included.

Following a specified length of storage time at the desired temperature, the dishes are removed and weighed again to determine weight loss of sample. The results are noted as per cent of original weight lost due to evaporation.

APPENDIX VIII

THE UNIQUE ROLE OF SELENIUM ADDITIVES

(R. L. Peeler)

Dialkyl selenides have been known as effective high temperature antioxidants since the early work of Denison and Condit[1]. They tested a series of selenides in petroleum oils at 840°F and found them to be superior to other available inhibitors. Cohen, et al.,[2] compared several dialkyl selenides with other additives in di(2-ethylhexyl) sebacate. It was concluded that the selenides were among the most effective high temperature oxidation inhibitors.

The outstanding characteristics of the dialkyl selenides, as far as ANP lubricants are concerned, lies in their unique effectiveness as inhibitors of radiation damage. Early work in this field[3] showed the selenides to be clearly superior to the other available inhibitors. In fact, this additive was estimated to increase the usable life of the irradiated fluids by approximately a factor of two. More recently, oxygen absorption measurements[4], have shown the selenides to be alone among inhibitors in retaining antioxidant effectiveness at dosages of 10^8r. Viscosity change, another index of radiation damage, was also greatly reduced.

In the critical coking test for gas turbine lubricants, dialkyl selenides actually caused a reduction in coking following irradiation (see Table XLV, page 78). This effect is the reverse of that observed with the other inhibitors. As a result, fluids may now be formulated which meet 700° F coking requirements both before and after irradiation to 10^9r. The polyglycols, otherwise doubtful in stability, were especially benefited by the use of selenide inhibitors. The reduction in coking following irradiation is particularly marked with these fluids.

The principal drawback to the use of the dialkyl selenides is their corrosion of silver and copper at high temperatures. This reaction, in addition to causing damage to the metals, tends to remove the selenium from the lubricant and reduce the available inhibitor. Attempts to prevent this corrosion in high temperature tests with metal deactivators and chelating agents have so far been unsuccessful.

[1] G. H. Denison and P. C. Condit, "Oxidation of Lubricating Oils," Industrial and Engineering Chemistry, 41, 944, (1949).

[2] G. Cohen, C. M. Murphy, J. G. O'Rear, H. Rooker, and A. A. Zisman, Industrial and Engineering Chemistry, 48, 1766, (1953).

[3] "The Effects of Fission Radiations on Lubricants and Lubrication," (Final Report, California Research-NEPA Project Report No. NEPA 1844, April 30, 1951.) (SECRET)

[4] "Engine Oil Development" Shell Development Company Progress Report No. 4 on Contract AF 33(6160-3182 (April 16-July 18, 1956).

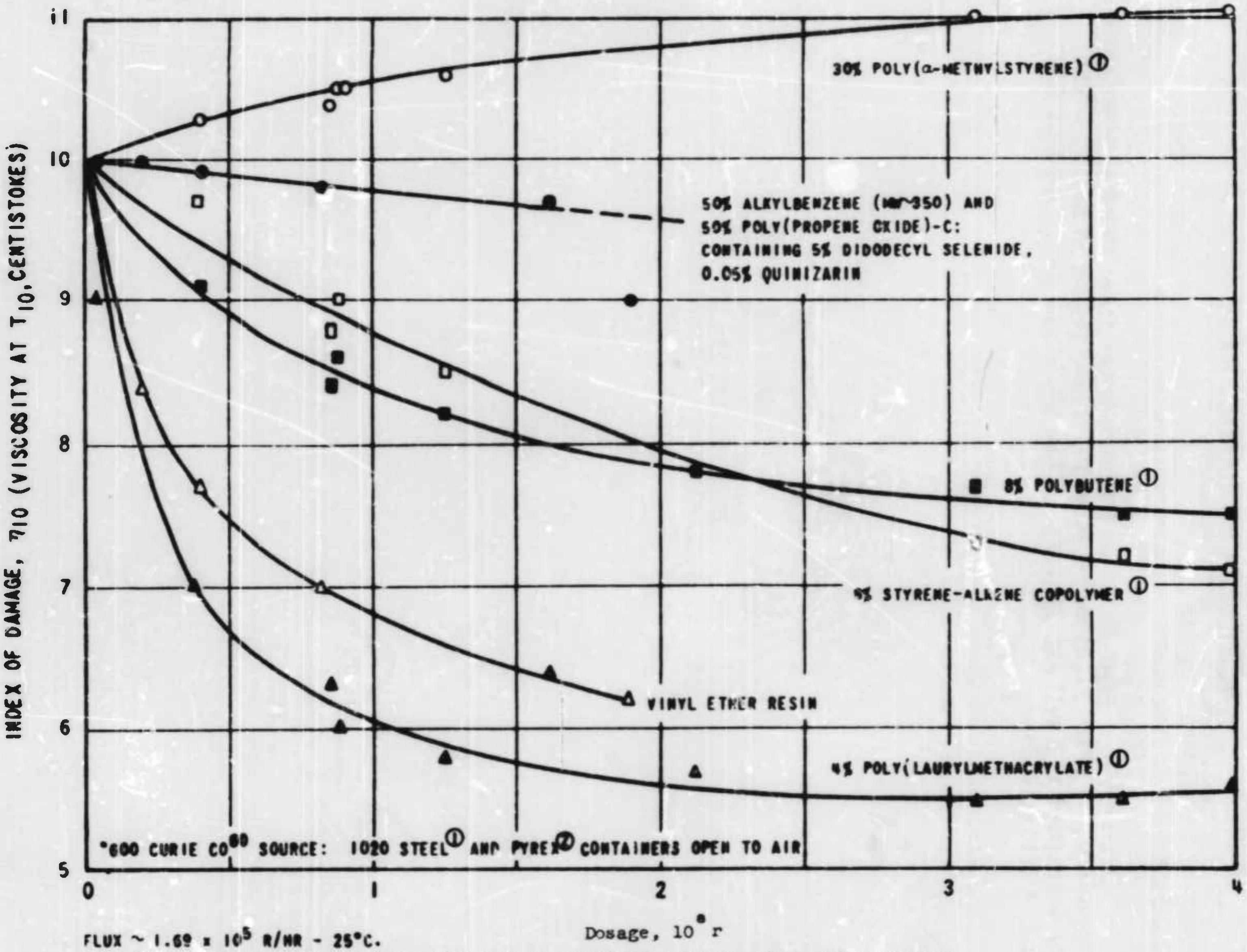
If the stability of the lubricant proves to be a limiting factor in the operation of several critical systems in nuclear powered aircraft, the additional stability provided by the dialkyl selenides may be sorely needed. In this case, it will probably be profitable to design components to exclude the reactive metals. This is a reversal of the usual procedure where the lubricant is designed to work in previously selected components. If copper, silver, and possibly lead and magnesium can be excluded from contact with the fluids, dialkyl selenides may help produce the most stable lubricants of any now known.

APPENDIX IX

STABILITY OF POLYMER THICKENERS TO GAMMA RAYS

(J. G. Carroll)

The attached Figures 42 and 43 are taken from California Research-AEC Report No. 7 (TID-5186) dated June 30, 1954, pages 58 and 59. The results described are self explanatory. This work was performed on AEC Contract AT(11-1)-174.



FLUX ~ 1.69 × 10^5 R/HR - 25°C.
BASE OIL: MIXED ALKYLBENZENE (MW ~ 250) WITH 5% DIDODECYL SELENIDE AND 0.05% QUINIZARIN.

FIG. 42 - STABILITY OF POLYMER THICKENERS TO GAMMA RAYS
SERIES G-4 AND G-10 IRRADIATED IN CALIFORNIA
RESEARCH CORPORATION SOURCE*

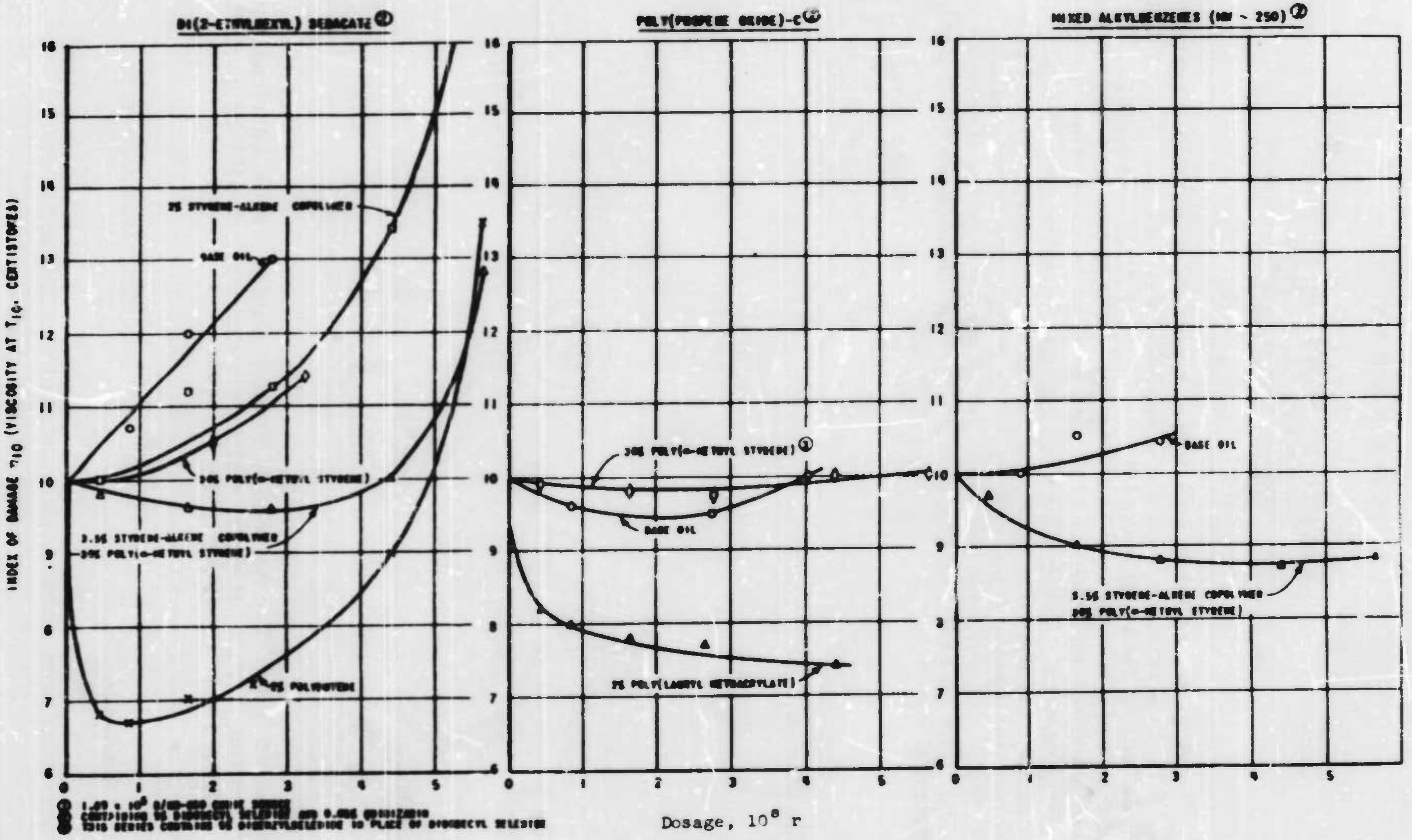


FIG. 43 - STABILITY OF POLYMER THICKENERS TO GAMMA RAYS SERIES G-11 IRRADIATED IN CALIFORNIA RESEARCH CORPORATION CO-60 SOURCE[1] IN PYREX CAPSULES AT 25°C OPEN TO AIR

APPENDIX X

VISCOSITY CHANGE WITH TIME[1] AFTER IRRADIATION

(J. G. Carroll)

Samples of lubricants were irradiated in a nuclear reactor at Hanford in 2S aluminum containers sealed under helium. The containers were allowed to decay in radioactivity 17 days prior to opening. The lubricants were transferred to screw cap vials in air, and viscosities were determined after the lapse of 1, 8, and 35 days from the time the containers were first opened. Table LXXXVIII summarizes the data obtained. It may be noted that the changes occurring in viscosity between the one and the eight-day determinations are insignificant. In the 35-day determinations, one sample increased in viscosity by 16%, though the majority of the increases are less than 1%. The largest changes took place with uncompounded or lightly compounded fluids.

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[1] Abstracted from "The Effects of Fission Radiations on Lubricants and Lubrication," (Final Report, California Research-NEPA Project) Report No. NEPA 1844, April 30, 1951, p. 39.

TABLE LXXXVIII

VISCOSITY CHANGE WITH TIME AFTER IRRADIATION

Samples Irradiated in Hanford "F" File for About 35.7 Hours and a Dosage of 1 x 10^{18} Neutrons/cm^2 in Sealed Containers at 8 ± 2°C

Identity	Viscosity at 100°F, Centistokes				Viscosity at 210°F, Centistokes			
		After Pile Exposure *				After Pile Exposure *		
	Original	1 Day	8 Days	35 Days	Original	1 Day	8 Days	35 Days
Poly(propene oxide)	56.1 56.1	137 136	142 137	159 148	9.6 9.6	16.9 17.8	15.8 17.6	14.0 -
Alkylbenzene (m.w. = 250) Containing 4% Poly(lauryl methacrylate) and 2% Didodecyl Selenide	12.8 12.8	7.8 7.7	8.0 7.7	8.6 7.8	3.5 3.5	2.1 2.1	2.2 2.1	2.2 2.2
Didecyl Terephthalate Containing 2% Didodecyl Selenide	53.1 53.1	81.5 77.5	- 78.1	- 78.5	6.9 6.9	9.0 8.6	9.0 8.7	- 8.4
Poly(propene oxide)-B Containing 5% Didodecyl Selenide and 2% Iodobenzene; Blend Saturated with Quinizarin	19.3 19.3	15.4 15.1	14.6 14.9	- 15.4	4.5 4.5	3.7 3.7	3.6 3.7	- 3.6
Alkylbenzene (m.w. = 350) Containing 2% Didodecyl Selenide	122 122	145 141	144 143	155 143	8.1 8.1	9.1 8.9	9.1 9.0	10.0 8.9
Di(2-ethylhexyl) Sebacate Containing 20% Methylnaphthalene, 5% Didodecyl Selenide and 2% Iodobenzene; Blend Saturated with Quinizarin	8.5 8.5	10.0 10.0	10.1 10.0	10.3 10.0	2.5 2.5	2.8 2.5	2.8 2.8	2.8 2.8

* From NEPA 1844, page 75.

APPENDIX XI

FILTER RESIDUE TEST

Outline of Method

The fuel sample is filtered through a tared Gooch crucible. Material adhering to the test unit is dissolved in a suitable solvent. The gums are precipitated, and the mixture is also filtered through the Gooch crucible. The crucibles are washed, dried, cooled, and weighed. The filter residue, corrected for adsorption, is calculated as mg per 500 ml.

Apparatus

Asbestos - Powminco, medium fiber, Gooch grade, acid washed; made by Powhatan Mining Company, Woodlawn, Baltimore, Maryland.

Filter Paper - Whatman No. 2, 32 mm diameter; Whatman No. 12 fluted.

Crucibles - Gooch, Bitumen, porcelain, Coors, size No. 2A, capacity 26 ml.

Funnel - 6-inch diameter.

Constant Humidity Vessel - An air-tight vessel (such as a desiccator) containing saturated sodium dichromate solution. This provides a relative humidity of 52%.

Screen - 100 mesh.

Oven - at 90° F ± 5° F, for drying crucible.

I. Preparation of Gooch Filters

A. Concentrated Asbestos Slurry

Weigh out 100 grams of medium fiber asbestos into a 2-liter beaker. Add 1500 ml of distilled water and stir to make a slurry. Heat the slurry on a hot plate until boiling starts. Decant the water layer above the slurry, and dilute the remainder to a volume of 4 liters.

B. Dilute Asbestos Slurry

Shake the concentrated asbestos slurry. Dilute 1 liter with 3 liters of distilled water to prepare the dilute asbestos slurry.

C. Preparation of Mat

Shake the dilute asbestos slurry well and pour out an 800-ml portion. Place a Gooch crucible in a crucible holder on a vacuum filter flask; with the vacuum off, insert a filter paper disk (cut to size of the crucible from Whatman No. 2 filter paper) in the bottom of the crucible. Fill the crucible with freshly agitated asbestos slurry, turn the vacuum on, and allow to suck dry. Tamp the asbestos layer with a glass or stainless steel tamper. Add a second measureful of fine asbestos slurry. Suck dry with the aid of vacuum but do not tamp the second layer.

Dry the crucible in an oven at 190°F + 5°F for five hours, store in the constant humidity vessel for five hours, weigh to 0.1 mg. The dry asbestos pad should weigh from 0.3 to 0.4 gram.

II. Filtration

Fit a tared Gooch crucible with asbestos pad on a crucible holder set in the neck of a suction flask. Mount a separatory funnel over the crucible so that the stem of the funnel extends well into the crucible. Pour the 500-ml sample into the separatory funnel, stopper the funnel, start the suction, and then open the stopcock, thus obtaining a self-feeding system.

After the sample has passed through the filter, save the filtrate, undiluted, for determination of adsorption factor. Add 500 ml of filtered petroleum ether to a separatory funnel. With vacuum on, adjust the stopcock by hand, washing down the inside walls of the crucible. Stopper the funnel and filter the remainder of the petroleum ether.

Suck the crucible dry and place it in the oven at 190°F + 5°F for 1.5 to 2 hours. Allow the crucible to stand in the constant humidity vessel for 5 hours, and weigh to the nearest 0.1 mg.

III. Determination of Adsorption Factor

Filter the undiluted filtrate through a Gooch crucible which has been tared so that the actual weight of filter mat is known. Wash, dry, etc., as in II.

IV. Calculations

1. Adsorption Factor

$$F = \frac{\text{mg gain in wt of crucible (in III)}}{\text{gram filter mat in crucible (in III)}}$$

2. Filter Residue, mg = mg gain in weight of crucible (in II) - K

where K = F x grams filter mat in crucible (in II)

APPENDIX XII

THE DETERMINATION OF HYDROGEN BY BETA-RAY ABSORPTION

(K. L. Hall)

Theory

The absorption of beta particles by matter is approximately exponential:

$$A_x = A_o e^{-\mu x} \qquad \text{Equation 1}$$

where A_x is the activity in counts per second measured through x cm of absorber, A_o is the activity with no absorber, and μ is the linear absorption coefficient. For beta emitting nuclei, the curve of transmitted activity versus thickness deviates from linearity with increasing absorber thickness. That is, the effective absorption coefficient increases such that beta particles have a finite range.

It is common to plot the activity on semilogarithmic paper against surface density of the absorber in mg/cm^2. The latter is the thickness multiplied by the density, ρ x. The resulting absorption curves are very nearly independent of the composition of the absorber. The reason for this is that the principal interaction of beta particles with matter is with electrons. The number of electrons per gram depends on the ratio of Z, the atomic number, to A, the mass number. The electron density or the number of electrons per cubic centimeter, is $NZ\rho/A$ where N is Avogadro's number and ρ is the density. The absorption coefficient is proportional to the electron density so Equation 1 becomes

$$A_x = A_o e^{-k\frac{NZ\rho}{A}x} \qquad \text{Equation 2}$$

where, k is a proportionality constant. The factor Z/A is approximately 1/2 for all elements except hydrogen, and in these cases the absorption curve depends only on the surface density, ρ x. For example, Z/A for helium is 2/4, carbon 6/12, for oxygen 8/16, etc. With heavier elements Z/A becomes less than 1/2 and with increasing Z interaction with nuclei becomes important. This causes the attenuation to become greater, but the difference in beta particle range using aluminum and platinum absorbers is only about 20%. Hydrogen is unique in that its Z/A = 1 - greater than any other element. This becomes the basis for its analysis.

For hydrocarbons the exponent is found by summing the absorption coefficients over the atoms in the hydrocarbon molecule. Thus,

$$k\frac{NZ\rho}{A}x = kN\rho x\left(\frac{6}{12}C + H\right) = kNx\frac{\rho}{2}(H + 1) \qquad \text{Equation 3}$$

In Equation 3, C and H are the weight fraction of carbon and hydrogen in the molecule, respectively. The beta activity transmitted through a fixed thickness of absorber using a counting system with fixed geometry is plotted on semilog paper versus the function: $\rho(H + 1)/2$

Calibration

For a long-lived source of beta radiation the strontium-90-yttrium-90 equilibrium mixture was selected. Strontium-90 has a 25-year half-life and emits a weak beta-ray. However, its daughter yttrium-90 is also radioactive with a 61-hour half-life and emits a 2.2 Mev beta-ray. It is the yttrium-90 which is actually counted, its amount remaining constant due to its long-lived parent.

The sample cell consisted of a small glass cylinder about 25 mm in diameter and 7 mm high to which were cemented beryllium windows, 10 mils thick. The cell had a small inlet and outlet glass tube for filling. (Beryllium windows were not required with beta-rays but they are for X-rays and the same cell was also used in X-ray work.) The sample cell was placed between the beta-ray source and an end window Geiger tube and counted in the usual manner. A series of hydrocarbons ranging from 1-methylnaphthalene (7.0 weight per cent H) to n-pentane (16.7 weight per cent H) was counted and the smooth curve relating the observed counting rate and the expression, $\rho(H + 1)/2$, was obtained. The compounds used to define this calibration curve were of high purity except for methylnaphthalene which was used to extend the curve to higher density liquids. The curve was slightly concave towards the origin (which is expected as explained in the above section).

Analysis

For routine determination of the hydrogen content of an unknown liquid, a sample was first counted and the value of $\rho(H + 1)/2$ was read from the calibration curve. Its API gravity obtained earlier was converted to density at 60°F, and the density was corrected to the temperature at which the sample was counted by reference to National Bureau of Standards Circular C410. The value of the abscissa was read and H calculated.

The major error in this determination arises from the uncertainty in the calibration curve. An error in the abscissa is magnified tenfold in the final value of H. It is estimated that the H values obtained have a precision of about 1%.

The introduction of oxygen, nitrogen, sulfur, phosphrous, chlorine, etc., should cause little effect since their Z/A values are approximately equal to that of carbon. However, with heavier elements some deviation may be expected. Several liquids containing these elements were measured. Their purities were unknown. The deviations from the hydrocarbon curve for an amine (19% nitrogen), a ketone (16% oxygen), and an alcohol (22% oxygen) were not great. Water (89% oxygen) and thiophene (38% sulfur) fell considerably below the curve. From this it appears that the presence of less than 1% of these elements in a sample should not interfere with the analysis.