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EFFECTS OF RADIATION ON AIRCRAFT LUBRICANTS AND FUELS

CALIFORNIA RESEARCH CORPORATION
RICHMOND, CALIFORNIA

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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

APRIL 1958

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

Carpenter Litho & Prtg. Co., Springfield, O.
500 — June 1958

FOREWORD

This report was prepared by California Research Corporation under USAF Contract No. AF 33(616)-3184. This contract was initiated under Project No. 2133, "Radiation Effects (Materials)," Task No. 73071, "Nuclear Radiation Resistant Material." The work was administered under the direction of the Materials Laboratory, Directorate of Laboratories, Wright Air Development Center, with Lt. W. L. R. Rice acting as project engineer.

This is the second Summary Report issued on this contract and covers research conducted from December 1, 1956, to November 30, 1957. The first Summary Report covered developments from the inception of the contract in September 195 to November 30, 1956.

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, J. T. Querin, B. W. Hotten, H. L. Peeler, M. A. Pino, N. P. Shields, J. M. Stokely, F. A. Stuart, and D. R. Wilgus.

ABSTRACT

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

Aromatic base materials were needed in the lubricant work, and most of these had to be synthesized. Exploratory synthesis evolved alkaryl ethers, alkaryl esters, alkylbenzenes, alkyl diphenyl ethers, and diarylalkanes. Chemical structure was correlated with physical properties and also with oxidation, thermal, and radiation stability. Although esters were inferior, each class had members with good radiation stability. Over-all, the alkyl diphenyl ethers offer the most promise for lubricant development. Polymers were also synthesized. These were used in an alkyl diphenyl ether to improve viscosity index and to increase viscosity. Compared to conventional thickeners, alkylated poly(α-methylstyrenes) (APAMS) and poly(alkylphenoxyethyl methacrylates) (APEMS) show promise for use in future radiation resistant lubricants.

The grease research produced CALRESEARCH 159, a material of enhanced radiation stability. It is a selenide-inhibited alkylbiphenyl gelled with an aromatic salt. Promise of improved products was shown in work on new oils, e.g., tris(phenoxyphenyl)dodecylsilane, on new gelling agents, e.g., sodium N-p-tolylterephthalamate or mixtures of aromatic salts; and on new additives, e.g., N, N'-di-2-naphthyl-p-phenylenediamine.

Many formulations of various hydraulic fluids were evaluated before and after irradiation. The alkyl diphenyl ethers looked best in radiation stability and in thermal stability at 700°F. CALRESEARCH 216 evolved from the formulation work. It is an alkyl diphenyl ether inhibited with a selenide and thickened with a polybutene. Chemical inhibitors improved oxidation stability both before and after gamma irradiation. Aromatic hydrocarbon additives in MLO 8200 fluid reduced viscosity change and gassing caused by irradiation. This fluid was shown to be usable to about 10^{10} ergs/g C of gamma radiation. Original and irradiated aromatic base fluids operated satisfactorily in aircraft piston pumps at 275°F. Isothermal bulk modulus was found to decrease markedly in a gas-liquid system such as would prevail under irradiation.

The alkyl aromatics were found best as base materials for gas turbine oils. Esters, mineral oils, and polyglycols tested were deficient in radiation or thermal stability. CALRESEARCH 230 was developed in the work; it is a selenide-inhibited alkyl diphenyl ether containing a petroleum bright stock and other additives. The alkyl diphenyl ethers showed good oxidation stability before and after irradiation. Their tendency towards high coking and low lubricity was improved by additives. Irradiation lowered coking in these bases and also in alkylbiphenyls. In all base stocks, foaming increased after irradiation, with or without silicone being present. Coking was reduced by blending with high boiling materials, e.g., bright stocks. Certain oil soluble dyes showed synergism with the beneficial dialkyl selenides in oxidation tests.

The thermal stability of nine jet fuels (five JP-4's, three JP-5's, and an RP-1) was studied in the CFR coker. Original stocks and samples irradiated for three different levels were tested. Low level irradiation (0.8×10^{10} ergs/g C) impaired thermal stability. Higher level radiation (8×10^{10} ergs/g C) improved thermal stability. An equation was developed by which it was possible to predict increase in viscosity with irradiation at any dosage once a single dosage point was known.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:

R. T. Schwartz

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

LUBRICANT PRODUCT SUMMARY

The lubricant development work was guided by pattern nonnuclear product specifications. Radiation resistance was added to these stringent requirements such that aromatic base stocks were needed rather than conventional fluids. Aromatic stocks have not been used extensively in lubricants. Thus, a program including synthesis, formulation, and testing was called for. This approach yielded four preferred products for use in the presence of radiation. Data on these are discussed in the following paragraphs.

Greases

Table I summarizes data on CALRESEARCH 159. The product is usable from about -10°F to 350°F. After a gamma dosage of 7.2×10^{10} ergs/g C, worked penetration, oxidation stability, and bearing performance were somewhat impaired. However, little change was caused in water resistance, evaporation at 400°F, wear properties, or copper corrosion. Pumpability, work stability, and low temperature torque actually improved slightly after this exposure.

Hydraulic Fluids

Data on CALRESEARCH 216 are in Table II. Irradiation caused an initial decrease in viscosity followed by a moderate increase. After 11.7×10^{10} ergs/g C, viscosity at 400°F was about the same as initially, while viscosity at 0°F increased threefold. Irradiation also: lowered slightly the initial pour point of -20°F; lowered the flash point drastically; increased vapor pressure slightly; worsened foaming; improved wear and film strength; and caused gassing of about 1 ml/ml - 10^{10} ergs/g C. Oxidation stability of CALRESEARCH 216 was good at 400°F and at 500°F. This property worsened with irradiation but was still tolerable after 11.7×10^{10} ergs/g C. Hydrolytic stability at 400°F was similarly affected. Operation in a piston-type hydraulic pump was satisfactory initially and after a dosage of 4.4×10^{10} ergs/g C.

Engine Lubricants

CALRESEARCH 230 data are in Table III. The fluid, with a pour point of -15°F, gave low coking and an excellent result in the WADC deposition test. Oxidation stability was fair. Irradiation to 0.99×10^{10} ergs/g C produced no change in pour point and load carrying capacity. Only slight changes in viscosity, flash point, evaporation, and deposition values were observed. Foaming was more seriously degraded while oxidation stability was drastically changed.

Gear Lubricants

Development work on this product was minor during the contract year as planned. The need for a gear lubricant could probably be filled by a suitable engine oil containing an extreme pressure agent. Table IV notes some properties of such a fluid.

TABLE I

PROPERTIES OF A RADIATION RESISTANT GREASE - CALRESEARCH 159[a]

Property or Test						
Radiation Dosage, 10^{10} ergs/g C	0			7.2[b]		
Dropping Point, °F	500+			580+		
ASTM Worked Penetration	261			330		
Work Stability						
Penetration after 100,000 strokes	325			307		
Norma Hoffmann Bomb						
Copper Corrosion, 100 hours at 212°F	slight stain			slight stain		
Oxidation, 100 hours at 250°F, psi	9			24		
Dirt Content						
25 Microns	>7600			>7600		
50 Microns	>1600			>1600		
Water Resistance						
Per Cent Loss	0			0		
Evaporation, per cent						
22 Hours at 300°F	1.7			3.1		
22 Hours at 400°F	21			18.5		
Apparent Viscosity, poises						
0°F at 12 sec^{-1}	7000			2600		
0°F at 20 sec^{-1}	5000			2000		
Low Temperature Torque						
Temperature, °F	-65	0	40	-65	0	40
Starting Torque, g-cm	-	2767	554	-	1106	554
Running Torque, g-cm	-	553	185	10,325	369	344
Navy Gear Wear Test, weight loss						
5-lb Load, mg/1000 Cycles	2.0			1.8		
10-lb Load, mg/1000 Cycles	5.7			5.0		
Bearing Performance						
10,000 rpm, hours at						
300°F	1577	634		306	265	
350°F	279	188	400	195	196	45

[a] 83% C_{16-18}-alkylbiphenyl, 12% sodium N-octadecylterephthalamate, 5% didodecyl selenide, 0.1% quinizarin.
[b] 200 g irradiated in tin-plated can open to air; MTR Canal Source.

TABLE II

PROPERTIES OF A RADIATION RESISTANT HYDRAULIC FLUID - CALRESEARCH 216[a]

Radiation Dosage, 10^{10} ergs/g C	0	1.0[b]	5.3[c]	11.7[c]
Viscosity, cs, °F				
400	2.58[e]	2.01[e]	1.96[e]	2.25[e]
210	12.00	9.839	10.2	13.35
100	85.26	70.18	82.6	121.8
0	4857	4153	6280	12,000
Pour Point, °F	-20	-25	-35	-35
Flash Point, °F	480	460	430	280
Spontaneous Ignition Temp., °F	1000	980	1010	960
Bulk Modulus (adiabatic), psi				
At 0 psi and 77°F	290,000	-	-	-
Foaming				
Volume, ml	170	180	250	550
Stability, min	1	0.9	5	2.5
Gassing During Irradiation, ml/ml	-	1.1[d]	7.5[d]	11.4[d]
Density at 68°F, g/ml	0.925			
Acid Number, mg KOH/g	0.17	0.01	nil	1.34
Vapor Pressure at				
400°F, mm Hg	5.8	5.1	-	6.5
500°F, mm Hg	14.2	25	-	29
Oxidation Corrosion (48 hr at 500°F)				
Weight Change, mg/cm²				
Fe	-1.24	-0.39	-0.48	-0.61
Al	0	+0.13	+0.03	0
Insolubles, %	1.0	1.0	0.5	0.4
Viscosity Change, 100°F, %	+78	+84	+142	+562
Viscosity Change, 210°F, %	+20	+38	+61	+184
Neutralization Number Change	5.3	5.0	5.4	5.2
Hydrolytic Stability				
100 hours in pressure bomb with 5% water at 400°F				
Viscosity Change				
At 100°F, %	-6.4	-5.5	-12.6	-13.2
At 210°F, %	-2.6	-4.0	-8.3	-
Insolubles, %	0.62	0.13	0.23	0.17
Four-Ball Wear, mm				
2 hours, 167°F 4 kg	0.64	-	-	-
10 kg	0.67	-	-	-
40 kg	0.78	0.86	-	0.51
Mean Hertz Load (screening test), kg	20	-	-	-
Hydraulic Pump Test, 3000 psi				
150 hours at 160°F				
100 hours at 275°F	OK	-	OK[e]	-

[a] 84% C_{16-18}-alkyl diphenyl ether 14% Polybutene 12B, 2% bis(tridecyl) selenide, 0.1% silicone solution.

[b] 600 ml irradiated in aluminum container open to air; [redacted] Canal Source.

[c] 200 ml irradiated in tin-plated can open to air, [redacted] Canal Source.

[d] 10 ml irradiated in 410 stainless steel capsule under helium.

[e] At 415°F.

[f] 1-gallon sample irradiated in stainless steel can open to air; 4.4 x 10^{10} ergs/g C in [redacted] Canal Source.

TABLE III

PROPERTIES OF A RADIATION RESISTANT ENGINE OIL - CALRESEARCH 230[a]

Dosage, 10^{10} ergs/g C	0		0.99[b]	
Viscosity, cs, °F				
415	1.41		-	
210	6.25		6.63	
100	39.6		43.8	
0	2502		2114	
Pour Point, °F	-15		-15	
Flash Point, °F	485		455	
Spontaneous Ignition Temp., °F	980		930	
Foaming, Sequence 1 - Max. Vol., ml	0		285	
Time to Clear, min	0		2	
Sequence 2 - Max. Vol., ml	0		55	
Time to Clear, min	0		0.5	
Sequence 3 - Max. Vol., ml	0		60	
Time to Clear, min	0		2.3	
Evaporation, 6-1/2 hr at 400°F, Wt. %	12.8		13.2	
Mean Hertz Load (screening test), kg	26		26	
Panel Coking, 4 hr at 700°F, mg	60		-	
WADC Deposition Test, Model F	0.67		1.03	
Oxidation-Corrosion, 48-hr test on 25-ml sample; air flow = 1-1/4 liter/hr				
Temperature, °F	400	500	400	500
Weight Change, mg/cm²				
Fe	+0.26	0.0	+0.38	+0.58
Al	+0.16	0.0	+0.48	+0.36
Viscosity Change, 100°F, %	58.1	+193	Tar	+525
Viscosity Change, 210°F, %	+35.6	+98.6	+2880	+150
Neutralization Number Change	5.0	5.8	3.3	4.8
Insolubles, %	Nil	1.33	Nil	2.2

[a] 81.7% C_{16-18}-alkyl diphenyl ether, 15% 210 Bright Stock, 2% didodecyl selenide, 1% tricresyl phosphate, 0.2% Petrol Black A, 0.001% silicone solution.

[b] 600-ml sample in aluminum container open to air; MTR Canal Source.

TABLE IV

PROPERTIES OF A PROSPECTIVE RADIATION RESISTANT GEAR OIL[a]

Radiation Dosage, 10^{10} ergs/g C	0	6.5[b]
Viscosity, cs, °F		
210	6.59	8.49
100	49.45	71.89
-65	-	-
Pour Point, °F	-20	-20
Oxidation-Corrosion (72 hours at 347°F, 5 liters of air/hour)	Probably Acceptable	
Weight Change, mg/cm^2		
Fe		
Al		
Mg		
Appearance		
Viscosity Change, %, °F		
130		
-40		
Insolubles, %		
Load Carrying Ability		
Mean Hertz Load, kg	45	44

[a] 93% C_{16-18}-alkylbiphenyl, 5% sulfurized olefin, 2% dibenzyl selenide.
[b] 600-ml sample in aluminum container open to air; MTR Canal Source.

Table of Contents

		Page
1	Introduction	1
	1.1 Objectives	1
	1.2 Scope	1
	1.3 Approach	1
	1.4 Organization of the Report	4
2	Exploratory Materials	5
	2.1 Introduction	5
	2.2 Base Fluids and Additives	5
	2.3 Viscosity Index Improvers	39
3	Lubricating Greases	55
	3.1 Introduction	55
	3.2 Radiation Resistant Grease: CALRESEARCH 159	55
	3.3 New Gelling Agents	58
	3.4 Oil Variation in Greases	65
	3.5 Inhibitor Variation in Greases	69
	3.6 Status, Conclusions, and Recommendations	72
4	Hydraulic Fluids	75
	4.1 Introduction	75
	4.2 Evaluation of Base Stocks	77
	4.3 Evaluation of Additives	91
	4.4 Evaluation of Formulations	117
	4.5 Evaluation of Thermal Stability	125
	4.6 Hydraulic Pump Tests	131
	4.7 Bulk Modulus	139
	4.8 Results of Cooperative Tests	140
	4.9 Conclusions	144
	4.10 Recommendations	145
5	Engine Oils	147
	5.1 Introduction	147
	5.2 Viscosity Changes of Various Irradiated Base Stocks and Effect of Inhibitors	147
	5.3 Evaluation of Various Base Stocks	149
	5.4 Formulations	169
	5.5 Results of Cooperative Tests	177
	5.6 Miscellaneous	180
	5.7 Status, Conclusions, and Recommendations	180

Table of Contents (Cont'd)

		Page
6	Gear Lubricants	182
	6.1 Introduction	182
	6.2 Test Results	182
	6.3 Status, Conclusions, and Recommendations	184
7	Jet Fuels	185
	7.1 Introduction	185
	7.2 Test Fuels	185
	7.3 Test Procedures	186
	7.4 Test Results	186
	7.5 Status	210
	7.6 Conclusions	210
	7.7 Recommendations	210

List of Appendixes

		Page
I	Test Methods	211
II	Synthesis of Diarylalkanes	219
III	Synthesis of 500-Pound Batch of C_{14-16}-Alkyl Diphenyl Ether	221
IV	Ten-Pound Preparation of Polydodecyl Diphenyl Ether	223
V	Synthesis of Bis(tridecyl) Selenide	224
VI	Polymerization of Alpha-Methylstyrene	225
VII	Alkylation of Poly(alpha-methylstyrene)	226
VIII	Preparation of A ylphenoxyethyl Methacrylate	227
IX	Polymerization Alkylphenoxyethyl Methacrylate	228
X	Isothermal Bulk Modulus of Hydraulic Fluid - Hydrogen Mixtures	229
XI	Calculation of Bulk Modulus	246
XII	Calculation of Radiation-Induced Viscosity Change for Jet Fuels	248

List of Illustrations

Figure No.		Page
1	Thermal Stability of Exploratory Base Fluids	24
2	Thickening Power of APAMS in C_{14-16}-Alkyl Diphenyl Ether	44
3	Viscosity Index Improving Characteristics of APAMS in C_{14-16}-Alkyl Diphenyl Ether	45
4	Thickening Power of Polymers in C_{14-16}-Alkyl Diphenyl Ether	47
5	Radiation-Induced Viscosity Loss as a Function of Polymer Structure	51
6	Viscosity Loss of Polymers During Gamma Irradiation	52
7	Viscosity Index-Viscosity Relationship of Polymers During Gamma Irradiation	53
8	Effect of Co^{60} Irradiation on Crystallite Structure of Na Benzoate: Na N-octadecylterephthalamate Grease	60
9	Effect of Co^{60} Irradiation on Crystallite Structure of Na N-octadecylterephthalamate: Na Dibenzyldithiocarbamate Grease	61
10	Effect of γ-Irradiation on Consistency of Grease	66
11	Correlation Between ASTM Bomb Oxidation and Navy High Speed Bearing Tests	73
12	Shear Stability in Sonic Oscillator Test	103
13	Radiation Stability of Thickened C_{14-16}-Alkyl Diphenyl Ether Blends	106
14	Effect of Aromatic Additives on Gas Evolution of Oronite 8200 Fluid	115
15	Effect of Additives on Radiation-Induced Gassing of Oronite 8200 Fluid	116
16	Vapor Pressures of Hydraulic Fluids	122
17	Radiation-Induced Viscosity Change of CALRESEARCH 216	123
18	Pump Parts After Test NY-9	134
19	Pump Parts After Test NY-10	135
20	Pump Parts After Test NY-11	136
21	Pump Parts After Test NY-12	137
22	Viscosity Change of Hydraulic Fluids in Pump Tests	138
23	Comparison of Calculated and Experimental Values for Two-Phase Bulk Modulus of Hydrogen - 8200 Fluid Mixtures at 200° F	141
24	Effect of Irradiation on Viscosities of Inhibited and Uninhibited Base Stocks	148
25	Coke Formation of Various Blends	172
26	Typical Effects of Gamma Irradiation on API Gravity, Initial Boiling Point, and 80% Distilled Point of Jet Fuels	189
27	Typical Effects of Gamma Irradiation of Viscosity of Jet Fuels	190

List of Illustrations (Cont'd)

Figure No.		Page
28	Correlation of Measured and Calculated Viscosities at 100°F, JP-4 and JP-5 Fuels	192
29	Filter Pressure Drop as a Function of Time - J-813 Coker Tests	194
30	Filter Pressure Drop as a Function of Time - J-852 Coker Tests	195
31	Filter Pressure Drop as a Function of Time - J-782 Coker Tests	196
32	Filter Pressure Drop as a Function of Time - J-872 Coker Tests	197
33	Filter Pressure Drop as a Function of Time - J-770 Coker Tests	198
34	Filter Pressure Drop as a Function of Time - J-728 Coker Tests	199
35	Filter Pressure Drop as a Function of Time - J-771 Coker Tests	200
36	Filter Pressure Drop as a Function of Time - J-748 Coker Tests	201
37	CFR Fuel Coker Tests of Three Irradiated JP-4 Jet Fuels	203
38	CFR Fuel Coker Tests of Two Irradiated JP-4 Jet Fuels	204
39	CFR Fuel Coker Tests of Three Irradiated JP-5 Type Jet Fuels	205
40	Relationship Between Peroxide Number and Thermal Stability (Irradiated Samples of J-1118)	208
41	Effect of Irradiation on Thermal Stability	209
42	Correlation of Mean Hertz Load with Screening Test	217
43	Sketch of P-V-T Cell	232
44	Pressure-Volume Measurements for Hydrogen - 8200 Fluid Mixtures at 200°F	234
45	Isothermal Bulk Modulus of Hydrogen - 8200 Fluid Mixtures at 80°F	235
46	Isothermal Bulk Modulus of Hydrogen - 8200 Fluid Mixtures at 200°F	236
47	Isothermal Bulk Modulus of Hydrogen - 8200 Fluid Mixtures at 300°F	237
48	Isothermal Bulk Modulus of Hydrogen - C_{14-16}-Alkyl Diphenyl Ether Mixtures at 80°F	238
49	Isothermal Bulk Modulus of Hydrogen - C_{14-16}-Alkyl Diphenyl Ether Mixtures at 200°F	239
50	Isothermal Bulk Modulus of Hydrogen - C_{14-16}-Alkyl Diphenyl Ether Mixtures at 300°F	240
51	Isothermal Bulk Modulus of Hydrogen - MIL-O-5606 Fluid Mixtures	241
52	Solubility of Hydrogen in Hydraulic Fluids	243
53	Bunsen Solubility Coefficient for Hydrogen Dissolved in Hydraulic Fluid	244

List of Illustrations (Cont'd)

Figure No.		Page
54	Viscosities at 100° F as a Function of Radiation Dosage	249
55	Correlation of Measured and Calculated Viscosity at 0° F, JP-4 Fuels	251
56	Correlation of Measured and Calculated Viscosity at 0° F, JP-5 Fuels	252

List of Tables

Table No.		Page
I	Properties of a Radiation Resistant Grease - CALRESEARCH 159	vi
II	Properties of a Radiation Resistant Hydraulic Fluid - CALRESEARCH 216	vii
III	Properties of a Radiation Resistant Engine Oil - CALRESEARCH 230	viii
IV	Properties of a Prospective Radiation Resistant Gear Oil	ix
V	Properties of Alkaryl Ethers	7
VI	Properties of Esters	8
VII	Properties of Alkylbenzenes	9
VIII	Properties of Alkyl Diphenyl Ethers	11
IX	Properties of Diarylalkanes	13
X	Properties of Miscellaneous Compounds	15
XI	Physical Properties of Intermediates	17
XII	Influence of Alkyl Group on Properties of Alkyl Diphenyl Ethers	19
XIII	Effect of Chemical Structure on Physical Properties	21
XIV	Evaluation of Alkaryl Ethers	25
XV	Evaluation of Alkyl Diphenyl Ether	26
XVI	Evaluation of Esters	28
XVII	Evaluation of Alkylbenzenes and Miscellaneous Compounds	29
XVIII	Evaluation of Diarylalkanes	31
XIX	Viscosity Loss of Base Fluids at 700° F	34
XX	Comparative Radiation Stability of Exploratory Base Fluids	37
XXI	Exploratory Base Fluids - Summary Conclusions	38
XXII	Polymerization of Alpha-Methylstyrene	41
XXIII	Summary Molecular Weight, Viscosity, and Viscosity Index Data of Partially Alkylated Poly(alpha-methylstyrenes)	42
XXIV	Polymerization Data of Alkylphenoxyethyl Methacrylate	46
XXV	Stability of Viscosity Index Improvers in C_{14-16}-Alkyl Diphenyl Ether to Gamma Rays	48
XXVI	Inspections on Pile-Irradiated Greases	57
XXVII	Status of Field Tests on CALRESEARCH 159	57
XXVIII	Gelling Power and Radiation Resistance of Mixed Salts	59
XXIX	p-Tolylterephthalamate Greases	63
XXX	Exploratory Isocyanate Derivatives as Gelling Agents	64
XXXI	Effect of Irradiation at 350° F on Experimental Greases	67
XXXII	Oil Evaporation at 350° F, 1-g Oil in 2-Inch Diameter Dish After 24 Hours at 350° F	68
XXXIII	Greases Containing New Synthetic Oils	70
XXXIV	Comparison of Antioxidants at 5% Concentration in Radiation Resistant Greases	71

List of Tables (Cont'd)

Table No.		Page
XXXV	Key to Additive Code	76
XXXVI	Properties of Fluids Based on C_{14-16}-Alkyl Diphenyl Ether	78
XXXVII	Properties of Fluids Based on Dodecyl Diphenyl Ether	82
XXXVIII	Properties of Fluids Based on Tetradecyl Diphenyl Ether	83
XXXIX	Properties of Fluids Based on C_{16-18}-Alkylbiphenyl (Distilled)	84
XL	Properties of Fluids Based on Naphthenic White Oil	87
XLI	Properties of Fluids Based on UCON DLB 144E	90
XLII	Inspections of Irradiated Silicones	92
XLIII	Fluids Based on C_{14-16}-Alkyl Diphenyl Ether with Selenide and Sulfide Inhibitors	93
XLIV	Fluids Based on C_{14-16}-Alkyl Diphenyl Ether with Amine and Phenolic Inhibitors	94
XLV	Analysis of Insolubles from Corrosion Tests	95
XLVI	Miscellaneous Oxidation and Corrosion Tests	96
XLVII	Effect of Selenide Concentration on 500° F Oxidation and Corrosion Tests - 86% C_{14-16}-Alkyl Diphenyl Ether + 14% PB 128 with Varying Selenide Concentration	98
XLVIII	Properties of Fluids Based on C_{14-16}-Alkyl Diphenyl Ether, 14% Polybutene 128, and 0.001% Dimethyl Silicone	99
XLIX	Effect of Irradiation on Oxidation Stability Dornte Test - Uncatalyzed Oxygen Absorption at 400° F	101
L	Properties of Fluids Based on C_{14-16}-Alkyl Diphenyl Ether, 2% Bis(tridecyl) Selenide, and 0.001% Dimethyl Silicone	104
LI	Effect of Selenide Inhibitors on Radiation Stability 410 Stainless Steel Capsules Under Helium	107
LII	Effect of Inhibitors on Radiation Stability 410 Stainless Steel Capsules Under Helium	108
LIII	Effect of Inhibitors on Radiation Stability of C_{14-16}-Alkyl Diphenyl Ether Under Helium in 410 Stainless Steel Capsules at 400° F	110
LIV	Effect of Hydrogen Acceptors on Radiation Stability 410 Stainless Steel Capsules Under Helium	111
LV	Effects of High Gamma Dosage on Base Stocks and Blends	112
LVI	Effect of Additives on the Radiation Stability of Oronite 8200 Fluid Irradiations in Tin-Plated Cans - 200-ml Samples Open to Air and in Capsules Sealed Under Helium - 10-ml Samples	114
LVII	Effect of Aromatics on Oxidation Stability of Oronite 8200 Fluid Oxidation and Corrosion Tests, 48 Hours at 500° F	118
LVIII	Properties of CALRESEARCH 216	119

List of Tables (Cont'd)

Table No.		Page
LIX	Oxidation and Corrosion Tests on CALRESEARCH 216 Before and After Irradiation, 48 Hours at 500° F	124
LX	Properties of n-Nonyl Diphenyl Ether Blend Additives: 13% PB 128 + 2% $C_{13}Se$ + 0.001% DC	126
LXI	Properties of Oronite 8200 Fluid and Hexa(2-ethylbutoxyl)disiloxane Base Stock	127
LXII	Properties of Commercial Silicate Ester Hydraulic Fluids	129
LXIII	Thermal Stability Tests Under Helium in 410 Stainless Steel Capsules	130
LXIV	Results of New York Air Brake Hydraulic Pump Tests Model 66WA300, Pressure, 3000 psi, Full Delivery, 3450 rpm, Weight Loss in Milligrams	133
LXV	Effect of Irradiation on Adiabatic Bulk Modulus of Hydraulic Fluids at Atmospheric Pressure and 76° F	142
LXVI	Properties of Oronite 8200 Fluid Following Irradiation in NARF SPIT No. 2 Tests	143
LXVII	Lubricants Based on C_{14-16}-Alkyl Diphenyl Ether	150
LXVIII	Lubricants Based on Tetradecyl Diphenyl Ether	153
LXIX	Lubricants Based on C_{16-18}-Alkylbiphenyl (Distilled)	155
LXX	Lubricants Based on C_{16-18}-Alkylbiphenyl (Bottoms)	156
LXXI	Lubricants Based on Diisooctyl Terephthalate	159
LXXII	Lubricants Based on Naphthenic White Oil	162
LXXIII	Lubricants Based on UCON DLB 144E	165
LXXIV	Lubricants Based on Di(2-ethylhexyl) Azelate	166
LXXV	Lubricants Based on Diisooctyl Azelate	167
LXXVI	Lubricants Based on Di(2-ethylhexyl) Sebacate	168
LXXVII	Effects of Additives on Properties of C_{14-16}-Alkyl Diphenyl Ether	170
LXXVIII	Coke Tests at 700° F on C_{14-16}-Alkyl Diphenyl Ether Blends	171
LXXIX	Inhibiting Effect of Petrol Black A in Formulations Containing Tricresyl Phosphate	173
LXXX	Effects of Irradiation on Properties of Gas Turbine Oil Formulations	174
LXXXI	Effects of Bright Stock on Properties of Base Stocks	176
LXXXII	Comparison of Oxidation-Corrosion Test Results at 500° F Run at California Research Corporation and at WADC	178
LXXXIII	Micro Ryder Gear Loading Tests on Exploratory Blends	177
LXXXIV	Corrosion During Irradiation	181
LXXXV	Viscosity and Film Strength of Gear Oils	183
LXXXVI	Identity of Jet Fuels	185
LXXXVII	Laboratory Inspections on Fuels J-746 and J-770	187
LXXXVIII	Weight Loss of Fuel on Irradiation	188
LXXXIX	Summary of CFR Fuel Coker Tests on Irradiated Fuels	193

1 INTRODUCTION*

1.1 Objectives

The research and development on this contract had three objectives, as follows:

a. To develop four specific lubricants having enhanced resistance to nuclear radiation.

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

c. To provide technical service to personnel in the Air Nuclear Power program on problems pertaining to the present and projected uses of organic fluids.

1.2 Scope

For the four specific lubricants, performance requirements were based on the most recent nonnuclear high temperature specifications. Temperature limits were extended 50° F to 100° F or higher, radiation levels were set in the range from 10^8 to 10^9 roentgens (87×10^8 to 87×10^9 ergs/g C). This is the range in which all conventional lubricants show major property changes. Lubricant development work accounted for approximately 85% of the contract activity.

In the study of jet fuels, a survey was involved as no target specification for a radiation resistant fuel was given. Of concern was the stability of typical jet fuels to nuclear radiation. About 10% of the over-all effort was devoted to this work.

California Research personnel also served as consultants during the contract period on special problems of application for organic fluids in the ANP program. Such a function, which represented about 5% of contract effort, was 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 to others for test work. This activity was reported only to WADC and is not covered in this Summary Report.

1.3 Approach

1.3.1 Materials

Organic fluids used in advanced nonnuclear lubricant specifications are generally at the low end of the radiation stability scale. Lubricants made from aliphatic diesters, disiloxanes, and silicones show appreciable changes in properties after exposure to about 0.1×10^8 roentgens (8.7×10^8 ergs/g C). Chemical additives may be used to enhance the radiation stability[1] of base fluids, but the finished formulation is limited by the inherent characteristics of the base oil.

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

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* Manuscript released by authors January 1958 for publication as a WADC Technical Report

Polyphenyl compounds are the most stable of all organic species to radiation[1] but are not suitable for use as aircraft lubricants. However, these compounds may be modified chemically to yield materials of optimum compromise between radiation stability and lubricant performance. Broadly speaking, the alkyl aromatic class of organic fluids was found to be of most interest[2,3]. These fluids were the basis for the larger part of the lubricant development. Minimum work was programed with so-called "conventional" base materials; effort was sufficient only to establish optimum formulations. The alkyl aromatics used were mostly new materials which were specially synthesized for the work. It should be recognized that there is an inherent time lag between synthesis, formulation, and testing work. Thus this year's synthesis research will produce the base for next year's best formulations.

In the jet fuel survey, production fuels were investigated principally. Several of these are the same products under study by an Air Force-industry group for the development of a thermal stability test. The work on radiation stability should serve as a valuable adjunct to the extensive testing being conducted in the Air Force-industry program.

1.3.2 Irradiations

1.3.2.1 Sources Used

Almost all irradiations were made in the canal gamma source at the Materials Testing Reactor (MTR). The prevailing dose rate varied almost tenfold up to a maximum of 2×10^7 roentgens (17.4×10^8 ergs/g C) per hour. Samples were exposed for various dosages up to about 50×10^8 roentgens (44×10^{10} ergs/g C). The values for gamma dosage are considered accurate to about $\pm$ 10%[4].

A small number of irradiations were made in the California Research-AEC cobalt-60 source[5]. Prevailing dose rate was about 2.5×10^5 roentgens (22×10^6 ergs/g C) per hour. Accuracy of the dosage values here is about $\pm$ 5%.

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

[2] "Effects of Radiation on Aircraft Lubricants and Fuels," (California Research 1956 Summary Report on Contract AF 33(616)-3184) WADC Technical Report 56-646 (CONFIDENTIAL).

[3] "Engine Oil Development," (Shell Development Summary Report) November 1956, WADC TR 57-177.

[4] "Monitoring the MTR Canal Gamma Source - A Treatment of Reliability," (California Research-AEC Report No. 19) August 31, 1957.

[5] B. Manowitz, "Use of Kilocurie Radiation Sources," Nucleonics, 9, No. 2, p. 10, August 1951.

1.3.2.2 Units

Of the many units in which to express gamma dosage, the roentgen has been most popular and meaningful (though only approximately correct). Contract lubricant specifications were stated in terms of the roentgen. Measurements in the MTR Canal Source are both determined (by replacing the sample with the monitor) and reported in terms of the roentgen[1]. Thus the term became familiar and was used in planning irradiations.

Actually the roentgen cannot be applied to reflect correctly the energy absorbed in hydrocarbons. A more fundamental unit, ergs per gram, is preferred by Wright Air Development Center (WADC). This unit is referred to carbon as a standard and is expressed as ergs/g C. All gamma dosages in this report have been converted to ergs/g C by applying the simple factor, 87.1 ergs/g C per roentgen[2]. Thus the dosages reported are only approximate, true dosages in ergs/g C, which would vary with hydrogen-carbon ratio, etc., of material irradiated, would require a much more vigorous treatment. Corrections were not made for attenuation by the walls of irradiation containers. Calculations showed that this attenuation ranged from about 3% to 8%[3] for the various container configurations used. This error was ignored as it was well within the accuracy of measurement of radiation received by the samples.

1.3.2.3 Containers

As the exposure zone in the MTR Gamma Canal Source is under 18 feet of water, special containers were needed for the irradiation of samples. Several types of vessels were used, depending 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 are 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 OD aluminum pipe as an outer canister. Four-dram glass vials were a convenient type of inner container for exposing 10-ml samples. 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[4] of 410 stainless steel were substituted for the glass vials. In some cases the outer canister was provided with nichrome heaters.

[1] C. H. Hogg, "Gamma-Ray Dosage Rate Measurement," US AEC Document IDO-16205, November 22, 1955.

[2] Procedure requested by WADC personnel.

[3] Lower and upper limits assuming no or complete loss, respectively, of scattered gamma rays.

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

In many instances, quantities larger than 10 ml 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 held about 525 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.

1.3.3 Test Methods

Physical and chemical properties and performance in bench tests were measured by standard methods, whenever possible. In the few instances where special tests were used, the procedures are noted in the text. Appendix I cites standard methods by source and number; it also describes special tests.

1.4 Organization of the Report

The report is organized into six additional sections as follows:

Section II: Exploratory Materials - properties and test data on base fluids which were synthesized.

Section III: Lubricating Greases - development, test data, and status.

Section IV: Hydraulic Fluids - development, test data, and status.

Section V: Engine Lubricants - development, test data, and status.

Section VI: Gear Lubricants - status.

Section VII: Jet Fuels - test results.

2 EXPLORATORY MATERIALS (D. R. Wilgus, A. C. Ettling)

2.1 Introduction

The exploratory synthesis program for the contract year was designed to permit a systematic study and preliminary evaluation of a variety of chemical classes as possible base fluids for lubricant formulations. The program was, in part, a continuation and extension of the previous year's developments. Emphasis was placed on the preparation of alkaryl compounds in view of demonstrated radiation resistance of aromatic materials. The general classes of compounds explored were hydrocarbons, ethers, and esters. Variables which were studied included:

a. Nature, position, and number of alkyl chain attachments.

b. Alkyl chain structure.

c. Nature and position of aromatic nucleus.

d. Alkyl-to-aryl carbon ratio.

Correlations were made between structure and oxidative, thermal and radiation stabilities, and between physical properties.

In addition to the exploratory synthesis program, larger preparations of promising fluids were made to allow full-scale evaluation. Several batches of an alkyl selenide oxidation inhibitor with improved low temperature properties were synthesized. An investigation was initiated in the field of V.I. improvers for hydraulic fluids. In this the synthesis and preliminary evaluation of polymeric materials possessing resistance to radiation damage were carried out.

For all compounds synthesized, certain selected physical properties were obtained. These data are tabulated for the various organic classes and discussed in later sections. From this information, fluids were chosen for more extensive evaluations. Data on these selected fluids are also tabulated and discussed in later sections.

2.2 Base Fluids and Additives

Aluminum chloride-catalyzed alkylations with 1-olefins were used frequently in this work to introduce secondary alkyl groups on aromatic rings. Structural representations of these alkyl derivatives in Tables V through XXI depict attachment at the number two carbon of the olefin. Under the conditions employed, the point of attachment may be any carbon other than the terminal one of the paraffin chain. No attempt was made to determine the degree of concurrent meta and para orientation with the introduction of more than one secondary alkyl group. Normal alkyl groups introduced via acylation, followed by reduction, yielded only the para isomer, and these are represented accordingly in the tables.

The distillation of intermediate and final products was performed with simple laboratory apparatus using short Vigreaux columns. Temperature measurements were made with uncorrected thermometers, and pressures were measured by Dubrovin gages at a point in the system somewhat removed from the column head. Readings were unreliable at pressures below 1 mm.

Estimated pour points were made on small samples of fluids, as ASTM pour values did not always define true low temperature properties (e.g., n-nonyl diphenyl ether: ASTM pour, -45° F, small-scale pour, -20° F)[1]

2.2.1 Syntheses

2.2.1.1 Alkaryl Ethers

The ethers of Table V were synthesized by refluxing isopropanol solutions of alkali phenolates with appropriate alkyl halides. The high pour or melting points of these compounds are serious disadvantages. For example, 1,6-bis(phenoxy)hexane melted at 183° F, whereas, 1,6-diphenylhexane had a pour point of 5° F.

2.2.1.2 Esters

Most of the esters of Table VI were synthesized by alkylating[2] benzene or diphenyl ether with ethyl undecylenate using aluminum chloride catalyst. The 2-ethylhexyl esters were prepared by transesterification of the ethyl esters using litharge catalyst[3].

The synthesis of diisooctyl terephthalate was presented in the 1956 Summary Report[3]. Hydrogenation at 392° F and 2800 psi to the hexahydro derivative, using Raney nickel catalyst, lowered the viscosity and increased the viscosity index without changing the low pour point.

2.2.1.3 Alkylbenzenes

Four of the alkylbenzenes of Table VII, 2-phenylhexadecane, 10-phenyleicosane, 11-phenyldocosane, and 1-phenyl-9-octadecene, were not synthesized on this project but were available from other work. They were prepared by alkylating benzene with 1-octadecene using aluminum chloride catalyst. Only the last of the list had a sufficiently low pour point to be of interest, although all had good viscosity properties. Similarly, the sec-octadecylbenzenes had good viscosity but poor pour characteristics.

[1] An expeditious procedure for pour determinations consisted of charging 5 cc material to a small vial equipped with a low temperature thermometer. The vial was placed in a Dry Ice-acetone bath, and the temperature was gradually lowered. The vial was swirled intermittently, and the temperature at which the sample ceased to flow was observed. The material was allowed to liquefy and the procedure repeated.

[2] C. A. Thomas, "Anhydrous Aluminum Chloride in Organic Chemistry," ACS Monograph Series No. 87, p. 471, Reinhold Publishing Corporation, New York (1941).

[3] "Effect of Radiation on Aircraft Lubricants and Fuels," (California Research 1956 Summary Report on Contract AF 33(616)-3184) WADC Technical Report 56-646, Appendix I, p. 160.

TABLE V

PROPERTIES OF ALKARYL ETHERS

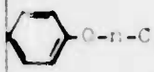
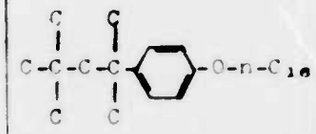
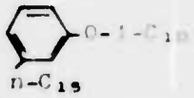
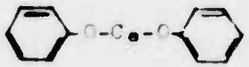
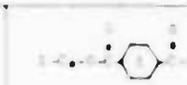
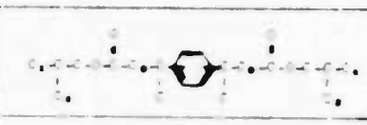
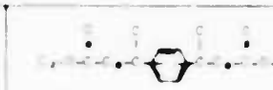
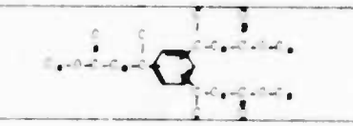
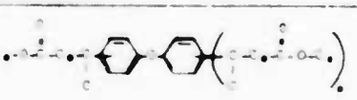
Structure				
Compound	n-Hexadecyl Phenyl Ether	n-Hexadecyl Octyl-(DIB)phenyl Ether	Isodecyl 3-n-Pentadecylphenyl Ether	1,6-Bis(phenoxy)hexane
Reference	←AOO-1-36→	←4806-15→	←4806-14→	←4805-15→
Distillation Fraction				
a. Boiling Range, °F at mm	-	463-475/0.7	463-475/0.6	-
b. Description	-	Heart Cut	Heart Cut	-
Physical Properties				
a. Viscosity, cs at 400°F	-	-	-	0.745 (414°F)
210°F	2.51	6.44	5.16	2.62
100°F	8.62	41.3	27.1	14.5 (extrap)
b. Temperature, °F, for a Viscosity (extrap)				
of 1 cs	380	525	502	348
of 2500 cs	-60	-3	-19	-13
of 13,000 cs	-79	-27	-42	-31
c. ASTM Slope (100°F to 210°F)	0.745	0.713	0.709	0.928
d. Viscosity Index	133	115	133	-51
e. Pour Point, °F	-	-	+12	-
f. Viscosity at Pour Point, cs (extrap)	-	-	460	-
g. Melting Point, °F	95	88	-	183
h. Refractive Index, n_D^{20}	-	-	1.4829	-

TABLE V

PROPERTIES OF ESTERS

Structure			
Compound	Dibenzyl hexahydroterephthalate	Carbethoxyethoxyethyl benzene	Bis(carbethoxyethoxyethyl) benzene
Reference	[illegible]	[illegible]	[illegible]
Distillation Fraction			
a. Boiling Range, °F at mm	[illegible]	[illegible]	Topped to [illegible]
b. Description	Heart Cut	[illegible]	Bottoms
Physical Properties			
a. Viscosity, cs at 210°F	[illegible]	[illegible]	[illegible]
100°F	[illegible]	[illegible]	[illegible]
b. Temp., °F, for a Viscosity of/cap			
10 cs	[illegible]	[illegible]	[illegible]
10,000 cs	[illegible]	[illegible]	[illegible]
15,000 cs	[illegible]	[illegible]	[illegible]
c. ASTM Slope (100°F to 210°F)	[illegible]	[illegible]	[illegible]
d. Viscosity Index	[illegible]	[illegible]	[illegible]
e. Pour Point, °F	[illegible]	[illegible]	[illegible]
f. Viscosity at Pour Point, cs (cstmp)	[illegible]	15,000	150,000
g. Density, 4°	[illegible]	[illegible]	[illegible]
h. Refractive Index, n_D^{20}	[illegible]	[illegible]	[illegible]

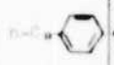
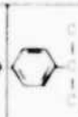
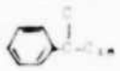
Structure			
Compound	Carbethoxyethylbenzene	Bis(carbethoxyethyl)benzene	Tris(carbethoxyethyl)benzene
Reference	[illegible]		
Distillation Fraction			
a. Boiling Range, °F at mm	[illegible]	[illegible]	[illegible]
b. Description	[illegible]	[illegible]	Mid Bottoms
Physical Properties			
a. Viscosity, cs at 210°F	[illegible]	[illegible]	[illegible]
100°F	[illegible]	[illegible]	[illegible]
b. Temp., °F, for a Viscosity of/cap			
10 cs	[illegible]	[illegible]	[illegible]
10,000 cs	[illegible]	[illegible]	[illegible]
15,000 cs	[illegible]	[illegible]	[illegible]
c. ASTM Slope (100°F to 210°F)	[illegible]	[illegible]	[illegible]
d. Viscosity Index	[illegible]	[illegible]	[illegible]
e. Pour Point, °F	[illegible]	[illegible]	[illegible]
f. Viscosity at Pour Point, cs (cstmp)	[illegible]	[illegible]	[illegible]
g. Density, 4°	[illegible]	[illegible]	[illegible]
h. Refractive Index, n_D^{20}	[illegible]	[illegible]	[illegible]

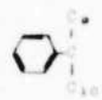
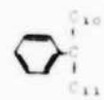
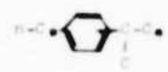
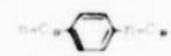
Structure			
Compound	[illegible] Diphenyl Ether	Bis(carbethoxyethyl) Diphenyl Ether	Tris(carbethoxyethyl) Diphenyl Ether
Reference	[illegible]		
Distillation Fraction			
a. Boiling Range, °F at mm	[illegible]	[illegible]	[illegible]
b. Description	Heart Cut	Heart Cut	Bottoms
Physical Properties			
a. Viscosity, cs at 210°F	[illegible]	[illegible]	[illegible]
100°F	[illegible]	[illegible]	[illegible]
b. Temp., °F, for a Viscosity of/cap			
10 cs	[illegible]	[illegible]	[illegible]
10,000 cs	[illegible]	[illegible]	[illegible]
15,000 cs	[illegible]	[illegible]	[illegible]
c. ASTM Slope (100°F to 210°F)	[illegible]	[illegible]	[illegible]
d. Viscosity Index	[illegible]	[illegible]	[illegible]
e. Pour Point, °F	[illegible]	[illegible]	[illegible]
f. Viscosity at Pour Point, cs (cstmp)	[illegible]	[illegible]	[illegible]
g. Density, 4°	[illegible]	[illegible]	[illegible]
h. Refractive Index, n_D^{20}	[illegible]	[illegible]	[illegible]

* Bottoms (Not applicable mm).

TABLE VII

PROPERTIES OF ALKYLBENZENES

Structure												
Compound	n-Nonyl-benzene	2-Phenyl-hexadecane	1-Phenyl-9-octadecene	sec-Octadecylbenzenes								
Reference	←4658-43→	←3048-13→	←560-7→	←4965-12→								
Distillation Fraction		-		-	255-	321-	332-	368-	373-	490-	517-	>600/0.8
a. Boiling Range, °F at mm	293/10	-	430-440/5	-	320/0.8	331/0.8	367/0.8	372/0.8	489/0.8	516/0.8	599/0.8	-
b. Description	Heart Cut	-		whole	0-4%	4-11%	11-13%	13-76%	76-79%	79-92%	92-95%	5% Btm
Physical Properties												
a. Viscosity, cs at 210°F	1.09	3.73	2.56	3.57	1.90	2.43	2.35	2.76	4.86	7.73	8.60	27.3
100°F	0.55	16.9	8.04	14.9	5.74	8.56	8.14	10.4	23.7	46.2	52.7	250
b. Temp., °F, for a Viscosity (extrap)												
of 1 cs	226	442	391	443	335	370	363	392	494	577	598	>770
of 2500 cs	-112	-32	-68	-40	-79	-58	-62	-52	-28	-8	-6	+34
of 13,000 cs	-	-53	-88	-62	-98	-76	-81	-72	-50	-33	-32	+2
c. ASTM Slope (100°F to 210°F)	0.841	0.741	0.704	0.716	0.747	0.764	0.764	0.754	0.695	0.659	0.645	0.582
d. Viscosity Index	126	125	165	140	-	117	117	121	143	135	135	127
e. Pour Point, °F	-40	+15	-25	+26	+55	+20	+2[a]	+26[a]	+20	+40[a]	+50[a]	+65
f. Viscosity at Pour Point, cs (extrap)	46	193	194	96	12	55	96	62	245	270	220	780
g. Density, D[illegible]	-	-	-	-	-	-	-	-	-	-	-	-
h. Refractive Index, n[illegible]	1.4839	-	-	1.4779	1.4590	1.4733	1.4718	1.4793	1.4805	1.4775	1.4789	1.4780

Structure				
Compound	10-Phenyleicosane	11-Phenyldocosane	sec-Octyl-n-nonylbenzene	Di(n-nonyl)benzene
Reference	←2359-3→	←2359-19→	←5044-13→	←5051-22→
Distillation Fraction				
a. Boiling Range, °F at mm	-	437/2.0	291-334/0.1	349-365/0.5
b. Description	-	-	Heart Cut	Heart Cut
Physical Properties				
a. Viscosity, cs at 210°F	3.11	3.70	2.75	2.83
100°F	13.3	17.0	10.8	9.80
b. Temp., °F, for a Viscosity (extrap)				
of 1 cs	405	440	384	412
of 2500 cs	-36	-30	-47	-63
of 13,000 cs	-57	-52	-67	-83
c. ASTM Slope (100°F to 210°F)	0.768	0.745	0.773	0.706
d. Viscosity Index	104	120	107	152
e. Pour Point, °F	+15	+35	-40[b]	+45
f. Viscosity at Pour Point, cs (extrap)	150	97	1600	28
g. Density, D[illegible]	-	-	0.8533	0.8560
h. Refractive Index, n[illegible]	-	-	1.4837	1.4830

[a] Estimate from small-scale run.

[b] Crystallized within ten hours at -20°F.

n-Nonylbenzene was synthesized by acylating benzene with pelargonyl chloride, followed by Wolff-Kischner reduction of the ketone. (See Appendix II.) A repetition of this process substituting n-nonylbenzene for benzene yielded di(n-nonyl)benzene. Alkylation of n-nonylbenzene with 1-octene yielded sec-octyl-n-nonylbenzene.

2.2.1.4 Alkyl Diphenyl Ethers

In order to permit extensive screening tests, a 500-pound batch of C_{14-16}(50/50)-sec-alkyl diphenyl ether was synthesized at an early date. The method of synthesis is found in Appendix III and was typical for the introduction of secondary alkyl groups on the aromatic ring of the many compounds synthesized, particularly for the alkyl diphenyl ethers of Table VIII. Normal alkyl groups were introduced by acylation, followed by reduction, as described in Appendix II. Two of the compounds in Table VIII were synthesized by the Ullmann reaction[1], involving the metathesis of an alkali phenolate with m-bromotoluene in the presence of activated copper. These were m-tolyl m-n-pentadecylphenyl ether and the intermediate m-tolylphenyl ether. The latter was acylated and reduced to obtain m-tolyl n-tetradecylphenyl ether.

The several higher molecular weight alkyl diphenyl ethers were prepared as grease bases. Of these, the poly-sec-dodecyl product proved to be the most suitable. Details of the preparation of 10 pounds of this material are given in Appendix IV.

2.2.1.5 Diarylalkanes

The method of synthesis of the diarylalkanes in Table IX is reported in Appendix II. This method is generally applicable for the introduction of normal alkyl groups into an aromatic nucleus. Secondary alkyl groups [as in phenyl(sec-tetradecylphenyl)isodecane] were introduced by the method given in Appendix III for a diphenyl ether derivative. The compound, dicyclohexylisodecane, was included in Table IX for convenience and was prepared by hydrogenating diphenylisodecane at 392°F and 2200 psi over Raney nickel catalyst. Unexpected difficulties were encountered in the synthesis of the three bis(butylphenyl)nonanes. Each contained about 5% of unreduced ketone. The contribution of the impurities to the properties has not been resolved, since attempts to completely purify these compounds have been unsuccessful thus far.

2.2.1.6 Miscellaneous Compounds and Intermediates

The properties of several compounds not fully characterized are given in Table X. The polyoctyl-m-terphenyl was prepared for use as a radiation resistant grease base. It was synthesized by aluminum chloride alkylation of m-terphenyl with 1-octene in carbon disulfide solvent. Polynonylphenyl was the

[1] "Organic Syntheses," Collective Volume II, p. 445, John Wiley and Sons, New York (1943).

TABLE XXIX

PROPERTIES OF ALKYL DIPHENYL ETHERS

Structure											
Compound	n-Nonyl Diphenyl Ether		n-Decyl Diphenyl Ether	n-Tetradecyl Diphenyl Ether	Dioctyl (50/50 mix) Alkyl Diphenyl Ether						
Reference	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]						
Distillation Fraction											
a. Boiling Range, °F at mm	[illegible]	[illegible]	[illegible]	[illegible]	-	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
b. Description	Heart Cut		Heart Cut	Heart Cut	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Physical Properties											
a. Viscosity, cs at 210°F	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
100°F	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
b. Temp., °F, for a Viscosity (extrap)											
of 1 cs	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
of 2000 cs	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
of 10,000 cs	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
c. ASTM Slope (100°F to 210°F)	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
d. Viscosity Index	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
e. Pour Point, °F	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
f. Viscosity at Pour Point, cs (extrap)	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
g. Density, [illegible]	[illegible]	[illegible]	-	-	-	-	-	-	[illegible]	-	-
h. Refractive Index, [illegible]	[illegible]	[illegible]	-	[illegible]	-	-	-	-	[illegible]	[illegible]	-
i. Flash Point (OCC), °F	-	-	-	-	[illegible]	-	-	-	-	-	-

Structure				
Compound	[illegible]-Ethyl n-Tetradecyl Diphenyl Ether	[illegible]-Ethyl sec-Pentadecyl Diphenyl Ether	[illegible]-Ethyl n-Nonyl Diphenyl Ether	[illegible]-Ethyl n-Tetradecyl Diphenyl Ether
Reference	[illegible]	[illegible]	[illegible]	[illegible]
Distillation Fraction				
a. Boiling Range, °F at mm	[illegible]	[illegible]	-	-
b. Description	Heart Cut	Heart Cut	[illegible]	[illegible]
Physical Properties				
a. Viscosity, cs at 210°F	[illegible]	[illegible]	[illegible]	[illegible]
100°F	[illegible]	[illegible]	[illegible]	[illegible]
b. Temp., °F, for a Viscosity (extrap)				
of 1 cs	[illegible]	[illegible]	[illegible]	[illegible]
of 2000 cs	[illegible]	[illegible]	[illegible]	[illegible]
of 10,000 cs	[illegible]	[illegible]	[illegible]	[illegible]
c. ASTM Slope (100°F to 210°F)	[illegible]	[illegible]	[illegible]	[illegible]
d. Viscosity Index	[illegible]	[illegible]	[illegible]	[illegible]
e. Pour Point, °F	[illegible]	[illegible]	[illegible]	[illegible]
f. Viscosity at Pour Point, cs (extrap)	[illegible]	[illegible]	[illegible]	[illegible]
g. Density, [illegible]	-	-	-	[illegible]
h. Refractive Index, [illegible]	-	[illegible]	[illegible]	[illegible]
i. Flash Point (OCC), °F	-	-	-	-

Structure												
Compound	[illegible]-Ethyl n-Nonyl Diphenyl Ether											
Reference	[illegible]						[illegible]					
Distillation Fraction												
a. Boiling Range, °F at mm	-	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	-	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
b. Description	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Physical Properties												
a. Viscosity, cs at 210°F	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
100°F	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
b. Temp., °F, for a Viscosity (extrap)												
of 1 cs	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
of 2000 cs	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
of 10,000 cs	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
c. ASTM Slope (100°F to 210°F)	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
d. Viscosity Index	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
e. Pour Point, °F	-	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
f. Viscosity at Pour Point, cs (extrap)	-	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
g. Density, [illegible]	-	-	-	-	-	-	-	-	-	-	-	-
h. Refractive Index, [illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	-	-	-	-	-	-
i. Flash Point (OCC), °F	-	-	-	-	-	-	-	-	-	-	-	-

[a] Estimate from semi-log plot.
[b] Crystallized within 24 hours at -20°F.

TABLE VIII (CONTINUED)

PROPERTIES OF ALKYL SILICATE ESTERS

Page 2 of 2

Structure											
Compound	Methyltrimethoxysilane (Methyl Ester)				Tetraethyl (Ethyl Ester)	Triethylmethoxysilane (Methyl Ester)					
Reference	[illegible]				[illegible]	[illegible]					
Distillation Fraction											
a. Boiling Range, °F at [illegible]	-	[illegible]	[illegible]	[illegible]	[illegible]	-	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
b. Description	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Physical Properties											
a. Viscosity, [illegible] at 210°F	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
100°F	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
b. Temp., °F, for a Viscosity (estimd)											
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
c. API Gravity (100°F to 210°F)	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
d. Viscosity Index	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
e. Pour Point, °F	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
f. Viscosity at Pour Point, cs (estimd)	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
g. Density, [illegible]	-	-	-	-	-	-	-	-	-	-	-
h. Refractive Index, [illegible]	-	-	-	-	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
i. Flash Point (COC), °F	-	-	-	-	-	-	-	-	-	-	-

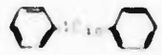
Structure									
Compound	[illegible] (Ethyl Ester)								
Reference	[illegible]								
Distillation Fraction									
a. Boiling Range, °F at [illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
b. Description	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Physical Properties									
a. Viscosity, cs at 210°F	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
100°F	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
b. Temp., °F, for a Viscosity (estimd)									
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
c. API Gravity (100°F to 210°F)	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
d. Viscosity Index	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
e. Pour Point, °F	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
f. Viscosity at Pour Point, cs (estimd)	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
g. Density, [illegible]	-	-	-	-	-	-	-	-	-
h. Refractive Index, [illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
i. Flash Point (COC), °F	-	-	-	-	-	-	-	-	-

Structure									
Compound	Triphenylmethoxysilane (Methyl Ester)								
Reference	[illegible]						[illegible]	[illegible]	
Distillation Fraction									
a. Boiling Range, °F at [illegible]	-	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	Trapped in [illegible] Mixture	Trapped in [illegible] Mixture	
b. Description	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]			
Physical Properties									
a. Viscosity, cs at 210°F	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	
100°F	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	
b. Temp., °F, for a Viscosity (estimd)									
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	
c. API Gravity (100°F to 210°F)	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	
d. Viscosity Index	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	
e. Pour Point, °F	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	
f. Viscosity at Pour Point, cs (estimd)	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	
g. Density, [illegible]	-	-	-	-	-	-	-	-	
h. Refractive Index, [illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	
i. Flash Point (COC), °F	-	-	-	-	-	-	-	-	

* Estimate from [illegible] Data.

TABLE IX

PROPERTIES OF DIARYLADKANES

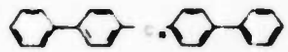
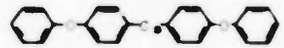
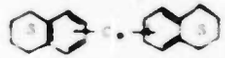
Structure					
Compound	1,6-Diphenylhexane	1,9-Diphenylnonane	1,10-Diphenyldecane	Diphenyliaodecane	Dicyclohexyliaodecane
Reference	4958-33	4658-30	4658-36	4658-31	5051-41
Distillation Fraction					
a. Boiling Range, °F at mm	273-200/0.3	307-396/0.5	305-369/0.5	333-369/0.15	297-326/0.5
b. Description	Heart Cut	Heart Cut	Heart Cut	Heart Cut	Heart Cut
Physical Properties					
a. Viscosity, cs at 210°F	1.21	2.41	2.70	2.51	3.63
100°F	5.71	8.17	10.3	10.6	18.6
b. Temperature, °F, for a Viscosity (extrap)					
of 1 cs	314	360	365	361	422
of 2500 cs	-56	-51	-49	-38	-24
of 13,000 cs	-83	-80	-68	-58	-44
c. ASTM Slope (100°F to 210°F)	0.811	0.745	0.763	0.835	0.791
d. Viscosity Index	98	130	112	58	78
e. Pour Point, °F	+5	+20	+55	-70	<-60
f. Viscosity at Pour Point, cs (extrap)	54	32	28	50,000	*52,000
g. Melting Point, °F	-	-	-	-	-
h. Density, D	0.9530	-	0.9371	-	-
i. Refractive Index, n_D^{20}	1.5412	1.5286	1.5269	1.5270	1.4756

Structure							
Compound	Phenyl-n-nonylphenyliaodecane	Phenyl-n-tetradecylphenyliaodecane				1,9-Di-p-tolylnonane	Di-p-tolyliaodecane
Reference	5057-21	4955-29				4658-17	4658-16
Distillation Fraction							
a. Boiling Range, °F at mm	405-517/0.5	410-468/0.7	469-520/0.7	521-612/0.7	612/0.7	379/1	390-425/2
b. Description	Heart Cut	C-11*	11-54*	54-79*	21* Btm		
Physical Properties							
a. Viscosity, cs at 210°F	0.47	4.50	7.31	10.2	23.9	2.76	3.76
100°F	32.0	24.2	51.9	82.5	973	10.4	23.3
b. Temperature, °F, for a Viscosity (extrap)							
of 1 cs	490	402	535	590	753	392	400
of 2500 cs	-19	-18	-13	-13	-42	-48	-6
of 13,000 cs	-37	-41	-21	-12	-13	-68	-26
c. ASTM Slope (100°F to 210°F)	0.720	0.718	0.714	0.682	0.618	0.754	0.846
d. Viscosity Index	126	112	110	112	112	121	14
e. Pour Point, °F	-35	-54*	-50	-45	-15	-	<-20
f. Viscosity at Pour Point, cs (extrap)	11,000	60,000	230,000	270,000	110,000	-	<7700
g. Melting Point, °F	-	-	-	-	-	92	-
h. Density, D	0.9094	0.9108	0.8974	0.8968	-	-	0.9421
i. Refractive Index, n_D^{20}	1.5141	1.5138	1.5063	1.5053	1.5020	-	1.5296

* Estimate from ab.-viscosity rec.

TABLE IX (continued)

PROPERTIES OF DIARYLALKANES

Structure					
Compound	1,9-Bis(biphenylyl)nonane	1,9-Bis(phenoxyphenyl)nonane	1,9-Bis(1,2,3,4-tetrahydronaphthyl)nonane		
Reference	4966-38	4658-27	4966-37		
Distillation Fraction					
a. Boiling Range, °F at mm	-	545-568/0.15	468-488/0.3	489/0.3	490-527/0.3
b. Description	-	Heart Cut	0-70%	70-80%	80-100%
Physical Properties					
a. Viscosity, cs at 414°F	2.07				
210°F	12.4	10.6	11.4	12.5	16.0
100°F	154 (extrap)	99.9	151	177	302
b. Temperature, °F, for a Viscosity (extrap)					
of 1 cs	605	580	560	562	580
of 2500 cs	+32	+23	+40	+43	+57
of 15,000 cs	+7	-9	+17	+19	+32
c. ASTM Slope (100°F to 210°F)	0.714	0.710	0.780	0.777	0.786
d. Viscosity Index	91	97	57	54	37
e. Pour Point, °F	-	-20	-20	+4	+12
f. Viscosity at Pour Point, cs (extrap)	-	58,000	400,000	45,000	75,000
g. Melting Point, °F	160-165	-	-	-	-
h. Density, D420	-	1.0516	-	-	-
i. Refractive Index, n_D^{20}	-	1.5746	1.5607	1.5608	1.5650

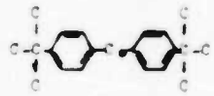
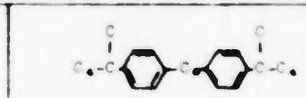
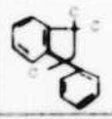
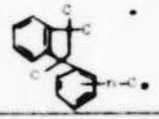
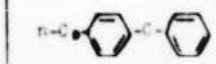
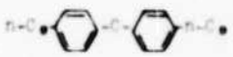
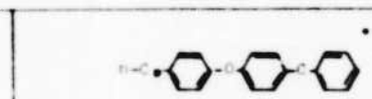
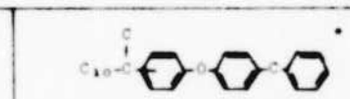
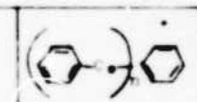
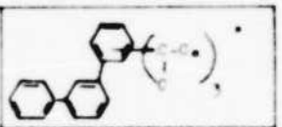
Structure					
Compound	1,9-Bis(n-butylphenyl)nonane	1,9-Bis(sec-butylphenyl)nonane	1,9-Bis(tert-butyl-phenyl)nonane	1,6-Bis(sec-hexylphenyl)hexane	
Reference	4658-25	4966-18	4966-32	4966-28	
Distillation Fraction					
a. Boiling Range, °F at mm	410-450/0.6	464-482/0.3	428-455/0.3	417-464/0.3	465-500/0.3
b. Description	Heart Cut	Heart Cut	Heart Cut	0-80%	80-100%
Physical Properties					
a. Viscosity, cs at 400°F	1.96				
210°F	7.53	7.72	8.44	8.77	10.5
100°F	47.5	64.6	80.5	107	132
b. Temperature, °F, for a Viscosity (extrap)					
of 1 cs	570	526	530	517	548
of 2500 cs	-4	+14	+21	+33	+37
of 15,000 cs	-28	-10	-3	+12	+19
c. ASTM Slope (100°F to 210°F)	0.678	0.750	0.764	0.709	0.786
d. Viscosity Index	127	91	78	40	55
e. Pour Point, °F	<-60	-35	-30	-25	-30
f. Viscosity at Pour Point, cs (extrap)	>200,000	150,000	180,000	470,000	1,000,000
g. Melting Point, °F	-	-	-	-	-
h. Density, D420	-	-	0.9181	-	-
i. Refractive Index n_D^{20}	1.5143	1.5148	1.5179	1.5281	-

TABLE X

PROPERTIES OF MISCELLANEOUS COMPOUNDS

Structure												
Compound	1,1,3-Trimethyl-3-phenylindane	n-Nonyl-1,1,3-trimethyl-3-phenylindane	Phenyl(n-nonylphenyl)methane		Bis(n-nonylphenyl)methane							
Reference	4806-31	5051-47	6158-15		5108-27				5158-22			
Distillation Fraction												
a. Boiling Range, °F at mm	217-228/0.5	284-370/0.5	-	329-352/0.5	-	320-401/0.5	402-511/0.5	511/0.5	-	360-417/0.5	464-496/0.5	497/0.5
b. Description	Heart Cut	Heart Cut	whole	0-22%	whole	0-24%	24-50%	44% Btm	whole	0-10%	20-54%	50% Btm
Physical Properties												
a. Viscosity, cs at 210°F	2.61	3.39	6.32	2.41	5.75	2.57	4.94	17.9	5.82	2.82	4.89	15.3
100°F	16.6[b]	20.7	36.5	8.09	58.8	8.86	24.3	187	29.7	9.84	22.8	142
b. Temperature, °F, for a Viscosity (extrap)												
of 1 cs	338	387	533	372	560	400	503	685	534	408	500	680
of 2500 cs	-4	-7	-13	-65	-12	-60	-26	7	-23	-62	-30	+26
of 13,000 cs	-21	-27	-37	-84	-37	-80	-49	36	-48	-82	-54	-2
c. ASTM Slope (100°F to 210°F)	0.987	0.882	0.646	0.736	0.672	0.735	0.690	0.685	0.669	0.709	0.682	0.646
d. Viscosity Index	-129	-12	131	133	135	137	143	110	145	150	152	114
e. Pour Point, °F	-	-60	-50[a]	-5[a]	-54[a]	-18[a]	-60[a]	-	-66[a]	+14[a]	+16[a]	-28[a]
f. Viscosity at Pour Point, cs (extrap)	-	700,000	40,000	105	55,000	250	30,000	-	60,000	69	247	90,000
g. Melting Point, °F	126	-	-	-	-	-	-	-	-	-	-	-
h. Density, D[illegible]	-	-	-	-	-	-	-	-	-	-	-	-
i. Refractive Index, n_D^{20}	1.5650	1.5235	1.5449	1.5190	-	-	-	-	-	-	-	-

Structure											
Compound	Benzyl n-Nonyl Diphenyl Ether				Benzyl sec-Dodecyl Diphenyl Ether					Polynonylphenyl	Polyoctyl m-Terphenyl
Reference	5158-32				5158-33					5658-19	5658-38
Distillation Fraction											
a. Boiling Range, °F at mm	-	374-441/0.5	442-475/0.5	476-510/0.5	-	416-468/0.5	469-498/0.5	499-538/0.5	539-608/0.5	-	Topped to 448/0.5
b. Description	whole	0-10%	10-45%	45-70%	whole	0-2%	2-41%	41-90%	90-70%	-	Bottoms
Physical Properties											
a. Viscosity, cs at 210°F	5.28	3.40	5.24	8.93	9.55	4.76	6.58	8.10	12.2	12.2	28.8
100°F	70.3	15.6	31.1	82.1	92.9	28.6	49.3	68.9	145	99.6	657
b. Temperature, °F, for a Viscosity (extrap)											
of 1 cs	539	426	487	547	557	461	508	539	587	500	677
of 2500 cs	+15	-30	-10	+22	+24	-8	+7	+15	+36	46	471
of 13,000 cs	-8	-50	-32	-2	+1	-29	-16	-8	+12	11	443
c. ASTM Slope (100°F to 210°F)	0.737	0.746	0.746	0.746	0.741	0.773	0.755	0.744	0.741	0.732	0.723
d. Viscosity Index	94	118	111	89	89	91	91	98	77	117	63
e. Pour Point, °F	-22[a]	-58[a]	-45[a]	-17[a]	-18[a]	-45[a]	-29[a]	-20[a]	-8[a]	-	+15
f. Viscosity at Pour Point, cs (extrap)	40,000	15,000	48,000	46,000	50,000	56,000	41,000	35,000	52,000	-	125,000
g. Melting Point, °F	-	-	-	-	-	-	-	-	-	-	-
h. Density, D[illegible]	-	-	-	-	-	-	-	-	-	-	0.9196
i. Refractive Index, n_D^{20}	-	-	-	-	-	-	-	-	-	1.5312	1.5520

[a] Not fully characterized.

[a] Estimate from small-scale run.

[b] Extrapolated - measured 8.39 cs at 130°F.

result of an attempt to prepare a polymer by the method of Appendix II using 1 mole of azelaic acid chloride with slightly less than 1 mole of benzene. The viscosity of the product indicated a lower molecular weight than desired.

The synthesis of 1,1,3-trimethyl-3-phenylindane was accomplished by dropping alpha-methylstyrene into a stirred mixture of benzene and concentrated sulfuric acid at 68° F. The structure was confirmed by infrared spectra. Acylation of the substituted indane and subsequent Wolff-Kischner reduction of the ketone were performed according to methods previously indicated. The viscosity-temperature characteristics of the resulting alkylphenylindane were too poor to allow further immediate interest in this class of materials.

The substituted diphenylmethanes and benzyl alkyl diphenyl ethers were of indefinite structure. These materials were prepared by reacting benzyl chloride or alkylbenzyl chloride with either an alkylbenzene or alkyl diphenyl ether using chloroform-modified aluminum chloride catalyst. Some of the heterogeneous products had good viscosity and pour characteristics, thereby being of interest in this study. An attempt to synthesize n-nonyl diphenylmethane by the method of Appendix II failed.

Some of the intermediates obtained in the synthesis of exploratory base fluids were purified during the course of the work. Certain physical properties of these intermediates are given in Table XI.

2.2.1.7 Bis(tridecyl) Selenide

It was shown in the 1956 Summary Report[1] that selenides are promising oxidation and radiation damage inhibitors. A principal difficulty was the solubility of the available didodecyl selenide in base oils at low temperatures. A bis(tridecyl) selenide was, therefore, synthesized from Enjay Oxo-tridecyl alcohol to obtain a material with better low temperature properties. Several batches of this selenide were made by the method described in Appendix V. The resulting product was a nonviscous liquid at -20° F and had a pour point of below -60° F.

2.2.1.8 Physical Property-Structure Relationships for Exploratory Base Fluids

A comparison of physical properties of members of a given structural class reveals certain trends which should be of material aid in tailoring base fluids with desirable functional characteristics.

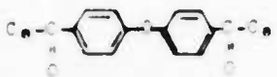
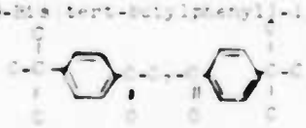
2.2.1.8.1 Alkaryl Ethers

Structural differences of substituent groups in this class produced unusually marked differences in physical properties. Isodecyl 3-n-pentadecylphenyl ether (A) and n-hexadecyl octyl(from diisobutylene)-phenyl ether (B) illustrate this point as they have nearly equivalent

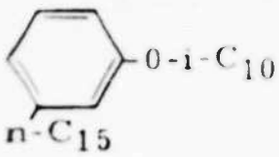
[1] "Effects of Radiation on Aircraft Lubricants and Fuels," (California Research 1956 Summary Report on Contract AF 33(616)-3184) WADC Technical Report 56-646.

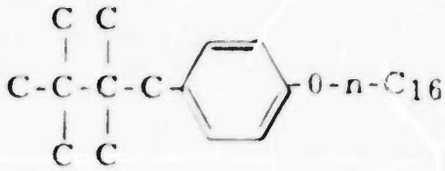
TABLE XI

PHYSICAL PROPERTIES OF INTERMEDIATES

	Boiling Point, °F at mm	Melting Point, °F	Viscosity, Centistokes 100°F	Viscosity, Centistokes 210°F
Nonanoylbenzene	237/1.0	-	-	-
m-Nonyl 2-ethylhexoylbenzene	394/0.15	-	-	-
Nonanoyl diphenyl ether	428/1.0	86	-	-
Dodecanoyl diphenyl ether	424-441/1.0	114	-	-
Dinonanoyl diphenyl ether	-	222	-	-
				
m-Methyl tetradecanoyl diphenyl ether	441-446/0.8	77-82	30.3	5.18
m-Nonyl 2-ethylhexoyl diphenyl ether	227-239/0.2	-	64.2	7.73
1,9-Diphenyl-1,9-nonandione	414/0.1	108.5	-	-
1,10-Diphenyl-1,10-decandione	-	100	-	-
Diphenyl isodecandione	400-440/0.4	-	-	-
1,9-Bis(n-butylphenyl)-1,9-nonandione	500/0.1	ca 52	40.1	10.4
1,9-Bis(sec-butylphenyl)-1,9-nonandione	517-529/0.3	-	-	-
1,9-Bis(tert-butylphenyl)-1,9-nonandione	459-545/0.35	-	83.2	21.7
				

molecular weights and alkyl-aryl carbon ratios. Substantial superiority in pour and viscosity-temperature characteristics is shown for Compound A.





	(A)	(B)
V.I.	133	116
Pour	+12° F	+88° F

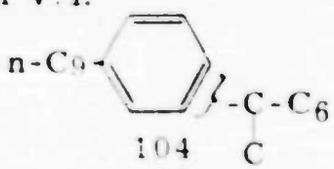
2.2.1.8.2 Esters

Enhancement of V.I. and no impairment of low temperature properties resulted from the hydrogenation of an aromatic diester. An increase in V.I. from 93 to 130 and concurrent lowering of viscosity level were accomplished by saturation of the aromatic ring in diisooctyl terephthalate.

Esters, prepared by the alkylation of aromatics with an olefinic monobasic acid ester, exhibited reasonably good viscosity indexes and satisfactory pour properties. The range of viscosities was quite broad, being dependent upon the nucleus, number of substitutions, and type of esterifying alcohol. The significance of position of attachment of second and third substituent groups has yet to be established.

2.2.1.8.3 Alkylbenzenes

The V.I. properties and moderately good pour of 1-phenyl-9-octadecene are noteworthy. Apparently isomerism about the double bond is responsible for the observed low temperature properties and imposes no sacrifice in viscosity-temperature characteristics. The olefinic character of this fluid probably limits its application as a lubricant. Unpublished API data have indicated the excellent V.I. of p-di(n-decyl)benzene. It melts, however, slightly above room temperature. Improvement in low temperature properties was explored by examining the nonyl homologue and certain di-alkyl derivatives with a sufficient amount of asymmetry. Para-di(n-nonyl)benzene was found to have good viscosity-temperature characteristics. Branching in one of the alkyl groups (sec-octyl group meta and/or para to the nonyl substituent) gave marked improvement in pour but at the expense of V.I.



V.I.	152	104
Pour	+45	-40

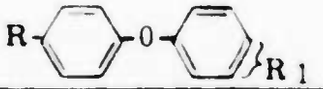
Another attempt was made to tailor a dialkylbenzene with optimum physical properties in which moderate branching occurred at a carbon removed from the point of attachment. Such is the case for p-2-ethylhexyl-nonylbenzene. Complications in initial syntheses removed this compound from further immediate consideration. The judicious adjustment of the normal chain length, as well as its branched chain counterpart on the para position of the aromatic ring, could conceivably result in an unsymmetrical dialkylbenzene with desirable properties.

2.2.1.8.4 Alkyl Diphenyl Ethers

Physical property-structure correlations for sec-alkyl diphenyl ethers were reported in the 1956 Summary Report[1]. The study was extended somewhat by the synthesis of higher molecular weight di- and tri-substituted derivatives as potential grease bases. The effect of n-alkyl substituents on physical properties was investigated. Table XII summarizes pertinent data on the various alkyl diphenyl ethers prepared. It illustrates the effects of chain length and nature of alkyl attachment on viscosity, V.I., and pour.

Table XII

Influence of Alkyl Group on Properties of Alkyl Diphenyl Ethers



Where R is:	Where R_1 is:	Viscosity, cs at 210°F	V.I.	Pour, °F
n-C_9	H	2.53	121	-20
n-C_{12}	H	3.24	143	+70
n-C_{14}	H	3.83	159	+75
n-C_{14}	sec-C_4	4.90	145	+50
n-C_9	sec-C_4	2.65	123	-35
n-C_9	sec-C_8	5.10	114	-60
n-C_9	sec-C_{12}	6.85	121	-49
n-C_9	n-C_9 (para)	5.34	147	+30
n-C_{15} (meta)	C_1 (meta)	4.38	142	+25

1 "Effects of Radiation on Aircraft Lubricants and Fuels," (California Research 1956 Summary Report on Contract AF 33(616)-3184) WADC Technical Report 56-646, p. 17.

The position of secondary alkyl attachments in the mixed n-, sec-alkyl diphenyl ethers was not established. However, the indicated structure is considered consistent with observed V.I. and low temperature properties. The sec-alkyl (C_4, C_8, C_{12}) n-nonyl diphenyl ethers offer the best compromise of properties, over a range of viscosity, for a functional fluid in this particular structural class.

2.2.1.8.5 Diarylalkanes

The properties of 1,9-diphenylnonane, reported in the 1956 Summary Report[1], stimulated an interest in the further investigation of the diarylalkanes as possible base fluids. A study was made to ascertain the effects of the following variables on general physical properties:

a. Paraffin bridge length and structure.

b. Type, position, and nature of attachment of substituent groups.

c. Saturated versus aromatic rings.

The influence of structure on viscosity, V.I., and pour is illustrated in Table XIII.

[1] "Effects of Radiation on Aircraft Lubricants and Fuels," (California Research 1956 Summary Report on Contract AF 33(616)-3184) WADC Technical Report 56-646.

Table XIII

Effect of Chemical Structure on Physical Properties

R_1-⬡-R_2-⬡-R_3					
Where R_1 is:	Where R_2 is:	Where R_3 is:	Viscosity, cs at 210°F	V.I.	Pour, °F
H	n-C_6	H	1.81	87	5
H	n-C_9	H	2.41	130	20
H	n-C_{10}	H	2.70	112	55
H	i-C_{10}	H	2.51	58	-70
H	O-C_6-O	H	2.62	-52	183 (mp)
C_1	n-C_9	C_1	2.76	121	92 (mp)
C_1	i-C_{10}	C_1	3.76	14	-20
n-C_4	n-C_9	n-C_4	7.53	127	<-60
sec-C_4	n-C_9	sec-C_4	7.72	91	-35
tert-C_4	n-C_9	tert-C_4	8.44	78	-30
fused C_4	n-C_9	fused C_4	11.4	57	-20
⬡	n-C_9	⬡	12.4	91	162 (mp)
⬡-O	n-C_9	O-⬡	10.6	97	-20
sec-C_6	n-C_6	sec-C_6	8.77	42	-25
H	i-C_{10}	n-C_9	5.48	126	-35
H	i-C_{10}	sec-C_{14}	7.31	110	-50
S-i-C_{10}-S			3.63	80	<-60

The following tentative generalizations can be made in regard to structure-property correlations with the diarylalkanes examined:

a. An increase in chain length of the normal paraffin bridge produces a progressive increase in viscosity, V.I., and pour. (The V.I. of 1, 9-diphenylnonane is an exception. No explanation is advanced for this apparent anomaly other than the unique contribution made by the odd number of carbon atoms.)

b. Branching of the paraffin bridge gives pronounced improvement in low temperature properties but a concomitant impairment of V.I.

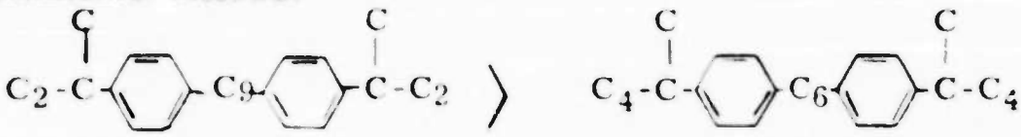
c. Replacement of carbon with oxygen, e.g., 1,6-bis(phenoxy)-hexane, has a deleterious effect on both pour and V.I.

d. Para methyl substituents degrade both pour and V.I. However, methyl groups in meta positions may lower pour points.

e. Isomeric butyl groups likewise lower the V.I. but appear to improve the low temperature properties. (The extent of contribution of impurities to observed pours and the probability of supercooled fluids have not been fully explored.) The pour of the n-butyl homologue is indeed surprising. The descending order of V.I. and pour for the butyl series is:

$$n\text{-}C_4 \rangle \ sec\text{-}C_4 \rangle \ tert\text{-}C_4 \rangle \ fused\ C_4$$

f. A preferred orientation of paraffin and aryl groups (with a nearly constant alkyl-aryl carbon ratio, equivalent molecular weights, and like mode of alkyl attachments) follows:



g. The phenoxy-substituted diarylalkane, 1, 9-bis(phenoxyphenyl)-nonane, exhibits surprisingly good properties in view of its symmetry and high aromatic content.

h. Improvement in V.I. with a moderate sacrifice in low temperature properties can be accomplished by:

1. Incorporating mono-alkyl (either normal or secondary) substituent groups.

2. Saturating terminal aromatic rings.

2.2.2 Evaluation of Compounds

Thermal and radiation stability tests were conducted on the majority of exploratory base fluids. Oxidation-corrosion and lubricity tests were performed on compounds of special interest. Preliminary evaluation results are given in Tables XIV to XVIII, inclusive.

2.2.2.1 Thermal Stability

Screening tests were conducted at 700° F for a 20-hour period in stainless steel capsules under a helium atmosphere. (See Appendix 1.) Measured gas evolution and viscosity change after this treatment were considered sufficient indication of relative thermal stability. Although the method has several inherent disadvantages, it was an expedient means for the preliminary evaluation of exploratory compounds.

A direct comparison of relative stabilities of synthesized base fluids in particular structural classes is given in Figure 1. Precise correlations were not established between structures and thermal stability in view of the nature of the materials evaluated. However, certain trends are noteworthy, and some generalizations can be made in regard to thermal characteristics and structural differences. With the exception of 1,6-bis-(phenoxy)hexane, the alkaryl ethers (Table XIV) showed considerable changes in viscosity under the test conditions and further demonstrated the weakness of this structural class in a high temperature environment.

The alkyl diphenyl ethers (Table XV) were in most instances more stable than the alkaryl ethers. n-Dodecyl diphenyl ether was particularly promising of the mono-substituted diphenyl ethers investigated. An intercomparison of mono- and dialkyl derivatives with a relatively constant alkyl-aryl carbon ratio revealed a superiority in thermal properties of alkyl groups with primary carbon attachments on the aromatic ring. Such is evidenced in the following order of stability: m-tolyl m-n-pentadecylphenyl ether > sec-butyl n-nonyl diphenyl ether > C_{14-16}(50/50)-sec-alkyl diphenyl ether. An increase in chain length of olefin (C_8 to C_{12}) in the monoalkylation of n-nonyl diphenyl ether resulted in impaired thermal stability of the dialkyl compound. The presence of bis(tridecyl) selenide oxidation inhibitor in these particular base stocks had an adverse effect on high temperature properties. Test data on n-nonyl and di-n-nonyl diphenyl ethers appeared to be anomalous. These compounds need further evaluation. An intercomparison of di- and poly-sec-alkyl diphenyl ethers indicated a significant thermal superiority for the poly-substituted derivative.

None of the exploratory dibasic acid esters (Table XVI) exhibited satisfactory thermal properties at 700° F. Certain of the alkylbenzenes under study (Table XVII) showed surprisingly good stability. sec-Octyl-n-nonylbenzene was promising, and di(n-nonyl)benzene was the most outstanding base fluid evaluated in any of the structural classes investigated. Enhanced thermal stability of normal alkyl groups with primary carbon attachments on the aromatic ring was again demonstrated. Trends were indicated in the thermal characteristics of diarylalkanes (Table XVIII) in which aromatic rings were coupled with aliphatic chains at primary carbon atoms. As might be expected, an increase in length of the paraffin or presence of branching had a deleterious effect on thermal properties. No ready explanation can be given for the poor behavior of 1,9-diphenylnonane. Check runs need to be conducted on this material.

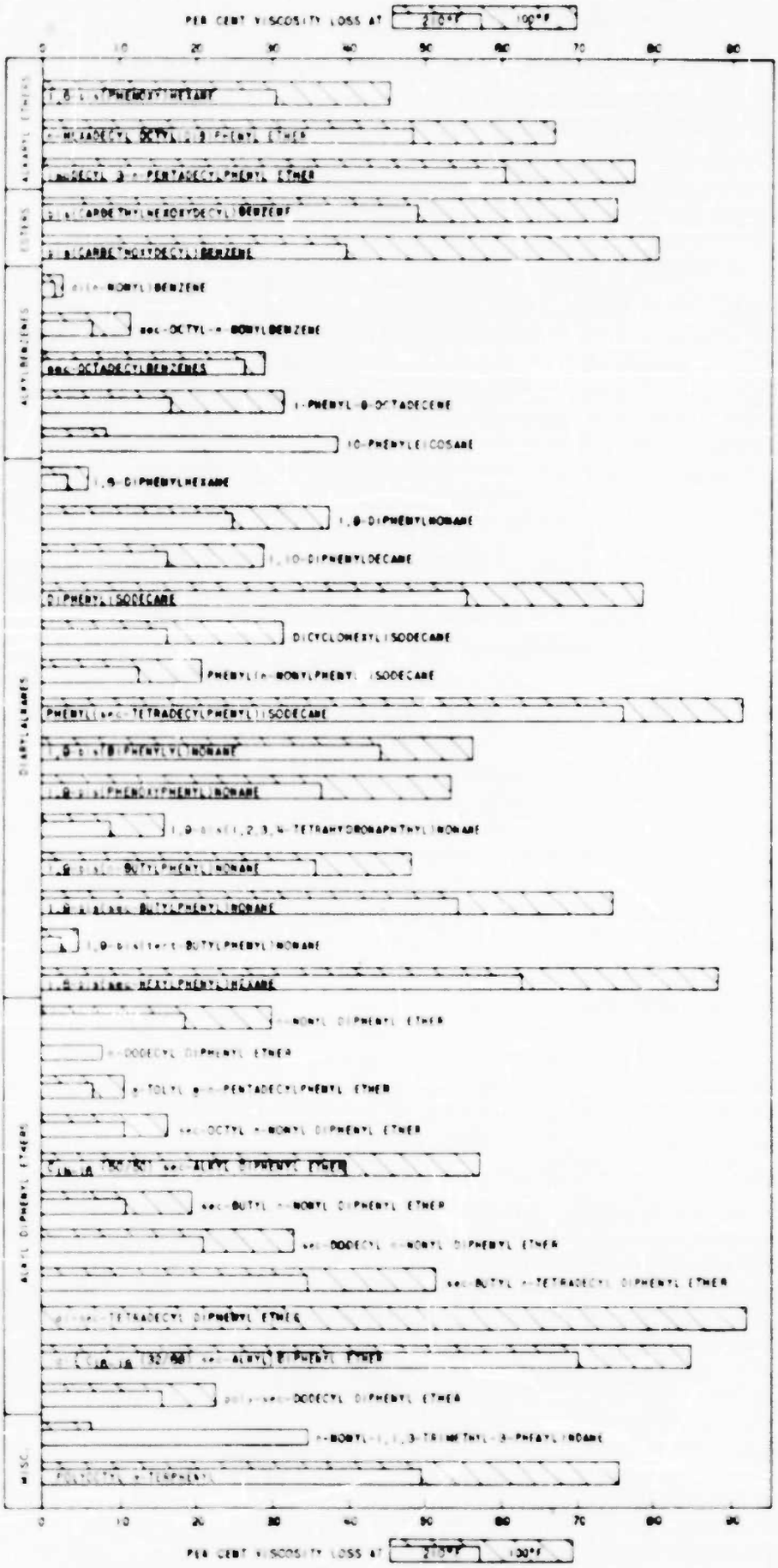
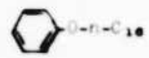
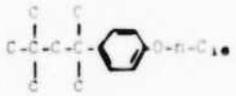
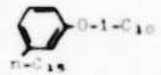


FIG. 1 - THERMAL STABILITY OF EXPLORATORY BASE FLUIDS
CAPSULE TESTS, 20 HOURS AT 700°F

TABLE XIV

EVALUATION OF ALKARYL ETHERS

Structure				
Compound	n-Hexadecyl Phenyl Ether	n-Hexadecyl Octyl(DIB)-phenyl Ether	Isodecyl 3-n-Pentadecyl-phenyl Ether	1,6-Bis(phenoxy)hexane
Reference	← AGO-1-36 →	← 4896-15 →	← 4896-14 →	← 4965-15 →
Distillation Fraction				
a. Boiling Range, °F at mm	-	463-475/0.7	463-475/0.5	-
b. Description	-	Heart Cut	Heart Cut	-
Physical Properties				
a. Viscosity, cs at 100°F	8.62	41.3	27.1	14.5[a]
at 210°F	2.51	6.44	5.16	2.62
				0.745[b]
b. Temperature, °F, for a Viscosity (extrap)				
of 1 cs	380	525	502	348
of 2500 cs	-60	-3	-19	-13
of 13,000 cs	-79	-27	-42	-31
c. ASTM Slope (100°F to 210°F)	0.745	0.713	0.709	0.928
d. Viscosity Index	133	115	133	-51
e. Pour Point, °F	-	-	+12	-
f. Viscosity at Pour Point, cs (extrap)	-	-	460	-
g. Melting Point, °F	95	88	-	183
h. Refractive Index, n_D^{60}	-	-	1.4829	-
Thermal Stability, Capsule, 20 hours at 700°F				
a. Gas Evolved, ml gas/g fluid	14.5	5.9	23.8	32.3
b. Viscosity Change at 100°F, %	-26.8	-67.1	-77.4	-45.5
at 210°F, %	+40.3	-48.5	-60.3	-30.6
Oxidation Stability, 48 hours at °F	400	400	400	-
a. Additive, %	2% Parabar 441	2% Parabar 441	2% Parabar 441	-
b. Viscosity Change at 100°F, %	+214	-33.3	+86.1	-
at 210°F, %	+174	+7.8	+47.5	-
c. Neutralization No.	3.0	8.5	11.0	-
d. Metal Weight Change, mg/sq cm Al	+0.61	+0.29	-0.06	-
Steel	+0.32	+0.06	-0.16	-
Cu	-4.3	-1.5	-0.65	-
Ag	+0.77	+0.16	-0.06	-
Be-Cu	-5.1	-0.42	-0.77	-
e. Insolubles, %	trace	trace	trace	-
f. Evaporation, %	2.4	0.4	0.3	-
Radiation Stability[c], Dosage, 10^{10} ergs/g C	0.96 | 3.83 | 0.17 | 5.40 (400°F)	0.70 | 2.70	0.92 | 4.27	0.60 | 2.79
a. Gas Evolved, ml gas/g fluid	- | 7.8 | 0.5 | 13.7	1.8 | 5.5	0.9 | 1.7	- | -
b. Viscosity Change at 100°F, %	+12.2 | +62.5 | +1.16 | +67.5	+0.73 | +12.8	+1.14 | +14.8	+314[a] | -17.2[a]
at 210°F, %	+9.16 | +46.2 | -0.80 | +31.5	-0.31 | +6.06	+0.19 | +8.9	+47.4 | +2.67
				-1.88[b] | +12.3[b]
Lubricity, Mean Hertz Load (Screening Test), kg	~21	~14	~16.5	-

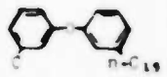
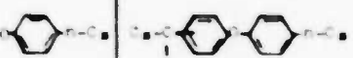
[a] Extrapolated.

[b] At 415°F.

[c] All samples uninhibited.

TABLE XV

EVALUATION OF ALKYL DIPHENYL ETHER

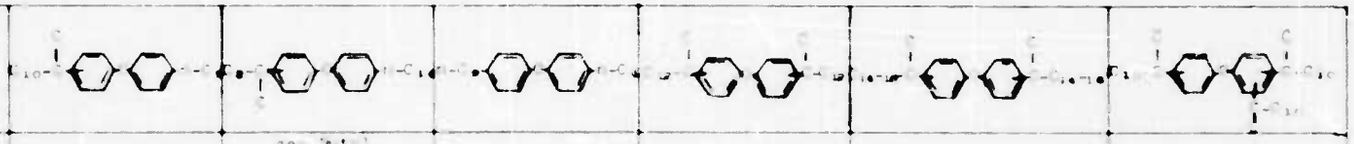
Structure						
Compound	n-Nonyl Diphenyl Ether	n-Dodecyl Diphenyl Ether	C_{14-16}(50/50)sec-Alkyl Diphenyl Ether	m-Tolyl m-n-Pentadecylphenyl Ether	sec-Butyl n-Nonyl Diphenyl Ether	sec-Octyl n-Nonyl Diphenyl Ether
Reference	← 4[illegible]5-4 →	← 4956-8 →	← 4658-28 →	← 5051-18 →	← 5108-15 →	← 5158-9 →
Distillation Fraction						
a. Boiling Range, °F at mm	5[illegible]-[illegible]/[illegible]	365-370/0.5	-	428-435/0.5	-	-
b. Description	Heart Cut	Heart Cut	Whole	Heart Cut	Bottoms	Whole
Physical Properties						
a. Viscosity, cs at 100°F	9.08	12.6	26.8	20.6	9.71	29.2
at 210°F	2.55	3.24	4.85	4.58	2.65	5.10
b. Temperature, °F, for a Viscosity (extrap) of 1 cs	378	425	475	470	387	486
of 2500 cs	-58	-49	-24	-50	-53	-12
of 13,000 cs	-74	-71	-36	-52	-73	-35
c. ASTM Slope (100°F to 210°F)	0.759	0.737	0.741	0.713	0.785	0.736
d. Viscosity Index	121	183	114	142	123	114
e. Pour Point, °F	-20	+70	-15	+25	-35	-60[a]
f. Viscosity at Pour Point, cs (extrap)	360	23	2600	160	730	150,000
g. Density, D^{60}_{60}	0.9609	-	-	-	-	-
h. Refractive Index, n^{20}_{D}	1.5284	-	-	1.5156	-	-
i. Flash Point (COC), °F	-	-	415	-	-	-
Thermal Stability, Capsule, 20 hours at 700°F						2% Tridecyl Selenide
a. Gas Evolved, ml gas/g fluid	5.0	0.63	30.6	1.01	1.30	1.2 / 18.6
b. Viscosity Change at 100°F, %	-30.0	+1.30	-57.5	-10.7	-19.4	-16.4 / -78.1
at 210°F, %	-18.5	-8.03	-39.6	-6.6	-10.9	-10.8 / -59
Oxidation Stability, 48 hours at °F	500	500	400	400	500	-	500	500
a. Additive, %	none	2% tridecyl selenide	2% Parabar 441	none	2% Parabar 441	2% Parabar 441	-	none	2% tridecyl selenide
b. Viscosity Change at 100°F, %	(solid)	(solid)	+48.7	+42.9	+47.3	+545	-	+2710	+14930
at 210°F, %	(solid)	(solid)	+24.5	+23.7	+27.4	+220	-	+677	+2100
c. Neutralization No.	(solid)	-	7.0	5.9	3.4	7.3	-	10.3	15.7
d. Metal Weight Change, mg/sq cm Al	0.0	+0.06	+0.02	-0.32	-0.05	0.0	-	0.00	0.00
Steel	-22.2	-0.47	+0.35	-0.34	+0.03	-0.22	-	-0.03	-0.72
Cu	-0.64	-27.1	-0.70	-3.24	-1.69	-1.05	-	-0.46	-22.18
Ag	-0.03	-71.8	+0.22	-3.04	-0.06	-0.03	-	0.00	-21.54
90-Cu	+0.52	-14.3	+0.48	-0.24	-0.49	-0.46	-	+0.75	-4.29
e. Insolubles, %	solid	plugged	trace	-	-	1.42	-	1.9	plugged
f. Evaporation, %	20.8	20.5	0.4	-	-	1.89	-	9.1	5.5
Radiation Stability[b] dosage, 10^{10} ergs/g C	1.15	5.10	0.60 / 2.70	(Tabulated in Sections IV and V)		1.24 / 5.84	0.01 / 4.37	-	-
a. Gas Evolved, ml gas/g fluid	1.0	2.4	1.0 / 1.8			1.1 / -	0.4 / 1.1	-	-
b. Viscosity Change at 100°F, %	+6.1	+27.6	+2.5 / +11.5			+7.24 / +45.7	+1.13 / +8.76	-	-
at 210°F, %	+3.1	+15.4	+1.5 / +7.2			+3.65 / +32.9	+0.76 / +5.29	-	-
Lubricity, Mean Hertz Load (Screening Test), kg	~10		~17	~15	~13	-	-	-

[a] Estimate from small-scale run

[b] All samples uninhibited.

TABLE XV (continued)

EVALUATION OF ALKYL DIPHENYL ETHER

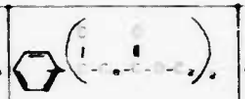
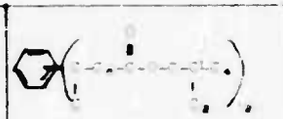
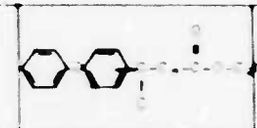
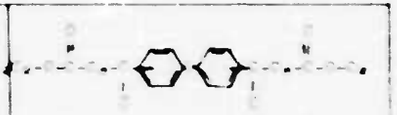
Structure												
Compound	sec-Octadecyl n-Nonyl Diphenyl Ether		sec-Butyl n-Tetradecyl Diphenyl Ether		Di-n-nonyl Diphenyl Ether		Di-sec-tetradecyl Diphenyl Ether		Di[C$_{10-14}$ (92/5)sec-alkyl] Diphenyl Ether		Poly-sec-dodecyl Diphenyl Ether	
Reference	4158-10		4659-41		4965-41		4993-1		5097-4		4999-2	
Distillation Fraction												
a. Boiling Range, °F at mm	-		-		471-500/0.1		-		-		-	
b. Description	whole		bottoms		Heart Cut		whole		whole		whole	
Physical Properties												
a. Viscosity, cs at 100°F	17.2		21.6		26.1		111		85.0		140	
at 210°F	6.96		4.00		5.34		12.0		11.1		15.2	
b. Temperature, °F, for a Viscosity (extrap)												
of 1 cs	521		407		518		667		664		677	
of 2500 cs	-3		-29		-27		20		11		26	
of 15,000 cs	-20		-51		-56		-7		-13		-2	
c. ASTM Slope (100°F to 210°F)	0.705		0.67		0.660		0.655		0.66		0.655	
d. Viscosity Index	121		145		147		131		121		115	
e. Pour Point, °F	-45		-50		-45		-25		20		-45	
f. Viscosity at Pour Point, cs (extrap)	9,500		50		175		31,000		1700		550,000	
g. Density, 20/4	-		0.920		-		-		-		-	
h. Refractive Index, n$^{20}_{D}$	-		1.5177		1.5150		1.4990		1.4980		1.5043	
i. Flash Point (COC), °F	-		-		-		-		-		-	
Thermal Stability, Capsule, 20 hours at 750°F	-	2% tridecyl selenide										
a. Gas Evolved, ml gas/g fluid	1.00	0.80	1.10		1.7		11.4		6.1		0.90	
b. Viscosity Change at 100°F, %	-12.0	-61.0	-51.0		(two phases)		-20.7		-64.8		-22.0	
at 210°F, %	-31.0	-43.7	-34.7				(gels)		-71.0		-15.9	
Oxidation Stability, 48 hours at °F	400	400	-		400		400		400		400	
a. Additive, %	none	2% tridecyl selenide	-		2% Paratac 441		2% Paratac 441		2% Paratac 441		2% Paratac 441	
b. Viscosity Change at 100°F, %	+1030	(plugged)	-		(gelled)		+51.0		+35.2		+72.5	
at 210°F, %	+413	-	-		-		+14.4		+26.6		+40.0	
c. Neutralization No.	17	-	-		-		4.4		2.7		5.5	
d. Metal Weight Change, mg/dm^2 in: Al	0.03	0.00	-		-0.03		-0.13		-0.33		-0.35	
Steel	0.08	-1.71	-		-0.30		-0.07		-0.10		0.0	
Cu	-0.23	-17.0	-		-0.7		-0.45		-0.32		-0.65	
Ni	0.09	-18.5	-		-1.0		-0.37		-0.25		-0.6	
Mg-Cu	-1.18	-5.04	-		-0.74		-0.14		-0.29		-0.10	
e. Insolubles, %	1.0	plugged	-		-		trace		trace		trace	
f. Evaporation, %	4.4	7.6	-		-		nil		1.7		nil	
Radiation Stability, Dosage, 10^{18} ergs/g C	-	-	1.34	5.34	0.91	4.27	0.62	1.76	0.93	4.14	0.97	4.1
a. Gas Evolved, ml gas/g fluid	-	-	1.0	1.0	0.8	1.7	1.0	2.7	1.6	6.1	1.0	1.2
b. Viscosity Change at 100°F, %	-	-	+0.37	+41.0	+27.1	+41.5	+3.5	+14.1	+7.1	+35.7	+8.18	+40.5
at 210°F, %	-	-	+5.08	+27.5	+14.4	+26.7	+1.0	+10.5	+5.9	+29.6	+5.34	+27.6
Lubricity, Mean Hertz Load (Screening Test), kg	-		-		-		-20		-10		-10	

* Estimate from small-scale run.

\- All samples unfiltered.

TABLE XVI

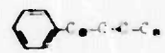
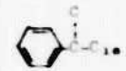
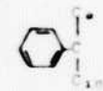
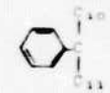
EVALUATION OF ESTERS

Structure					
Compound	Diisooctyl Hexahydroterephthalate	Bis(carbethoxydecyl)benzene	Bis(carbethylhexoxydecyl)benzene	Carbethoxydecyl Diphenyl Ether	Bis(carbethoxydecyl) Diphenyl Ether
Reference	5559-10	5051-12	5051-7	5051-38	5051-38
Distillation Fraction					
a. Boiling Range, °F at mm	365-391/<1	482-532/0.8	Topped to 486/0.5	374-410/0.5	554-603/0.5
b. Description	Heart Cut	Heart Cut	Bottoms	Heart Cut	Heart Cut
Physical Properties					
a. Viscosity, cs at 100°F	20.0	39.2	82.0	25.7	87.4
at 210°F	4.18	6.57	11.3	4.53	10.6
b. Temperature, °F, for a Viscosity (extrap)					
of 1 cs	400	540	555	468	601
of 2500 cs	-28	-10	+9	-13	+16
of 13,000 cs	-50	-34	-18	-34	-8
c. ASTM Slope (100°F to 210°F)	0.732	0.689	0.641	0.768	0.686
d. Viscosity Index	130	128	126	98	111
e. Pour Point, °F	< -60	< -60	-50	< -60	-55
f. Viscosity at Pour Point, cs (extrap)	> 30,000	> 125,000	180,000	> 170,000	1,000,000
g. Density, D_{4}^{20}	-	-	0.9256	-	-
h. Refractive Index, n_D^{20}	-	1.4809	1.4779	1.5187	1.5038
Thermal Stability, capsule, 20 hours at 700°F					
a. Gas Evolved, ml gas/g fluid	48.6	91.1	42.7	-	-
b. Viscosity Change at 100°F, %	(solid)	-75.0	-80.7	-	-
at 210°F, %	(solid)	-49.0	-39.7	-	-
Oxidation Stability, 48 hours at °F	400	500	-	500	500
a. Additive, %	2% Parabar 441	2% Parabar 441	-	2% Parabar 441	2% Parabar 441
b. Viscosity Change at 100°F, %	+87.5	Not Enough	-	Not Enough	Not Enough
at 210°F, %	+55.5	Sample	-	Sample	Sample
c. Neutralization No.	8.1	solid	-	solid	solid
d. Metal Weight Change, mg/sq cm Al	+0.13	-0.06	-	-0.03	-0.51
Steel	+0.38	-68.8	-	-38.5	-37.1
Cu	-14.2	-0.52	-	-2.90	-2.32
Ag	+0.26	-0.13	-	-0.22	-0.16
Be-Cu	-0.83	-0.19	-	-3.32	-2.91
e. Insolubles, %	trace	solid	-	solid	solid
f. Evaporation, %	5.2	14.5	-	8.3	10.5
Radiation Stability[a], Dosage, 10^{10} ergs/g C	0.70 / 2.70	0.90 / 4.14	1.13 / 5.31	1.13 / 5.31	1.13 / 5.31
a. Gas Evolved, ml gas/g fluid	1.9 / 7.6	1.8 / 5.4	1.6 / 6.1	0.9 / 2.4	0.9 / 3.4
b. Viscosity Change at 100°F, %	+6.50 / +80.0	+12.8 / +57.8	+5.29 / +58.4	+2.53 / +19.2	+5.25 / +106.0
at 210°F, %	+4.07 / +44.5	+8.5 / +40.8	+2.92 / +39.8	+0.88 / +11.2	+3.49 / +29.2
Lubricity, Mean Hertz Load (Screening Test), kg	-15	-15	-	-	-

[a] All samples uninhibited.

TABLE XVII

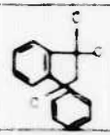
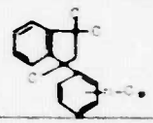
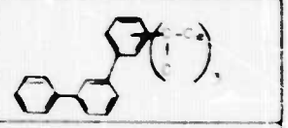
EVALUATION OF ALKYLBENZENES AND MISCELLANEOUS COMPOUNDS

Structure						
Compound	n-Nonylbenzene	2-Phenylhexadecane	1-Phenyl-9-octadecene	sec-Octadecylbenzenes	10-Phenyleicosane	11-Phenyldocosane
Reference	← 4658-43 →	← 3048-13 →	← 560-7 →	← 4965-12 →	← 2359-3 →	← 2359-19 →
Distillation Fraction						
a. Boiling Range, °F at mm	293/10	-	430-440/5	-	-	437/2.0
b. Description	Heart Cut	-	-	Whole	-	-
Physical Properties						
a. Viscosity, cs at 100°F	2.55	16.9	8.04	14.9	13.3	17.0
at 210°F	1.09	3.73	2.56	3.57	3.11	3.7
b. Temperature, °F for a Viscosity (extrap)						
of 1 cs	226	442	391	443	405	440
of 2500 cs	-112	-32	-68	-40	-36	-30
of 13,000 cs	-	-53	-88	-62	-57	-52
c. ASTM Slope (100°F to 210°F)	0.841	0.741	0.704	0.716	0.768	0.745
d. Viscosity Index	126	125	165	140	104	120
e. Pour Point, °F	-40	+15	-25	+26	+15	+35
f. Viscosity at Pour Point, cs (extrap)	46	193	194	96	150	97
g. Density, D	-	-	-	-	-	-
h. Refractive Index, n_D^{20}	1.4639	-	-	1.4779	-	-
Thermal Stability, Capsule, 20 hours at 700°F						
a. Gas Evolved, ml gas/g fluid	-	-	9.2	0.68	3.44	-
b. Viscosity Change at 100°F, %	-	-	-31.3	-29.1	-8.4	-
at 210°F, %	-		-16.8	-26.4	-38.7	-
Oxidation Stability, 48 hours at °F	-	-	400	-	400	-
a. Additive, C	-	-	2% Parabar 441	-	2% Parabar 441	-
b. Viscosity Change at 100°F, %	-	-	+386	-	+19.9	-
at 210°F, %	-	-	+163	-	+12.6	-
c. Neutralization No.	-	-	6.8	-	5.8	-
d. Metal Weight Change, mg/sq cm Al	-	-	0.0	-	+1.5	-
Steel	-	-	-1.35	-	+1.4	-
Cu	-	-	-0.16	-	-5.4	-
Ag	-	-	-0.16	-	+1.6	-
Be-Cu	-	-	+0.03	-	-7.5	-
e. Insolubles, %	-	-	trace	-	4.8	-
f. Evaporation, %	-	-	nil	-	10.8	-
Radiation Stability*, Dosage, 10^{10} ergs/g C	1.24 / 5.84	0.61 / 2.79	0.61 / 2.70	0.61 / 2.79	0.61 / 2.70	0.91 / 4.27
a. Gas Evolved, ml gas/g fluid	1.4 / 4.7	0.7 / 1.8	1.1 / 2.6	0.7 / 1.8	1.5 / 3.5	1.1 / 3.4
b. Viscosity Change at 100°F, %	+3.57 / +25.9	-51.0 / -46.7	+10.3 / +36.0	-29.6 / -24.9	+5.3 / +21.0	+1.5 / +18.0
at 210°F, %	+0.99 / +15.8	-34.4 / -30.3	+5.9 / +23.1	-23.3 / -19.3	+4.8 / +13.7	+1.4 / +12.9
Lubricity, Mean Hertz Load (Screening Test), kg	-	-	-	-	~13	-

* All samples uninhibited.

TABLE XVII (continued)

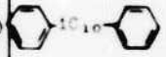
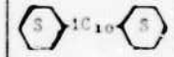
EVALUATION OF ALKYLBENZENES AND MISCELLANEOUS COMPOUNDS

Structure										
Compound	sec-Octyl-n-nonylbenzene		Di(n-nonyl)-benzene		1,1,3-Trimethyl-3-phenylindane		n-Nonyl-1,1,3-trimethyl-3-phenylindane		Polyoctyl m-Terphenyl	
Reference	5044-13		5051-22		4843-31		5051-47		4668-38	
Distillation Fraction										
a. Boiling Range, °F at mm	291-334/0.1		349-365/0.5		217-228/0.5		283-370/0.5		Topped to 450/0.5	
b. Description	Heart Cut		Heart Cut		Heart Cut		Heart Cut		Bottoms	
Physical Properties										
a. Viscosity, cs at 100°F	10.8		9.80		8.39 (130°F) 16.6 (extrap)		20.7		652	
at 210°F	2.75		2.83		2.61		3.39		28.8	
b. Temperature, °F, for a Viscosity (extrap)										
of 1 cs	384		412		338		388		677	
of 2500 cs	-47		-63		-4		-7		471	
of 15,000 cs	-87		-83		-21		-27		443	
c. ASTM Slope (100°F to 210°F)	0.775		0.706		0.987		0.882		0.721	
d. Viscosity Index	107		152		-139		-12		66	
e. Pour Point, °F	-40		-45		126 (mp)		-60		+15	
f. Viscosity at Pour Point, cs (extrap)	1600		2[illegible]		-		700,000		125,000	
g. Density, D[illegible]	0.8633		0.8560		-		-		0.9300	
h. Refractive Index, n[illegible]	1.4837		1.4850		1.5650		1.5235		1.5520	
Thermal Stability, Capsule, 20 hours at 700°F										
a. Gas Evolved, ml gas/g fluid	1.09		0.91		-		14.5		1.33	
b. Viscosity Change at 100°F, %	-11.1		-2.55		-		-6.32		-75.4	
at 210°F, %	-6.55		-1.77		-		-34.8		-49.8	
Oxidation Stability, 48 hours at °F	-		500		-		-		500	
a. Additive, %	-		none	1% tridecyl selenide	-		-		2% Parabar +41	
b. Viscosity Change at 100°F, %	-		+21.00	solid	-		-		-	
at 210°F, %	-		+28.0	solid	-		-		+151	
c. Neutralization No.	-		35.5	solid	-		-		7.0	
d. Metal Weight Change, mg/sq cm Al	-		0.0	+0.09	-		-		-0.03	
Steel	-		0.0	-0.[illegible]	-		-		-0.03	
Cu	-		-0.[illegible]	-27.4	-		-		-0.42	
Ag	-		0.0	-71.4	-		-		-0.06	
Br-Cu	-		+0.[illegible]	-7.10	-		-		-0.07	
e. Insolubles, %	-		plugged	solid	-		-		0.0	
f. Evaporation, %	-		19.8	17.6	-		-		3.15	
Radiation Stability, Dosage, 10^{10} ergs/g C	1.24	5.84	1.24	5.84	1.24	5.84	1.13	5.31	1.24	5.84
a. Gas Evolved, ml gas/g fluid	1.0	2.3		9.2	-	-	1.0	2.3	0.9	2.3
b. Viscosity Change at 100°F, %	-1.57	+23.1	(empty	+68.3	+5.47	+8.44	+3.98	+31.2	+4.76	+30.1
at 210°F, %	-0.36	+16.0	capsule)	+44.6	+1.53	+4.22	+3.25	+18.6	+4.45	+10.4
Lubricity, Mean Hertz Load (Screening Test), kg	-		-		-		-		-	

* All samples uninhibited.

TABLE XVIII

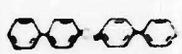
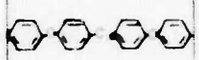
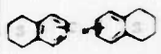
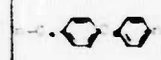
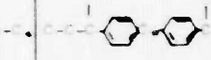
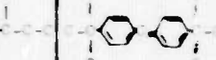
EVALUATION OF DIARYLALKANES

Structure							
Compound	1,6-Diphenyl-hexane	1,9-Diphenyl-nonane	1,10-Diphenyl-decane	Diphenyl-isodecane	Dicyclohexyl-isodecane	Phenyl(n-nonyl-phenyl)isodecane	Phenyl(tetradecyl-phenyl)isodecane
Reference	← 4996-33 →	← 4658-32 →	← 4658-35 →	← 5136-04 →	← 5051-41 →	← 5051-21 →	← 4995-29 →
Distillation Fraction							
a. Boiling Range, °F at mm	271-280/0.5	307-308/0.5	365-369/0.5	331-369/0.15	298-326/0.5	460-518/0.5	410-612/0.7
b. Description	Heart Cut	Heart Cut	Heart Cut	Heart Cut	Heart Cut	Heart Cut	
Physical Properties							
a. Viscosity, cs at 100°F	5.71	8.17	10.3	10.6	18.6	31.0	57.6
at 210°F	1.81	2.41	2.70	2.51	3.63	5.48	7.85
b. Temperature, °F, for a Viscosity (extrap)							
of 1 cs	314	368	386	363	422	498	545
of 2500 cs	-60	-61	-49	-38	-24	-14	7
of 15,000 cs	-83	-80	-68	-58	-44	-37	-18
c. ASTM Slope (100°F to 210°F)	0.811	0.745	0.763	0.835	0.791	0.720	0.714
d. Viscosity Index	98	130	112	58	78	125	110
e. Pour Point, °F	+5	+20	+55	-70	<-60	-35	-50
f. Viscosity at Pour Point, cs (extrap)	51	48	28	60,000	>62,000	11,000	250,000
g. Melting Point, °F	-	-	-	-	-	-	-
h. Density, D_4^{20}	0.9896	-	0.9371	-	-	0.9094	-
i. Refractive Index, n_D^{20}	1.5412	1.5288	1.5269	1.5280	1.4768	1.5140	-
Thermal Stability, Capsule, 20 hours at 700°F							
a. Gas Evolved, ml gas/g fluid	0.27	2.29	4.23	15.7	1.45	1.17	13.6
b. Viscosity Change at 100°F, %	-6.0	-37.5	-29.0	-78.8	-31.3	-20.8	-91.3
c. Viscosity Change at 210°F, %	-3.3	-24.9	-16.3	-55.4	-16.3	-12.4	-75.9
Oxidation Stability, 48 hours at °F	500	500	500	500	500	-	-
a. Additive, %	2% Parabar 441	2% Parabar 441	2% Parabar 441	2% Parabar 441	2% Parabar 441	-	-
b. Viscosity Change at 100°F, %	lost	+1720	+178	+6580	+9.66	-	-
at 210°F, %	+300	+448	+90.0	+933	+7.17	-	-
c. Neutralization No.	32.3	17.2	8.23	14.4	6.29	-	-
d. Metal Weight Change, mg/sq cm Al	-0.06	0.0	0.0	-0.09	-0.16	-	-
Steel	-0.06	-15.1	-3.75	+7.40	+0.03	-	-
Cu	-2.42	-0.06	-0.06	-0.07	-0.09	-	-
Ag	0.3	-0.03	-0.06	-0.16	-0.16	-	-
Be-Cu	-1.77	-0.51	+0.03	-0.45	-0.06	-	-
e. Insolubles, %	Plugged	14.6	0.84	13.3	7.07	-	-
f. Evaporation, %	5.38	4.31	1.27	19.1	0.49		
Radiation Stability, dosage 10^{19} ergs/g C	1.15 | 5.10	1.15 | 5.10	1.15 | 5.10	0.60 | 2.79	1.13 | 5.31	1.24 | 5.84	0.90 | 4.14
a. Gas Evolved, ml gas/g fluid	1.0 | 1.7	1.2 | 2.4	1.1 | 2.6	3.6 | 0.6	3.3 | 16.2	1.7 | 4.8	1.2 | 3.4
b. Viscosity Change at 100°F, %	+4.2 | +16.7	+5.8 | +24.8	+13.5 | +44.5	-0.0 | +7.7	+7.37 | +72.3	+9.91 | +46.7	-0.4 | +20.2
at 210°F, %	+1.3 | +11.1	+2.8 | +15.8	+10.5 | +33.0	+2.8 | +4.4	+5.79 | +46.8	+5.83 | +35.8	+0.9 | +15.3
Lubricity, Mean Hertz Load (Screening Test), kg	-	~7	~18	-	-	-	~11

* All samples uninhibited.

TABLE XVIII (continued)

EVALUATION OF DIARYLALKANES

Structure							
Compound	1,6-Bis-(diphenyl)nonane	1,6-Bis(phenoxy-phenyl)nonane	1,6-Bis(1,2,3,4-tetrahydro-naphthyl)nonane	1,6-Bis(n-butyl-phenyl)nonane	1,6-Bis(sec-butyl-phenyl)nonane	1,6-Bis(tert-butylphenyl)-nonane	1,6-Bis(sec-hexyl-phenyl)hexane
Reference	4956-36	4958-27	4956-37	4958-29	4956-18	4956-30	4956-28
Distillation Fraction							
a. Boiling Range, °F at mm	-	543-568/0.15	468-488/0.3	410-450/0.6	464-482/0.3	428-466/0.3	417-504/0.3
b. Description	-	Heart Cut		Heart Cut	Heart Cut	Heart Cut	
Physical Properties							
a. Viscosity, cs at 100°F	134 (extrap)	99.9	151	47.5	64.6	80.5	110
at 210°F	12.4	10.6	11.4	7.53	7.72	8.44	8.00
	2.07 (414°F)						
b. Temperature, °F, for a Viscosity (extrap)							
of 1 cs	605	580	550	570	526	550	514
of 2500 cs	+32	+23	+40	-4	+14	+21	34
of 13,000 cs	+7	-2	+12	-28	-10	-4	12
c. ASTM Slope (100°F to 210°F)	0.714	0.710	0.786	0.878	0.750	0.764	0.807
d. Viscosity Index	97	97	57	127	91	78	47
e. Pour Point, °F	-	-20	-20	<-65	-45	-30	-25
f. Viscosity at Pour Point, cs (extrap)	-	58,000	400,000	>200,000	150,000	180,000	500,000
g. Melting Point, °F	150-165	-	-	-	-	-	-
h. Density, 20/4	-	1.0516	-	-	-	0.9851	-
i. Refractive Index, n_D^{20}	-	1.5746	1.5607	1.5143	1.5148	1.5179	-
Thermal Stability, Capsule, 20 hours at 700°F							
a. Gas Evolved, ml gas/g fluid	3.48	1.68	1.46	60.3	7.06	16.6	32.5
b. Viscosity Change at 100°F, %	-36.3	-53.3	-16.0	-48.2	-74.4	-4.0	-86.5
at 210°F, %	-44.2	-30.6	-9.04	-35.7	-54.1	-2.4	-62.8
Oxidation Stability, 48 hours at °F	500	500 500	500	400	-	500	-
a. Additive, %	2% Parabar 441	none 5% tribenzyl selenide	2% Parabar 441	2% Parabar 441	-	2% Parabar 441	-
b. Viscosity Change at 100°F, %	solid	solid -21.2	+215	+212	-	lost	-
at 210°F, %	+52.4	solid -10.8	+53.3	+95	-	+251	-
c. Neutralization No.	3.95	solid 1.27	3.61	11.2	-	15.5	-
d. Metal Weight Change, mg/sq cm Al	-0.09	0.0 0.0	0.0	-0.13 -0.16	-	-3.03	-
Steel	-1.12	-21.9 -0.71	-0.03	-0.10 -0.03	-	-3.29	-
Cu	-1.32	not run -26.5	-0.02	-0.13 -0.38	-	-0.25	-
Ag	-0.05	not run -86.0	-0.03	0.0 -0.13	-	-0.22	-
Pb-Cu	-0.03	not run -19.9	0.0	+0.29 -0.03	-	+0.16	-
e. Insolubles, %	2.65	solid 1.6	1.9	0.008 trace	-	0.50	-
f. Evaporation, %	0.0	1.2 0.57	0.0	- 6.6	-	1.5	-
Radiation Stability, Dosage 12^{10} ergs/g C	0.92 4.27	0.60 2.70	1.24 5.84	0.00 2.70	0.90 4.14	1.15 5.10	1.25 5.66
a. Gas Evolved, ml gas/g fluid	0.6 0.6	0.03 0.9	1.1 4.2	1.4 1.1	1.2 3.1	1.3 -	(0.3) 3.2
b. Viscosity Change at 100°F, %	+2.98 +10.4	+5.1 +14.7	+15.1 +75.3	+7.70 +15.1	+7.3 +26.4	+14.2 +50.1	+9.6 +51.3
at 210°F, %	(extrap) +0.051 +2.75 +0.48 (415°F)	+5.1 +9.4	+6.7 +36.1	+0.53 +5.84	+4.7 +16.4	+7.9 +26.8	+4.8 +28.7
Lubricity, Mean Hertz Load (Screening Test), kg	-	~23	-	-	-	~16	~11

* All samples uninhibited.

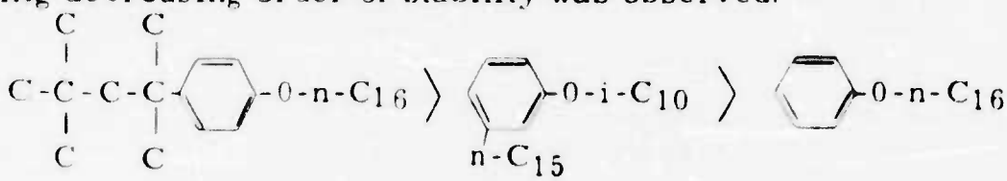
An interesting observation was the marked improvement in stability when the aromatic rings of diphenylisodecane were hydrogenated. The saturated derivative, dicyclohexylisodecane, was equivalent in stability to 1,10-diphenyldecane. Further measurable improvement was observed for the diphenylisodecane with an incorporated n-nonyl alkyl group. A striking variation in thermal properties was apparent in di-substituted (C_4) 1,9-diphenylnonanes. Here the only variation in structure is in the alkyl (C_4) substituents. The tert-butyl and fused C_4 (to give a tetralyl or 1,2,3,4-tetrahydronaphthyl structure) groups made substantial contributions to the thermal stability of the parent 1,9-diphenylnonane; whereas, normal and secondary butyl substituents appeared to give inferior qualities. The order of stability based on per cent viscosity change was as follows: 1,9-bis(tert-butylphenyl)nonane $\rangle$ 1,9-bis(1,2,3,4-tetrahydronaphthyl)nonane $\rangle$ 1,9-diphenylnonane $\rangle$ 1,9-bis-(n-butylphenyl)nonane $\rangle$ 1,9-bis(sec-butylphenyl)nonane. Phenyl- and phenoxy-substituted analogs were nearly equivalent in stability but were inferior to the parent compound in this regard.

The merits of assessing an order of thermal stability on the basis of a single property or test are questionable. However, an attempt was made to do this; and a tentative order of excellence is given in Table XIX for all exploratory compounds tested.

2.2.2.2 Oxidation-Corrosion

Quarter-scale oxidation-corrosion tests were performed only on preferred exploratory base stocks in Tables XIV through XVIII at temperatures of either 400° F or 500° F. (See Appendix I.) Parabar 441 and bis(tridecyl) selenide were used as oxidation inhibitors. The adverse effect of the selenide on metal corrosion (copper, silver) was anticipated. Results of runs at 500° F are of questionable significance because the correlation of these with engine data has yet to be established. Valid conclusions about relative oxidation stability of the various compounds examined do not appear to be justified in view of the limited reproducibility of the test (refer to Section 5 on gas turbine lubricants), as well as the small number of materials tested. Within these limits, certain trends are indicated in alkaryl ether, alkyl diphenyl ether, and diarylalkane structural classes.

Enhancement of oxidation stability by the tertiary octyl group was evidenced in the 400° F runs on the alkaryl ether series (Table XIV). The following decreasing order of stability was observed:



As might be expected, the susceptibility to oxidative breakdown in alkyl diphenyl ethers (Table XV) at 400° F increased with increasing paraffin content. Di [C_{16-18}(32/68)-sec-alkyl] diphenyl ether was an exception in this case. The descending order of stability based on viscosity increase at 400° F was as follows:

TABLE XIX

VISCOSITY LOSS OF BASE FLUIDS AT 700°F

(20 Hours - Helium Atmosphere - 410 Stainless Steel Capsules)

Base Fluid	Per Cent Viscosity Loss at 100°F
n-Dodecyl diphenyl ether Di(n-nonyl)benzene 1,9-Bis(tert-butylphenyl)nonane	<5
1,6-Diphenylhexane n-Nonyl-1,1,3-trimethyl-3-phenylindane 10-Phenyleicosane	5-10
m-Tolyl m-n-pentadecylphenyl ether sec-Octyl-n-nonylbenzene	10-15
1,9-Bis(1,2,3,4-tetrahydronaphthyl)nonane sec-Octyl n-nonyl diphenyl ether sec-Butyl n-nonyl diphenyl ether	15-20
Phenyl(n-nonylphenyl)isodecane Poly-sec-dodecyl diphenyl ether 1,10-Diphenyldecane sec-Octadecylbenzenes n-Nonyl diphenyl ether	20-30
1-Phenyl-9-octadecene Dicyclohexylisodecane sec-Dodecyl n-nonyl diphenyl ether 1,9-Diphenylnonane	30-40
1,6-Bis(phenoxy)hexane 1,9-Bis(n-butylphenyl)nonane	40-50
sec-Butyl n-tetradecyl diphenyl ether 1,9-Bis(phenoxyphenyl)nonane 1,9-Bis(biphenylyl)nonane C_{14-18}(50/50)sec-alkyl diphenyl ether	50-60
n-Hexadecyl octyl(DIB)phenyl ether	60-70
1,9-Bis(sec-butylphenyl)nonane Bis(carbethylhexoxydecyl)benzene Polyoctyl m-terphenyl Isodecyl 3-n-pentadecylphenyl ether Diphenylisodecane	70-80
Bis(carbethoxydecyl)benzene Di[C_{16-18}(32/68)sec-alkyl] diphenyl ether 1,6-Bis(sec-hexylphenyl)hexane	80-90
Phenyl(sec-tetradecylphenyl)isodecane Di-sec-tetradecyl diphenyl ether	90-92

di $[C_{16-18}(32/68)$-sec-alkyl] diphenyl ether

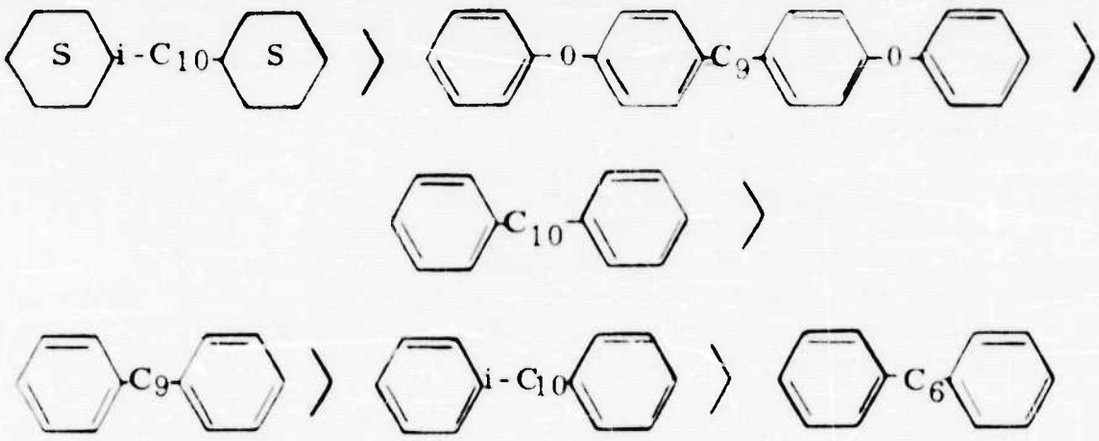
$C_{14-16}(50/50)$-sec-alkyl diphenyl ether $\cong$ n-dodecyl diphenyl ether

di-sec-tetradecyl diphenyl ether

poly-sec-dodecyl diphenyl ether

The gelation observed for di-n-nonyl diphenyl ether is attributed chiefly to impurities in the sample. The unexpectedly poor results from n-nonyl diphenyl ether and its sec-alkyl derivatives have not yet been explained.

A gradation in stability was apparent in the diarylalkane series in runs at 500° F (Table XVIII). Terminal phenoxy substituents on 1,9-diphenylnonane contributed substantially to oxidation resistance. Hydrogenation of aromatic rings in diphenylisodecane likewise enhanced the stability of the diarylalkane. This saturated derivative gave the most promising results of any exploratory compound tested thus far, with only a 10% gain in viscosity at 100° F. The parallel of a decrease in oxidation stability with a decrease in chain length of the coupling paraffin is indicated in the following observed order:



Test data are incomplete on the limited number of esters and alkylbenzenes examined (Tables XVI and XVII). The 1-phenyl-9-octadecene gave anticipated poor results, while the stability of 10-phenyleicosane was surprisingly good.

2.2.2.3 Radiation Stability

Irradiation of exploratory base stocks was conducted entirely at the MTR Canal Gamma Source. Ten milliliter, inhibitor-free samples were exposed in sealed stainless steel capsules under a helium atmosphere. Each fluid was irradiated at about 60° F at two dosage levels. Viscosity changes at 100° F and 210° F and the volume of gas evolved were measured after each exposure.

The majority of the compounds examined showed less than a 10% viscosity gain at 100°F after a dosage of 1.0×10^{10} ergs/g C. Substantial differences in viscosity change were observed with additional exposure up to 5.0×10^{10} ergs/g C. An index of damage, η_{10}[1], was adopted to permit an intercomparison of the relative radiation resistance of materials at a given dosage level. η_{10} is defined as the viscosity (centistokes) at that temperature, t_{10}, at which the viscosity of the original materials was 10 centistokes. Individual η_{10} values at two dosages were determined for the compounds tested. Logarithmic plots of these values as a function of dosage were made, and a dosage of 5.0×10^{10} ergs/g C was chosen for the interrelation of all fluids. Linearity was previously shown in a similar plot for butylbenzene, within the region of dosage of current concern[2].

Table XX broadly categorizes chemical classes and compounds as to their relative resistance to radiation. The apparent superiority of 1,9-bis(biphenyl)-nonane and the substituted indane must be qualified because these materials were solids at the exposure temperature; other materials were liquid. Only a few generalizations may be made in regard to structural differences and observed radiation resistance. Moderately stable compounds were found in each of the several chemical classes. Apparently the relative stability was not strictly a matter of per cent aromatic content; factors such as functional groups present and points of attachment also contribute. Most of the diarylalkanes and substituted diphenyl ethers exhibited only small differences in stability.

2.2.2.4 Lubricity

The Mean Hertz Load screening test (described in Appendix I) was used to evaluate the lubricity of selected base stocks (Tables XIV through XVIII). Representative fluids of the various structural classes exhibited moderately good lubricity, with values ranging from 10-23 kg. The majority of the samples tested gave values greater than 15. 1,9-bis(phenoxyphenyl)nonane was the best material of all with a value of 23.

2.2.3 Conclusions

The synthesis and evaluation of over 60 compounds, representing primarily five different structural classes, were involved in this preliminary effort to develop promising functional fluids for lubricant formulation. A summary of data from this study is given in Table XXI. An arbitrary rating scale was used to differentiate between the potentials of particular compounds. Base stocks with reasonably good physical properties were found in ester, alkylbenzene, alkyl diphenyl ether, and diarylalkane classes. Within the limits of the compounds studied and the significance of available screening test data, the following tentative conclusions were made:

[1] R. O. Bolt and J. G. Carroll, "The Radiolysis and Radiolytic Oxidation of Lubricants," Ind Eng Chem 50, No. 2, February 1958.

[2] "Research on the Radiation Stability of Organic Fluids," (California Research-AEC Report No. 6) TID 5148, October 30, 1953, p 84.

TABLE XX

COMPARATIVE RADIATION STABILITY OF EXPLORATORY BASE FLUIDS

(s) solid at ambient temperature

Index of Damage [illegible]	Alkaryl Ethers, Esters	Alkylbenzenes; Miscellany	Alkyl Diphenyl Ethers	Diarylalkanes
10-11		Polyoctyl m-terphenyl (orig. V_{100}=657 cs) 1,1,3-Trimethyl-3-phenylindane (s)		1,9-Bis(biphenylyl)nonane (s)
11-12	Isodecyl-3-n-pentadecylphenyl ether Carbethoxydecyl diphenyl ether n-Hexadecyl octyl(DIB)phenyl ether(s)	sec-Octyl-n-nonylbenzene 11-Phenyldocosane	sec-Butyl n-nonyl diphenyl ether	1,9-Bis(n-butylphenyl)nonane Diphenylisodecane 1,9-Bis(phenoxyphenyl)nonane
12-13	Bis(carbethoxydecyl) diphenyl ether	n-Nonyl-1,1,3-trimethyl-3-phenylindane	n-Dodecyl diphenyl ether Di-sec-tetradecyl diphenyl ether Di-[C_{16}-$_{18}$(32/68)sec-alkyl] diphenyl ether n-Nonyl diphenyl ether sec-Butyl n-tetradecyl diphenyl ether	Phenyl(sec-tetradecylphenyl)isodecane 1,6-Diphenylhexane 1,9-Bis(sec-butylphenyl)nonane 1,9-Diphenylnonane 1,6-Bis(sec-hexylphenyl)hexane 1,9-Bis(1,2,3,4-tetrahydronaphthyl)nonane 1,9-Bis(tert-butylphenyl)nonane
13-14	Bis(carbethylhexoxydecyl)benzene	10-Phenyleicosane	Di-n-nonyl diphenyl ether m-Tolyl m-n-pentadecylphenyl ether Poly-sec-dodecyl diphenyl ether	Phenyl(n-nonylphenyl)isodecane
14-16	Bis(carbethoxydecyl)benzene	n-Nonylbenzene		1,10-Diphenyldecane Dicyclohexylisodecane
17-18		1-Phenyl-9-octadecene		
19	n-Hexadecyl phenyl ether (s)			
20	Diisooctyl hexahydroterephthalate			

TABLE XXI

EXPLORATORY BASE FLUIDS - SUMMARY CONCLUSIONS

Rating Scale	Thermal Stability (Per Cent Viscosity Change at 100°F)	Radiation Stability (Mrs)	Oxidation-Corrosion (Per Cent Viscosity Gain at 100°F) 400°F ← Test → 500°F		Lubricity (Load (kg) for 1" scar)
1 = good	0-30	10-12	≤50	≤400	
2 = fair	30-60	12-14	50-100	400-1000	
3 = poor	>60	>14	>100	>1000	

Compound	Viscosity at 210°F (cs)	Viscosity Index	Pour (°F)	Thermal Stability	Radiation Stability	Oxidation-Corrosion	Lubricity
Alkaryl Ethers							
1. n-hexadecyl phenyl ether	2.51	133	95 (mp)	1	3	3	21
2. n-hexadecyl octyl DIB phenyl ether	6.44	116	68 (mp)	3	1	1[f]	14
3. isodecyl 3-n-pentadecylphenyl ether	5.16	133	12	3	1	2	16.5
4. 1,6-bis(phenoxy)hexane	2.62	-52	183 (mp)	2	-	-	-
Esters							
1. bis(octyl hexahydroterephthalate	4.18	131	<-60	3	3	2	16
2. carb(ethylhexoxy)decylbenzene	2.93	103	<-60				
3. bis(carbethoxydecyl)benzene	6.57	128	-35	3	3	3	15
4. tris(carbethoxydecyl)benzene	14.4	131	-5				
5. bis(carbethylhexoxydecyl)benzene	11.3	126	-50	3	2	-	-
6. carbethoxydecylbenzene	1.94	89	<-70				
7. carbethoxydecyl diphenyl ether	4.53	95	<-60	(a)	1	(b)	-
8. bis(carbethoxydecyl) diphenyl ether	10.6	112	-55	(a)	2	(b)	-
9. tris(carbethoxydecyl) diphenyl ether	19.0	117	-45				
Alkylbenzenes and Miscellaneous							
1. 10-phenyleicosane	3.11	105	15	1	2	1	13
2. 11-phenyldocosane	3.70	119	35	1	1	-	-
3. 2-phenylhexadecane	3.73	125	15				
4. 1-phenyl-9-octadecene	2.56	165	-25	2	3	3	-
5. sec-octadecylbenzenes	3.57	141	25	1	-	-	-
6. di(n-nonyl)benzene	2.83	153	45	1	-	3	-
7. sec-octyl-n-nonylbenzene	2.75	107	-40[e]	1	1	-	-
8. 1,1,3-trimethyl-3-phenylindane	2.61	-129	125 (mp)	-	1	-	-
9. n-nonyl-1,1,3-trimethyl-3-phenylindane	3.39	-12	-60	1	2	-	-
10. polyoctyl m-terphenyl	28.8	65	15	3	1	2[c]	-
11. n-nonylbenzene	1.09	125	-40	-	3	-	-
Alkyl Diphenyl Ethers							
1. C_{14}-C_{18}(30/50)sec-alkyl diphenyl ether	4.83	114	-15	2	(g)	1	15
2. di-sec-tetradecyl diphenyl ether	12.9	115	-25	3	2	2	20
3. di[C_{16}-C_{18}(32/68)sec-alkyl] diphenyl ether	11.3	121	20	3	2	1	19
*4. poly-sec-dodecyl diphenyl ether	15.2	115	-45[d]	1	2	2	18
*5. n-nonyl diphenyl ether	2.53	120	-45[d]	1	2	(b)	10
6. n-dodecyl diphenyl ether	3.24	143	70	1	2	1	17
7. n-tetradecyl diphenyl ether	3.83	159	75				
8. di-n-nonyl diphenyl ether	5.34	147	30	(b)	2	(b)	-
*9. sec-butyl n-nonyl diphenyl ether	2.65	123	-35	1	1	-	-
*10. sec-octyl n-nonyl diphenyl ether	5.10	115	-60	1	3	-	-
*11. sec-dodecyl n-nonyl diphenyl ether	6.86	121	-49	2	-	3	-
12. m-tolyl n-tetradecylphenyl ether	4.62	126	10				
*13. m-tolyl m-n-pentadecylphenyl ether	4.38	142	25	1	2	2	-
14. sec-butyl n-tetradecyl diphenyl ether	4.90	145	50	2	2	-	-
Diarylalkanes							
1. 1,6-diphenylhexane	1.81	98	5	1	2	3[c]	-
2. 1,9-diphenylnonane	2.41	130	25	2	2	3	7
3. 1,10-diphenyldecane	2.70	113	55	1	3	1	18
4. diphenylisodecane	2.51	58	-70	3	1	3	-
5. 1,6-bis(sec-hexylphenyl)hexane	8.77	42	-25	3	2	-	11
*6. 1,9-bis(n-butylphenyl)nonane	7.53	127	<-60	2	1	3	-
7. 1,9-bis(sec-butylphenyl)nonane	7.72	90	-35	3	2	-	-
8. 1,9-bis(tert-butylphenyl)nonane	8.44	78	-30	1	2	3[c]	16
9. 1,9-bis(1,2,3,4-tetrahydronaphthyl)nonane	11.4	95	-20	1	2	1	-
*10. 1,9-bis(phenoxyphenyl)nonane	10.6	97	-20	2	1	1[f]	23
11. 1,9-bis(biphenylyl)nonane	12.4	90	162 (mp)	2	1	1[c]	-
*12. phenyl(n-nonylphenyl)isodecane	5.48	125	-35	1	2	-	-
13. phenyl(sec-tetradecylphenyl)isodecane	7.83	110	-50	3	2	-	11
14. dicyclohexylisodecene	1.63	78	<-60	2	3	1	-
15. 1,9-di-p-tolylnonane	2.75	121	92 (mp)				
16. di-p-tolylisodecene	3.75	14	15				

* Metal phenolate.

[a] Faulty test.

[b] Inconclusive data.

[c] Extrapolated value.

[d] Crystallized after one day at -20°F.

[e] Crystallized after 10 hours at -20°F.

[f] Viscosity loss.

[g] Refer to Section IV.

a. Esters are inferior to the other classes in thermal characteristics at 700° F.

b. Within each class, there are members which exhibit good resistance to radiation.

c. Alkyl diphenyl ethers and diarylalkanes appear to be more stable than the other classes to oxidative effects, although few materials show much promise.

d. No pronounced differences occur among the classes in lubricating characteristics with the exception of 1, 9-bis-(phenoxyphenyl)nonane which is exceptionally good.

e. As a class, the alkyl diphenyl ethers offer most promise for further development as lubricant base stocks.

In consideration of all properties of compounds under study, the following candidates are of most interest:

Hydraulic Fluid and Gas
Turbine Lubricant Bases

a. 1, 9-bis(n-butylphenyl)nonane

b. 1, 9-bis(phenoxyphenyl)nonane

c. sec-butyl n-nonyl diphenyl ether

d. sec-octyl n-nonyl diphenyl ether

e. sec-dodecyl n-nonyl diphenyl ether

f. sec-octyl-n-nonylbenzene

Grease Bases

a. poly-sec-dodecyl diphenyl ether (50% bottoms)

b. 1, 9-bis(1, 2, 3, 4-tetrahydronaphthyl)nonane (boiling range, 490-527° F per 0.3 mm)

c. bis(n-nonylphenyl)methane (indefinite structure, 50% bottoms)

d. polyoctyl-m-terphenyl

2.3 Viscosity Index Improvers

Preliminary investigations were conducted in this field to provide ingredients for hydraulic fluids. Commercially available V.I. improvers, e.g., Paratone N and Acryloids, lose thickening power rapidly when exposed to radiation[1]. Initial studies were directed toward polymers containing aromatic rings to improve radiation stability.

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

2.3.1 Syntheses

A series of poly(alpha-methylstyrenes) was prepared by low temperature, solution polymerization techniques. Boron trifluoride gas and concentrated sulfuric acid were employed as catalysts. Methyl chloride was used as a diluent for the monomer. Regulation of reaction temperature afforded a convenient means of varying molecular weight. No effort was made to ascertain the breadth of molecular weight distribution for a given polymer preparation. Polymers were precipitated from benzene solution with methanol prior to the determination of intrinsic viscosities. The general viscosity-molecular weight range was indicated from the empirical relation $(\eta) = KM^a$ for a styrene[1] where η = intrinsic viscosity, $K = 1.03 \times 10^{-4}$, and $a = 0.74$.

Table XXII summarizes the polymerization conditions and pertinent data obtained from the series of runs. Further experimental details are given in Appendix VI.

The polymers were alkylated (HF catalysis) to varying degrees with propylene tetramer and/or n-1-dodecene to impart solubilizing characteristics. These olefins were chosen by virtue of their ready availability and their pertinence in a study of the effect of nature of attachment, configuration of the alkylating group, and degree of alkylation on radiation stability and V.I. improvement. Para substitution on the aromatic ring predominated for both olefins under the alkylating conditions employed. However, the nature of attachment differed. Propylene tetramer yielded attachments at tertiary carbon atoms; whereas, n-1-dodecene yielded secondary alkyl attachments[2]. Alkylations were performed in o-dichlorobenzene solvent at 41°F and at a constant rate of stirring. The mole ratio of polymer/solvent/olefin/hydrogen fluoride was 1/18/2.7/44 (weight ratio = 1/22.5/3.8/7.5). Alkylation time varied from one to six hours. Details of the alkylation procedure are in Appendix VII.

Attempts to measure degree of alkylation by carbon-hydrogen analyses were not entirely successful. Recourse to other methods of analyses, e.g., infrared, was not taken because neither V.I. improvement nor thickening power appeared to be primarily dependent on the length of alkylation time employed. The degree of alkylation was estimated to be in the range of 15-50%.

The solubility and V.I. improving properties of the partially alkylated poly(alpha-methylstyrenes) (APAMS) were determined in a typical base fluid, C_{14-16}-sec-alkyl diphenyl ether. Intrinsic viscosities, molecular weights, and viscosity-V.I. relationships in the alkyl diphenyl ether are summarized in Table XXIII. A comparison of intrinsic viscosities in benzene of the original poly(alpha-methylstyrenes) and the corresponding partially alkylated derivatives indicates little depolymerization occurring during alkylation.

[1] W. R. Krigbaum and P. J. Flory, J Polymer Sci 11, 37 (1953).

[2] Other projects at Cal Research.

TABLE XXII

POLYMERIZATION OF ALPHA-METHYLSTYRENE

Run No.	Methyl Chloride (cc)	Monomer (cc)	Catalyst Type	Catalyst (cc)	Stirring (rpm)	Reaction Temperature (°C)	Reaction Time (Hours)	Conversion (g)	Conversion (%)	Intrinsic Viscosity[d] (η)	Molecular Weight
4956-47-10	300	60	conc H_2SO_4	0.4	2600	-25 to -30	3	19	34	0.091	10,000
4956-47-9	300	60	conc H_2SO_4	0.4	2600	-48 to -52	3	24	43	0.230	33,000
4956-47-8	300	60	conc H_2SO_4	0.4	2600	-67 to -73	3	45	81	0.438	81,000
4956-50-4	500	50	BF_3	(c)	1300	-28 to -30	2	11	67	0.108	12,000
4956-45-6	500	50	BF_3	(c)	1300	-28 to -30	0.5	4	9	0.125	15,000
4956-45-4	500	50	BF_3	(c)	1300	-47 to -50	0.5	7	15	0.260	40,000
4956-50-2	500	50	BF_3	(c)	1300	-47 to -50	2.0	41	91	0.237	35,000
4956-50-3	500[a]	50	BF_3	(c)	1300	-45 to -50	2.0	42	93	0.483	91,000
4956-45-1	300	60	BF_3	(c)	1300	-48 to -73	0.5	54	98	0.654	138,000
4956-45-2	500	50	BF_3	(c)	1300	-54 to -72	0.5	42	93	0.638	133,000
5044-3-2	500	50	BF_3	(b)	1300	-70 to -76	0.5	41	90	1.036	256,000
4956-50-1A	500[a]	50	BF_3	(c)	1300	-70 to -72	2.0	41	90	1.048	257,000

[a] Contained 5 cc pyridine moderator.

[b] Gas on surface of reaction mixture.

[c] Methyl chloride solution of gas sprayed on surface of reaction mixture.

[d] Determined in benzene at 25°C.

TABLE XXIII

SUMMARY MOLECULAR WEIGHT, VISCOSITY, AND VISCOSITY INDEX DATA OF PARTIALLY ALKYLATED POLY(ALPHA-METHYLSTYRENES)

Alkylation No.	Poly(alpha-methylstyrene)			Alkylation Time (hours)	Polypropylated Poly(alpha-methylstyrene)		Blends in C_{14-18}-Alkyl Diphenyl Ether			
	Grams Alkylated	Intrinsic Viscosity[a] (η)	Molecular Weight		Grams Recovered	Intrinsic Viscosity[a] (η)	%	Viscosity, cs 100°F	Viscosity, cs 210°F	Viscosity Index
4956-49-14	5	0.091	10,000	1.5	5	0.091	2	33.3	5.7	123
							4	40.7	6.6	124
							6	51.1	7.8	124
4956-49-10	5	0.230	33,000	2.5	6	0.227	2	38.2	6.5	129
							4	53.7	8.6	133
							6	76.0	11.3	133
4956-49-8	10	0.438	81,000	1.5	10	0.391	2	47.1	8.0	136
							4	77.2	12.2	138
							6	126.0	18.3	136
4956-49-2	10	0.654	138,000	1.5	12	0.597	2	58.9	9.7	138
							4	117	17.7	137
							6	211	29.3	135
4956-49-3	10	0.654	138,000	2.5	10	0.552	2	59.2	9.3	134
							4	111	16.8	138
							6	195	27.1	135
5044-6-3	10	1.036	256,000	1.0	9	1.026	2	69.1	11.6	142
							4	147	22.4	139
							6	322	43.6	133
5044-6-4	10	1.036	256,000	2.5	9	1.000	2	70.3	11.8	142
							4	151	23.1	139
							6	314	43.1	134
5044-6-6	10	1.036	256,000	6.0	8	1.000	2	73.9	12.2	142
							4	169	25.7	138
							6	330	46.0	133
5044-6-1	10	1.048	257,000	1.0	8	1.146	2	78.1	12.9	142
							4	190	28.2	138
							6	402	52.6	132
5044-6-2	10	1.048	257,000	2.5	9	1.217	2	82.8	13.4	141
							4	194	29.0	138
							6	438	58.3	132
5044-6-5	10	1.048	257,000	6.0	9.5	0.987	2	78.8	12.3	138
							4	169	25.7	139
							6	326	45.4	133

[a] Determined in benzene at 25°C.

Thickening power of the APAMS as a function of molecular weight is illustrated in Figure 2. Similarly, the V.I. improving characteristics of the APAMS family are shown in Figure 3. The viscosity indexes of the upper molecular weight members of the series compare favorably with Paratone N (polybutene) and Parapol S-50 (isobutylene-styrene copolymer) and are slightly inferior to Acryloid 710 [poly(lauryl methacrylate)]. No significant differentiation could be made between poly(alpha-methylstyrenes) alkylated with propylene tetramer and those alkylated with n-1-dodecene in regard to thickening and V.I. improvement in the selected base fluid.

A further effort was made to synthesize aromatic, radiation resistant polymeric thickeners. Substitution of an alkylphenoxyethanol for lauryl alcohol in the methacrylate (Acryloid) series was explored. The monomer was prepared by oxyethylating an alkyl(C_{12})phenol and subsequently reacting the alkylphenoxyethanol with methacrylyl chloride. Details of the monomer synthesis are described in Appendix VIII. A limited number of solution polymerizations were carried out. Fifty per cent monomer solutions in benzene were treated with 0.1% to 1.0% α,α'-azodi-isobutyronitrile catalyst and the mixtures heated at reflux temperature (204° F) for a period of eight hours. The polymers were precipitated with methanol and dried to constant weight. Further polymerization details are given in Appendix IX.

No attempt was made to measure molecular weights of the products, but blends were made in C_{14-16}-alkyl diphenyl ether. Table XXIV summarizes the polymerization results as well as the thickening power and viscosity-temperature characteristics of the polymers in the chosen base fluid. The poly(alkylphenoxyethyl methacrylate) (APEM) prepared from 0.1% azonitrile catalyst at 4% to 6% concentration in the alkyl diphenyl ether exhibits V.I. improvement comparable to Acryloid 710 but is inferior in thickening power.

2.3.2 Irradiation Studies

Gamma exposure studies were undertaken to ascertain the relative stabilities of the APAMS and APEM polymers described. Comparative tests were also made with the commercial polybutenes, poly(alkyl methacrylates), and isobutene-styrene copolymers. The relative thickening power of these polymer types, in C_{14-16}-sec-alkyl diphenyl ether, is depicted in Figure 4. The upper and lower curves for a given polymer represent the limits of effectiveness of the various materials selected for intercomparison. In the irradiation work, different molecular weight polymers were used to thicken the inhibitor-free ether base oil to 10 + 0.3 centistoke at 210° F. These blends, approximately 8 cc each, were placed in Pyrex containers open to air and exposed in the cobalt-60 source at about 75° F. Viscosity measurements at 100° F and 210° F were made at appropriate intervals.

Table XXV summarizes the irradiation data obtained. The base fluid showed a small increase in viscosity and a constant viscosity index over the dosage range indicated. Gross differences were found in the radiation resistance of the polymer blends. The order of stability was APAMS $\rangle$ APEM $\rangle$ Parapols $\rangle$ polybutenes $\rangle$ Acryloids.

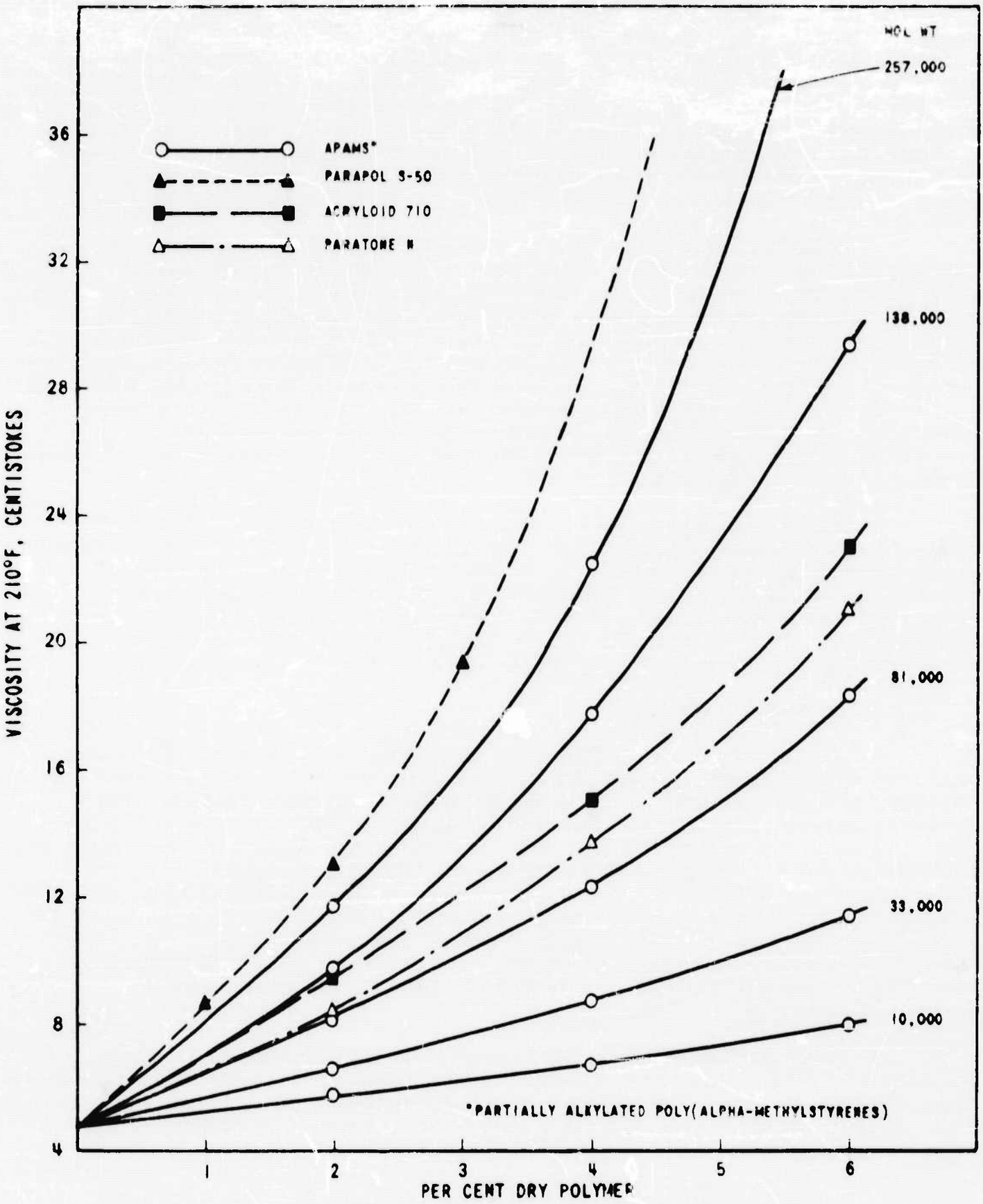


FIG. 2 - THICKENING POWER OF APAMS IN C_{14-18}-ALKYL DIPHENYL ETHER

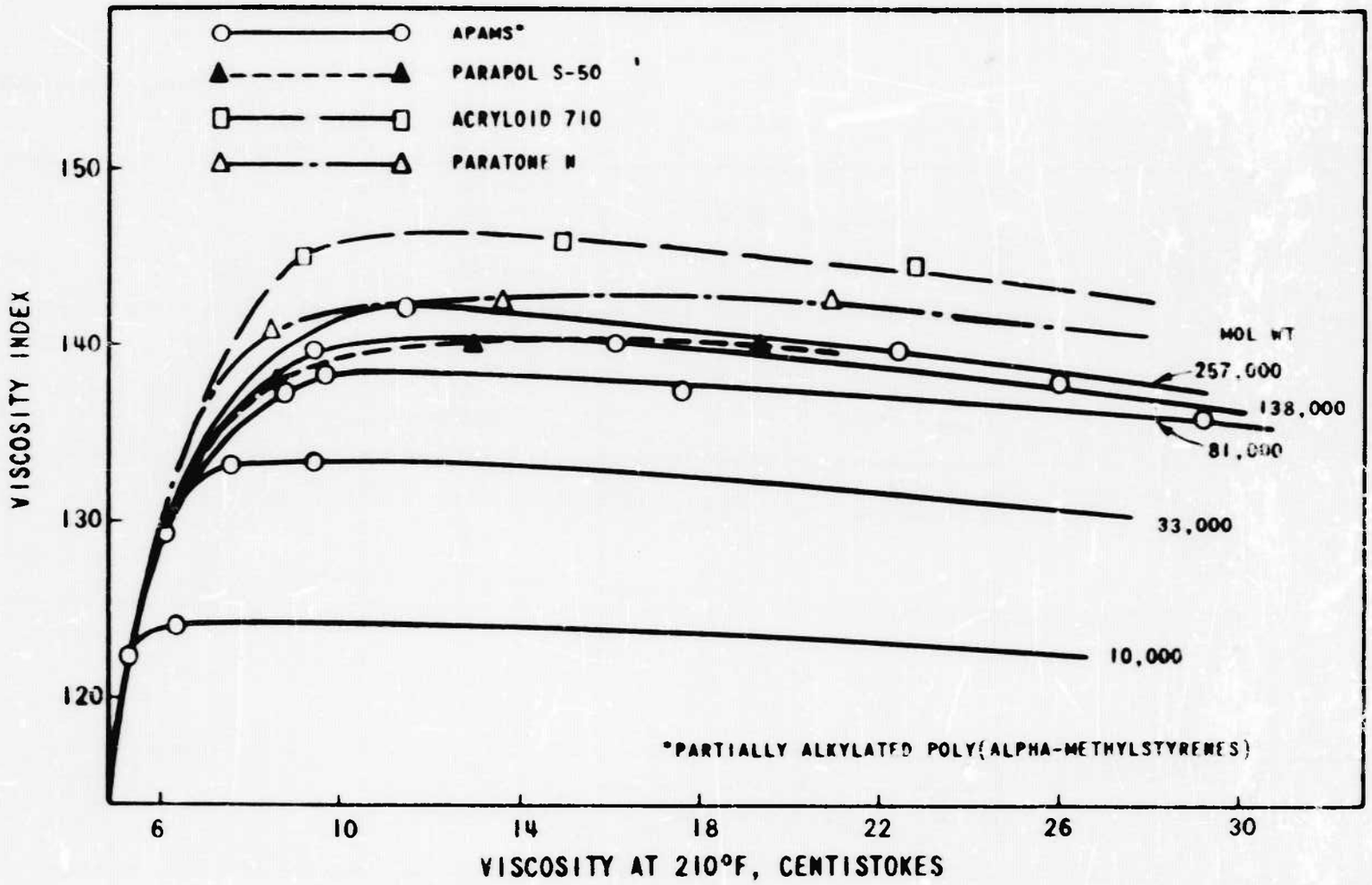


FIG. 3 - VISCOSITY INDEX IMPROVING CHARACTERISTICS OF APAMS IN C_{14-18}-ALKYL DIPHENYL ETHER

TABLE XXIV

POLYMERIZATION DATA OF ALKYLPHENOXYETHYL METHACRYLATE;
VISCOSITY-VISCOSITY INDEX RELATIONSHIP OF POLYMERS IN ALKYL DIPHENYL ETHER

Run No.	Per Cent Catalyst[a] (by wt)	Per Cent Conversion After Eight Hours	Blends in C_{14-18}-Alkyl Diphenyl Ether			
			Per Cent Polymer	Viscosity, cs		Viscosity Index
				100°F	210°F	
4896-37-16	1.0	75	2	31.5	5.53	124
			4	36.8	6.29	128
			6	43.0	7.17	132
4896-37-23	0.5	77	2	32.3	5.65	126
			4	38.6	6.57	130
			6	45.8	7.65	134
4896-37-28	0.2	72	2	34.7	6.11	134
			4	43.7	7.52	138
			6	56.3	9.46	139
4896-37-32	0.1	48	2	37.4	6.59	134
			4	51.4	8.87	141
			6	69.0	11.7	143

[a] α,α'-Azodi-iso-butyronitrile.

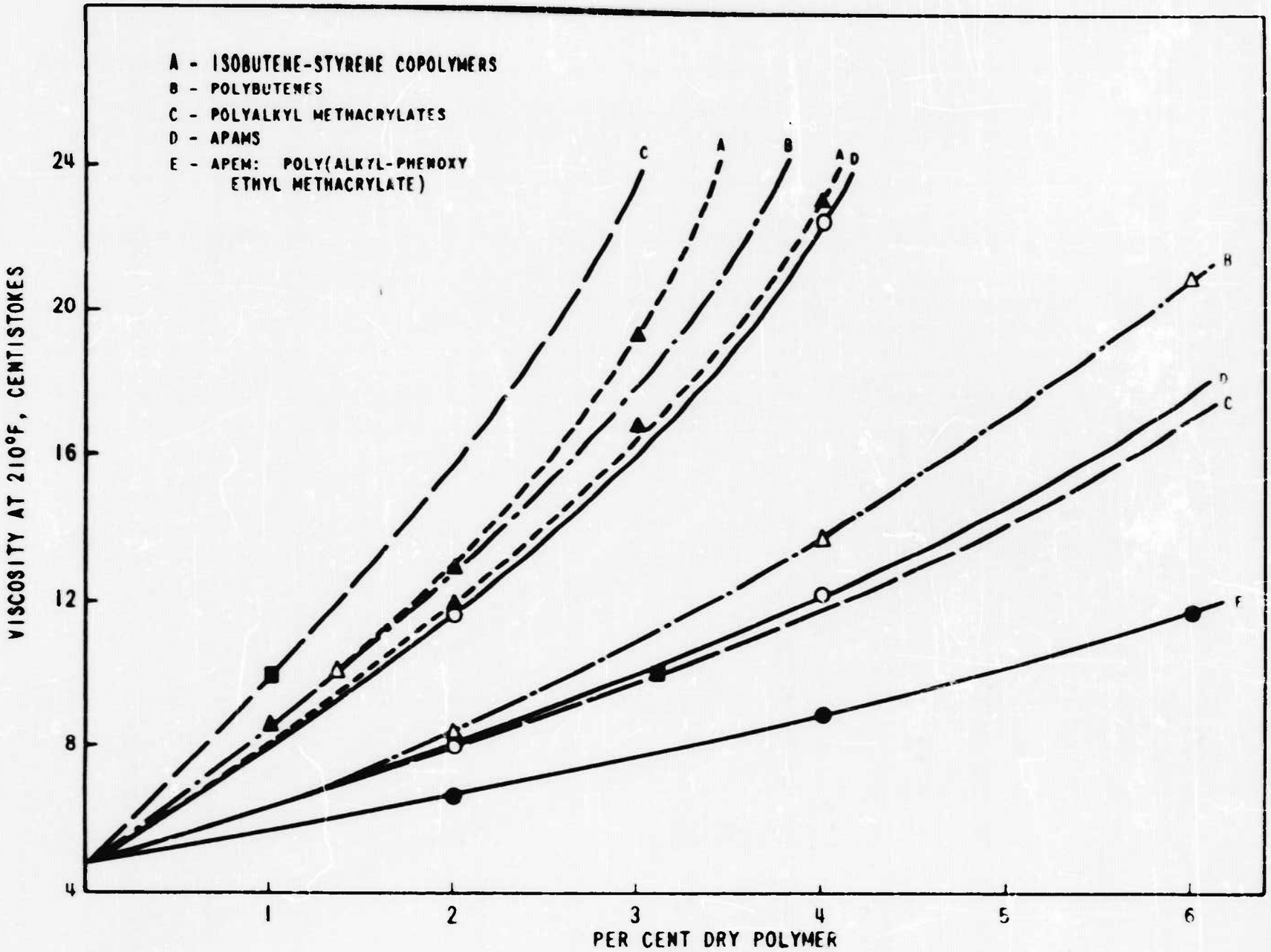


FIG. 4 - THICKENING POWER OF POLYMERS IN C_{14-16}-ALKYL DIPHENYL ETHER

TABLE XXV

STABILITY OF VISCOSITY INDEX IMPROVERS IN [illegible]-ALKYL DIPHENYL ETHER TO GAMMA RAYS

Blend No.	Polymer (Dry) Type	Polymer (Dry) Per Cent	Dosage (Ergs/g C)	Viscosity, cs 100°F	Viscosity, cs 210°F	Viscosity Index	Per Cent Viscosity Change at 210°F
[illegible]-24	none	-	0	26.8	4.83	114	-
			9.8 x 10^8	26.9	4.83	114	-
			25.1	-	4.90	-	+1.45
			39.3	27.6	4.92	114	+1.86
			58.4	28.0	4.98	115	+3.10
			87.1	28.8	5.05	114	+4.56
[illegible]-43-1	Acryloid 947	3.1	0	57.4	10.1	144	-
			9.8 x 10^8	46.9	8.23	141	-18.5
			25.1	-	7.21	-	-28.5
			39.3	39.0	6.77	134	-30.4
			58.4	37.4	6.49	132	-35.7
			87.1	36.8	6.28	128	-37.9
[illegible]-43-2	Acryloid 710	2.9	0	55.6	9.99	145	-
			9.8 x 10^8	44.1	7.62	140	-23.7
			25.1	-	6.63	-	-33.5
			39.3	36.0	6.32	132	-36.8
			58.4	35.0	6.09	129	-39.1
			87.1	34.5	5.91	126	-40.7
[illegible]-43-3	Acryloid 703	1.8	0	56.1	10.1	145	-
			9.8 x 10^8	40.8	7.27	140	-28.0
			25.1	-	6.31	-	-37.5
			39.3	34.2	6.01	130	-40.4
			58.4	33.2	5.83	128	-42.2
			87.1	33.1	5.73	124	-43.2
[illegible]-43-4	Acryloid 704	1.0	0	55.7	9.84	145	-
			8.7 x 10^7	53.8	9.67	145	-2.7
			9.8 x 10^8	36.9	6.58	137	-33.8
			25.1	-	5.90	-	-40.1
			39.3	32.0	5.65	127	-43.2
			58.4	31.4	5.54	125	-44.3
			87.1	31.0	5.50	123	-44.5
[illegible]-43-5	Acryloid 917	2.5	0	56.4	10.1	145	-
			9.8 x 10^8	45.7	7.98	140	-22.4
			25.1	-	6.97	-	-32.2
			39.3	37.9	6.59	133	-34.4
			58.4	36.5	6.31	130	-38.6
			87.1	-	6.17	-	-40.0
[illegible]-43-6	Acryloid 955	1.8	0	56.4	10.2	145	-
			9.8 x 10^8	41.5	7.34	139	-27.8
			25.1	-	6.42	-	-36.8
			39.3	34.7	6.11	131	-39.9
			58.4	33.5	5.89	128	-42.0
			87.1	33.4	5.81	124	-42.8
[illegible]-43-7	Paratone N	2.9	0	56.4	10.1	145	-
			15.0 x 10^8	-	7.70	-	-23.5
			29.5	41.0	7.05	135	-30.0
			48.8	39.1	6.51	126	-35.4
			86.4	37.4	6.31	127	-37.4
[illegible]-43-8	[illegible]	1.4	0	56.4	10.0	144	-
			15.0 x 10^8	-	6.80	-	-32.0
			29.5	37.5	6.28	129	-37.2
			48.8	34.8	6.02	128	-39.8
			86.4	34.0	5.91	127	-40.8
[illegible]-43-22	Parapol S-50	1.4	0	56.2	9.94	140	-
			14.9 x 10^8	45.1	7.70	134	-22.0
			30.5	42.4	7.09	131	-28.3
			45.4	41.2	7.02	134	-29.9
			87.4	39.5	6.52	125	-34.0
[illegible]-43-23	Parapol S-60	1.0	0	56.1	10.0	140	-
			14.9 x 10^8	45.3	8.01	135	-20.2
			30.5	44.8	7.44	132	-25.9
			45.4	43.1	7.17	131	-28.5
			87.4	41.1	6.78	128	-32.4

[a] Corrected for solvent effect.

[b] Poly(alkylphenoxyethyl methacrylate).

[c] Poly(alpha-methylstyrene) partially alkylated with propylene tetramer [alkylation time - hours] molecular weight.

[d] Poly(alpha-methylstyrene) partially alkylated with n-1-dodecene [alkylation time - hours] molecular weight.

TABLE XXV (continued)

STABILITY OF VISCOSITY INDEX IMPROVERS IN
Gamma-ALKYL DIPHENYL ETHER TO GAMMA RAYS

Blend No.	Polymer (Dry) Type	Polymer (Dry) Per Cent	Dosage (Ergs/G C)	Viscosity, cs 100°F	Viscosity, cs 210°F	Viscosity Index	Per Cent Viscosity Change at 210°F[a]
4896-43-25	APEM[b]	4.9	0	58.0	10.1	144	-
			14.9 x 10^8	50.3	8.49	139	-15.9
			30.5	46.0	7.74	135	-23.3
			45.4	44.5	7.41	132	-26.5
			86.4	42.2	6.98	130	-30.8
4896-43-12	APAMS (1.5) 81,000[d]	3.1	0	62.2	10.3	139	-
			15.0 x 10^8	-	9.52	-	-6.3
			29.6	55.9	9.07	136	-10.7
			48.8	53.2	8.65	135	-14.9
			86.4	50.8	8.22	133	-19.1
4896-43-13	APAMS (5) 81,000	2.6	0	62.2	10.3	140	-
			15.0 x 10^8	-	9.69	-	-5.9
			29.6	56.4	9.29	138	-9.8
			48.8	53.7	8.81	137	-14.5
			86.4	50.7	8.26	134	-19.8
			28.4 x 10^8	49.6	7.69	125	-
4896-43-14	APAMS (1) 138,000	2.1	0	62.3	10.3	140	-
			15.0 x 10^8	-	9.17	-	-11.6
			29.6	52.3	8.59	136	-16.9
			48.8	49.2	8.10	135	-21.5
			86.4	46.9	7.64	131	-26.1
4896-43-15	APAMS (2.5) 138,000	2.2	0	61.2	10.1	139	-
			15.0 x 10^8	-	9.17	-	-9.1
			29.6	53.1	8.67	136	-14.1
			48.8	50.5	8.25	134	-18.2
			86.4	48.3	7.78	130	-22.9
4896-43-16	APAMS (2.5) 257,000	1.8	0	60.1	10.2	142	-
			15.0 x 10^8	-	8.73	-	-14.3
			29.6	48.1	8.10	137	-20.5
			48.8	45.6	7.61	134	-25.3
			86.4	43.2	7.18	131	-29.6
4896-43-17	APAMS (6) 257,000	1.4	0	62.3	10.3	140	-
			15.0 x 10^8	-	8.99	-	-13.5
			29.6	50.0	8.32	136	-19.9
			48.8	47.0	7.75	133	-25.4
			86.4	44.0	7.31	131	-29.6
4896-43-18	APAMS (2.5) 133,000[d]	2.1	0	61.6	10.2	141	-
			14.9 x 10^8	55.7	9.20	138	-9.6
			30.5	52.3	8.62	136	-15.3
			45.4	49.0	8.30	138	-18.5
			86.4	46.1	7.72	134	-24.2
4896-43-19	APAMS (2.5) 257,000	1.4	0	57.5	9.73	141	-
			14.9 x 10^8	50.0	8.46	138	-13.0
			30.5	46.4	7.82	136	-19.5
			45.4	44.4	7.50	134	-22.9
			86.4	41.8	7.00	131	-28.4
4896-43-20	APAMS (6) 257,000	1.8	0	57.8	10.1	144	-
			14.9 x 10^8	51.3	8.69	139	-14.3
			30.5	47.6	8.05	137	-20.5
			45.4	45.8	7.72	135	-23.8
			86.4	42.7	7.21	133	-28.9

[a] Corrected for solvent effect.

[b] Poly(alkylphenoxyethyl methacrylate).

[c] Poly(alpha-methylstyrene) partially alkylated with propylene tetramer (alkylation time - hours) molecular weight

[d] Poly(alpha-methylstyrene) partially alkylated with n-1-dodecene (alkylation time - hours) molecular weight.

Dependence of stability on molecular weight was shown for the APAMS, polybutenes, and Acryloids. As might be expected, the lower molecular weight representatives in each class gave less viscosity loss. This is illustrated for the Acryloid and APAMS families in Figure 5. The APAMS were superior, but, in addition, considerable improvement in stability existed over a narrower concentration range for the APAMS than for the Acryloids. However, this may not be real because the polymers used were not of comparable molecular weight. Likewise the superiority of APEM over the Acryloids may be due to a molecular weight disparity rather than indicative of an inherent stability of the alkylphenoxyethyl group in the methacrylate monomer unit. Evaluation of lower molecular weight poly(alkyl methacrylate) homologues, with substantial V. I. improving characteristics, is suggested.

The Acryloid ashless detergent V. I. improvers, Acryloids 917 and 966, were indistinguishable from the other Acryloid polymeric thickeners in radiation resistance when compared in the same molecular weight range. Similarly, no stability differentiation could be made with poly(alpha-methylstyrenes) partially alkylated with propylene tetramer and n-1-dodecene. Data were insufficient to permit a valid intercomparison of the Parapols and APAMS on a molecular weight basis. At a constant alkyl-aryl carbon ratio, a significance in paraffin configuration in the polymers could possibly be established.

The viscosity loss with gamma irradiation for the various polymer classes under study is shown in Figure 6. A fixed concentration, 1.4%, was used in the alkyl diphenyl ether. The Acryloid curve is interpolated from Figure 5. By coincidence each blend had an original viscosity of 10 cs at 210°F. The APAMS were again superior. Figure 7 illustrates the V.I.-viscosity relationships for these polymers. The V.I. of the base fluid is 114, a point on the abscissa of the plot. The curvature of the dosage-level tie lines is of no particular significance. However, the points of intersection with the V.I.-viscosity curves are noteworthy. Although the polybutene and Acryloid give an initial measurable V.I. advantage, substantially less viscosity and V.I. losses are observed for the APAMS after the gamma irradiation indicated. No attempt was made to explore higher dosage regions where complicated secondary effects in thickening and V.I. could be anticipated.

2.3.3 Recommendations

Supplemental studies are warranted to further elucidate and qualify the APAMS as V.I. improvers for hydraulic fluids. Further investigations should include the determination of:

a. Optimum degree of poly(alpha-methylstyrene) alkylation to obtain maximum V.I. improvement.

b. Optimum length of paraffin alkylate for maximum V.I. effect.

c. Stability of lower molecular weight homologues (some sacrifice in V.I. improving characteristics is expected).

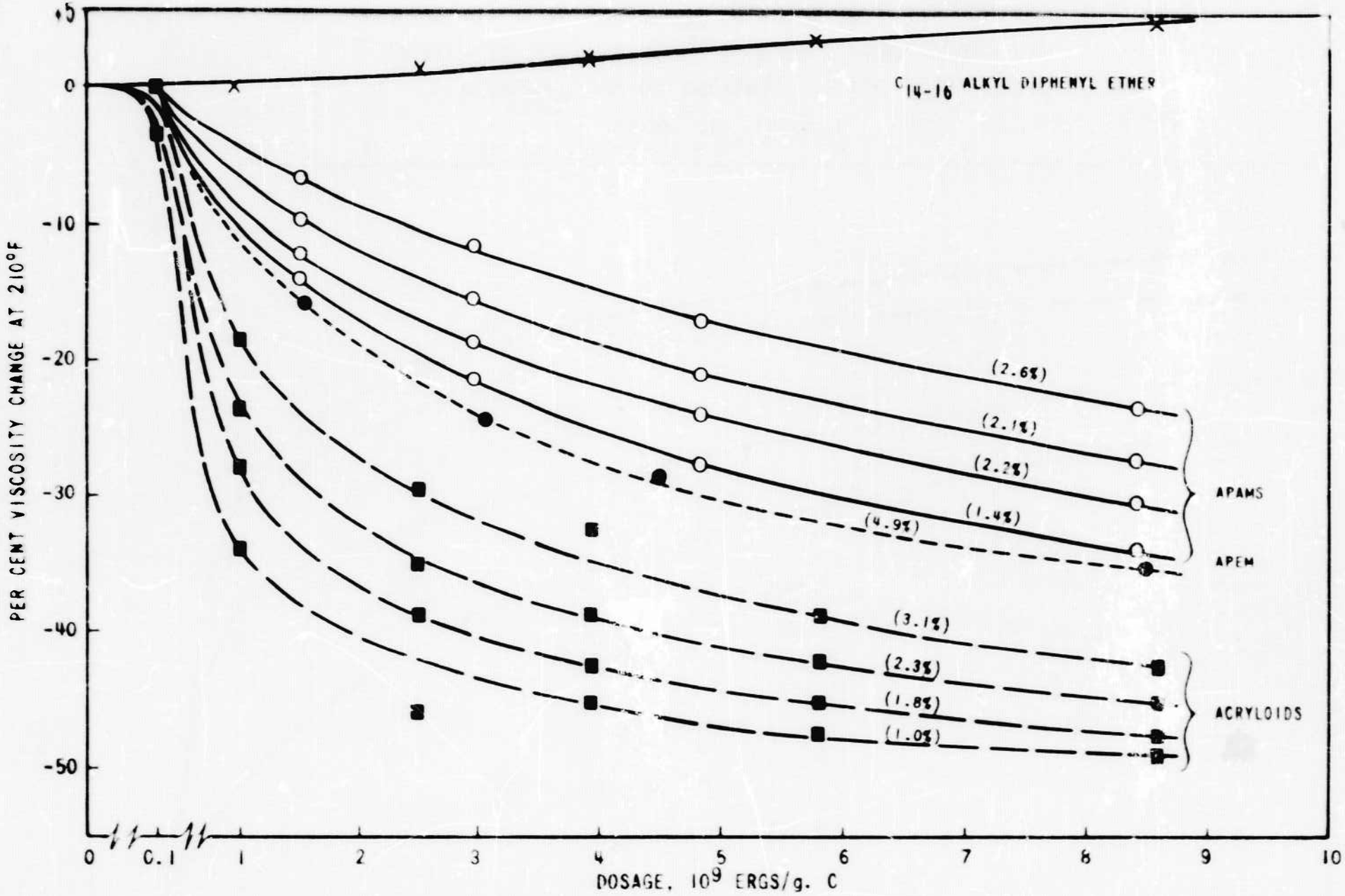


FIG. 5 - RADIATION INDUCED VISCOSITY LOSS AS A FUNCTION OF POLYMER STRUCTURE
ALL BLENDS IN C_{14-16}-ALKYL DIPHENYL ETHER,
V_{210} = 10 cs AT (PER CENT) CONCENTRATION

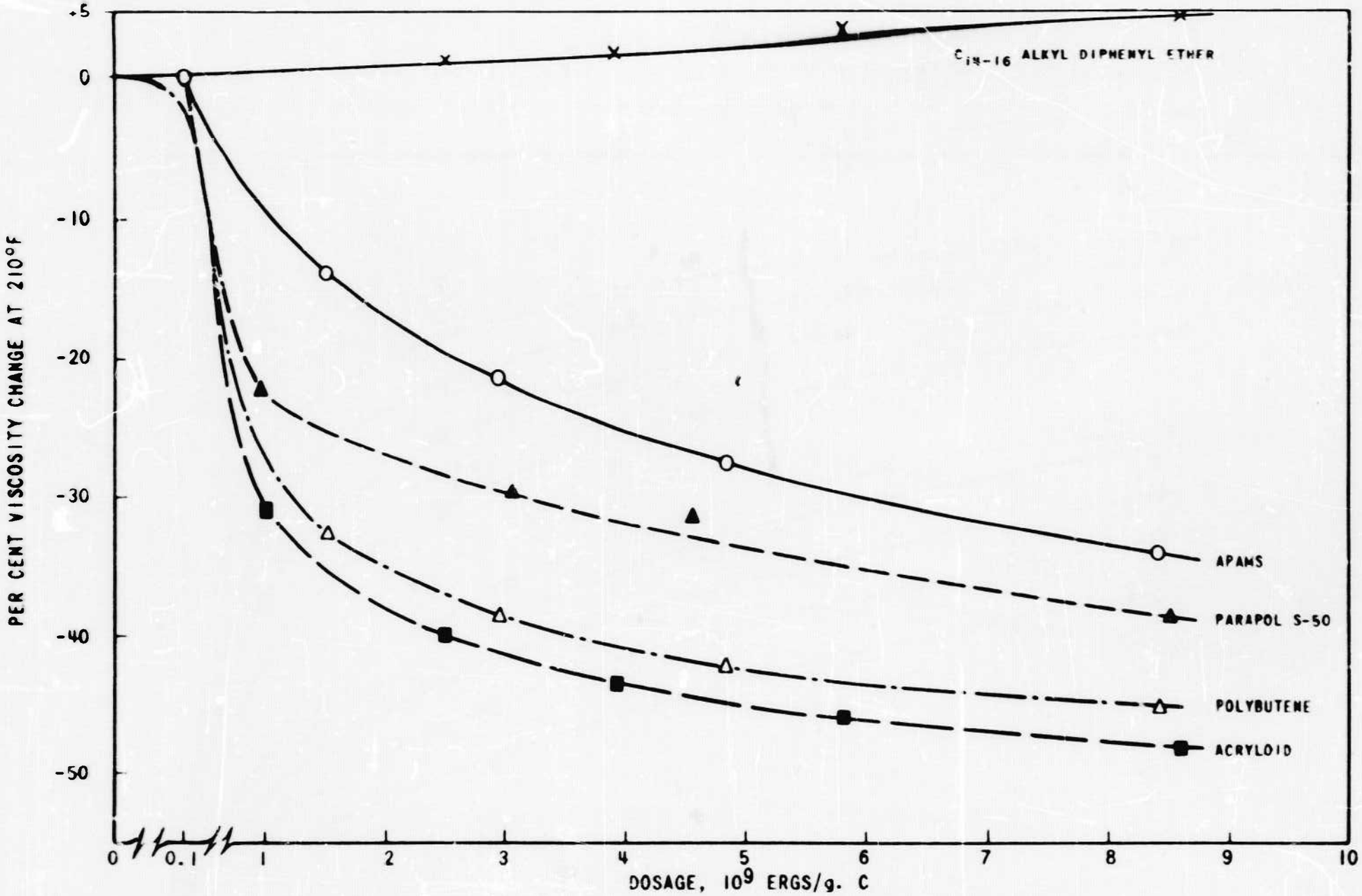


FIG. 6 - VISCOSITY LOSS OF POLYMERS DURING GAMMA IRRADIATION

POLYMER CONCENTRATION IN C_{14-16}-ALKYL DIPHENYL ETHER, 1.4%

ALL BLENDS V_{210} = 10 cs

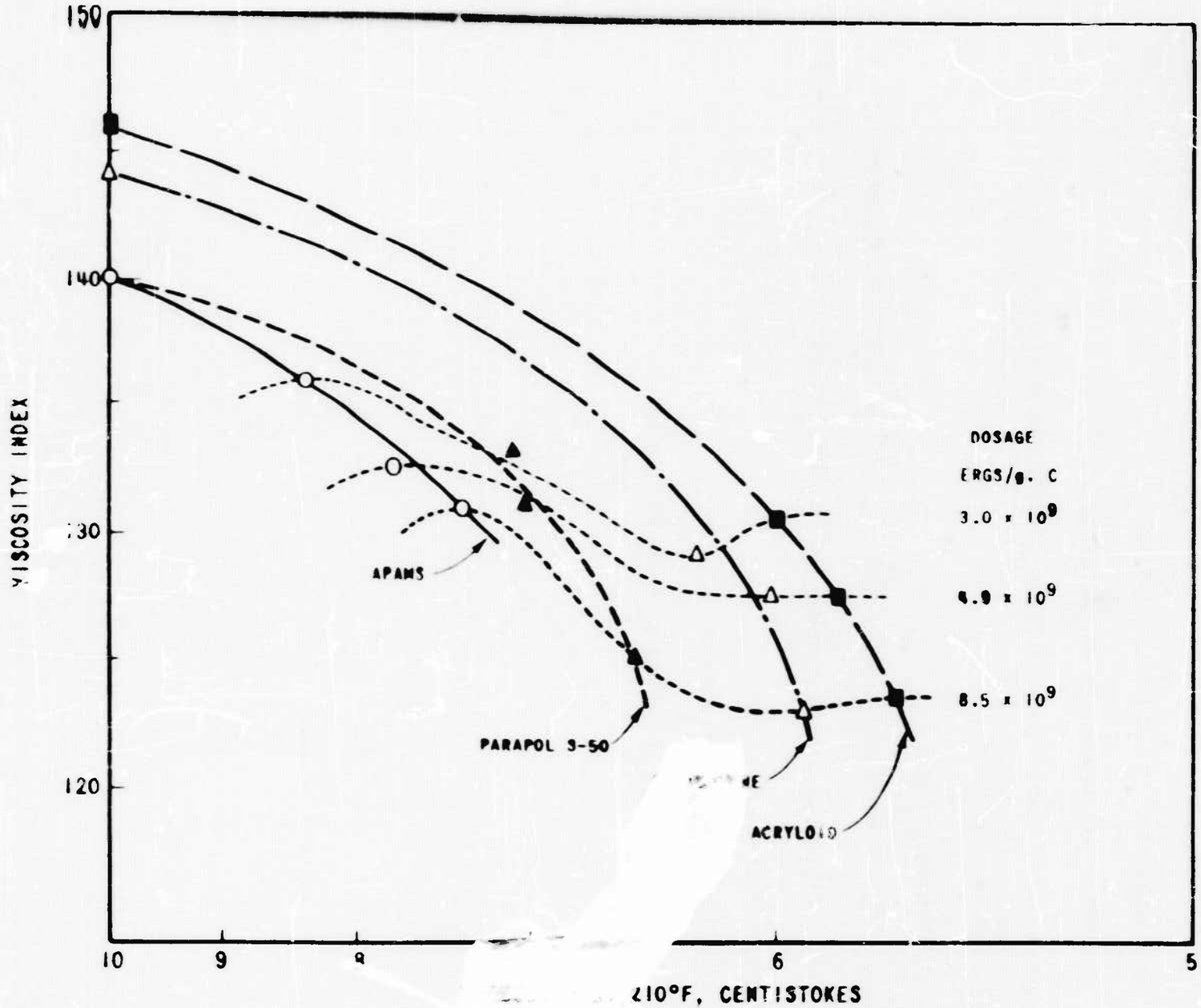


FIG. 7 - VISCOSITY INDEX - VISCOSITY RELATIONSHIP OF POLYMERS DURING GAMMA IRRADIATION

POLYMER CONCENTRATION IN C_{14-18}-ALKYL DIPHENYL ETHER, 1.4%

d. Solubility and V.I. improvement in other types of base fluids.

e. Shear and thermal properties.

f. Effect of inhibitors on radiation stability.

Other polymeric structural types containing appreciable aromaticity are worthy of evaluation as potential V.I. improvers for hydraulic fluids. These include alkylated derivatives of:

a. Polystyrenes

b. Poly(p-phenylstyrenes) and (p-phenyl-alpha-methylstyrenes)

c. Poly(p-phenoxystyrenes) and (p-phenoxy-alpha-methylstyrenes)

d. Polyphenyls

e. Butadiene-styrene copolymers

f. Poly(phenyl and phenoxyethyl acrylates)

3 LUBRICATING GREASES (B. W. Hotten)

3.1 Introduction

Previous research[1] showed that greases having much better radiation resistance than possessed by commercially available products could be made with the aid of synthetic alkyl aromatic oils and aromatic gelling agents. The 1957 program was aimed at further improvements in radiation resistance and other functional properties, such as life in bearings at high temperatures. Variations in gelling agents, oils, and the third important grease ingredient, additives, were studied.

Greases described in this section were made by the following general procedure. The saponifiable portion of the gelling agent, e.g., methyl-N-octadecylterephthalamate, was dissolved in the oil by heating to about 300° F. The mixture was cooled to about 150° F, and the saponifying agent, e.g., sodium hydroxide, dissolved in water was added. The mixture was heated to about 350° F to complete the saponification and dehydration. It was then pan cooled and milled through a 1/4-inch needle valve, opened about a half turn, at about 4000 psi pressure. Additives, when used, were put in just before the pan cooling. Grease mixtures that did not require saponification were heated directly to about 400° F, pan cooled, and milled.

3.2 Radiation Resistant Grease: CALRESEARCH 159

This most promising grease developed in previous research was evaluated thoroughly in laboratory tests and was made available for trial by potential users.

3.2.1 Composition

CALRESEARCH 159 had the following composition:

	Per Cent by Weight
Sodium N-octadecylterephthalamate	12
Didodecyl Selenide	5
Quinizarin	0.1
C_{16-18}-sec-alkylbiphenyl Oil	83

The oil was synthesized from C_{16-18}-alpha-olefins and biphenyl[1]. Fifty pounds of grease was made for test work.

[1] "Effects of Radiation on Aircraft Lubricants and Fuels," (California Research 1956 Summary Report on Contract AF 33(616)-3184) WADC Technical Report 56-646 (CONFIDENTIAL).

3.2.2 Properties

Some of the properties of the unirradiated grease were measured and reported earlier. The rest, plus the properties on an irradiated sample, were measured during 1957. All pertinent data are summarized in Table I, page vi. The irradiation was performed on a 5-pound sample in the MTR Canal Source in Idaho.

CALRESEARCH 159 softened 69 points in worked penetration as a result of irradiation to 7.2×10^{10} ergs/g C but, surprisingly, was stiffer than the unirradiated grease after 100,000 strokes. This stiffening may partly compensate for radiation softening in some dynamic applications. The grease gave moderate staining in the copper corrosion test both before and after irradiation. It passed the severe oxidation test before, but not after, irradiation. It failed the dirt count, probably because of undissolved quinizarin; this deficiency can be corrected in future batches by omission of quinizarin or use of a higher dissolution temperature. Evaporation and wear changed negligibly as a result of irradiation. Apparent viscosity and starting torque at 0° F dropped to less than half the original values, results probably related to the general radiation softening of the grease. Bearing life at 300° F had a geometric mean of 1000 hours before and 284 hours after irradiation; at 350° F it was 276 hours before and 120 hours after irradiation.

In general, the radiation effects of the high gamma dosage of 7.2×10^{10} ergs/g C were moderate. Typical commercial greases liquefy at about half this dosage and then become hard at higher levels.

A sample of CALRESEARCH 159 was also irradiated for about 13.4×10^{10} ergs/g C at 350° F. Duplicate bearing lives at 350° F after that were 147 and 174 hours. This is very good, considering the severity of treatment. A conventional sodium soap grease (Chevron OHT) was too hard to run at all in a bearing after such irradiation.

CALRESEARCH 159 and two commercial greases were subjected to the combined radiation of the Brookhaven pile. Dosage received was about 1.9×10^{18} slow neutrons[1] per square cm. Results are compared in Table XXVI.

[1] Slow neutrons by Co activation (below Cd cutoff).
Gamma radiation above 1 Mev by calorimeter $\cong 10^{18}$ per sq cm.
Fast neutrons above 1.6 Mev by Np^{237} activation $\cong 1.9 \times 10^{17}$ per sq cm.
Results from Contract AT(11-1)-174 research.

Table XXVI

Inspections on Pile-Irradiated Greases

Grease	Chevron OHT Grease		Chevron Industrial Grease Heavy		CALRESEARCH 159	
Sample No.	69-2	69-5	69-1	69-4	69-3	69-6
ASTM Unworked Penetration						
Original	289		208		261	
After Irradiation	53	103	45	45	296	296
Appearance						
After Irradiation	Rubbery		Very Hard		Smooth, Soft	

Only CALRESEARCH 159 was soft enough for further use after the exposure.

3.2.3 Field Tests

CALRESEARCH 159 was a joint development under this contract and also AEC Contract AT(11-1)-174[1]. Samples were distributed to various people having a need for a radiation resistant grease. The status of this test work is outlined in Table XXVII.

Table XXVII

Status of Field Tests on CALRESEARCH 159

Company	Status
General Electric Company, ANP Department	Planned for use in Idaho in hot cells for handling reactor cores.
General Motors Corporation, New Departure Division	Tests in progress on bearings.
General Dynamics Corporation, Electric Boat Division[a]	In use on USS Sea Wolf to lubricate primary coolant valves[b].
Oak Ridge National Laboratory[a]	Successfully tested in small bearings inpile and outpile.
WADC	Tests in progress.
Jack and Heintz, Inc.	Tests planned.
United Aircraft Corporation, Pratt and Whitney Division	Used to lubricate bearings in the MTR, further tests planned.

[a] Grease forwarded under AEC Contract AT(11-1)-174.

[b] Publicity releases not permitted without express permission of U.S. Navy Bureau of Ships.

[1] "Radiation Resistant Greases," (California Research-AEC Report No. 8) AECU 3148, June 30, 1956, p. 21.

3.3 New Gelling Agents

Research in 1956[1] showed that greases made with N-alkylterephthalamates as gelling agents lost less gel structure with irradiation than did those made with conventional soaps. As means of further improving radiation resistance, a sodium alkylterephthalamate was compounded with more highly aromatic salts or replaced completely by other higher aromatic compounds.

3.3.1 Mixed Salts

Results on a series of greases made from 1:1 molar ratios of sodium N-octadecylterephthalamate and other sodium salts are in Table XXVIII. The first grease listed (4669-40) is for reference, with no added salt.

Grease 4591-43 contained sodium benzoate as the added salt. It stiffened slightly after irradiation to 1.65×10^{10} ergs/g C and was softened about 20 penetration points from the original at 3.48×10^{10} ergs/g C. Electron micrographs of the hexane-washed and uranium-shadowed grease at the increasing irradiation dosages are in Figure 8. The very fine, curved crystallites are the terephthalamate, and the larger crystallites with a basket-weave pattern are the benzoate. The benzoate crystallites stabilized the terephthalamate gel structure despite the fact that the two sets of crystallites are discrete. In the micrographs damage is not evident to either crystalline phase.

Grease 4669-27 contained sodium p-biphenylcarboxylate. Unlike the benzoate grease, it softened about 30 penetration points initially and leveled off for the rest of the radiation dosage.

Grease 4669-12 contained crude sodium dibenzyldithiocarbamate as the added salt. The acid for this salt was made as follows:

> Eighty grams zinc dibenzyldithiocarbamate (Eastman) was refluxed in a mixture of 400-ml concentrated hydrochloric acid and 400-ml water for three hours. The reaction mixture was cooled and filtered and the filter residue washed with ice water. A neutral equivalent of 257 was found for the product (calculated 273).

When the grease was irradiated, its stability against softening was very good. In fact, there was a slight gain in stiffness. The composition of this grease is uncertain. It was hoped that dibenzyldithiocarbamic acid could be obtained by acid hydrolysis of the zinc salt. But such acids are unstable, and the product obtained may contain dibenzylamine hydrochloride and unreacted zinc salt. Electron micrographs of the irradiated grease are in Figure 9. As in the benzoate grease, there are two distinct crystalline phases; but the thiocarbamate crystallites are coarser than the benzoate. No crystal damage is evident from irradiation.

[1] "Effects of Radiation on Aircraft Lubricants and Fuels," (California Research 1956 Summary Report on Contract AF 33(616)-3184) WADC Technical Report 56-646 (CONFIDENTIAL).

TABLE XXVIII

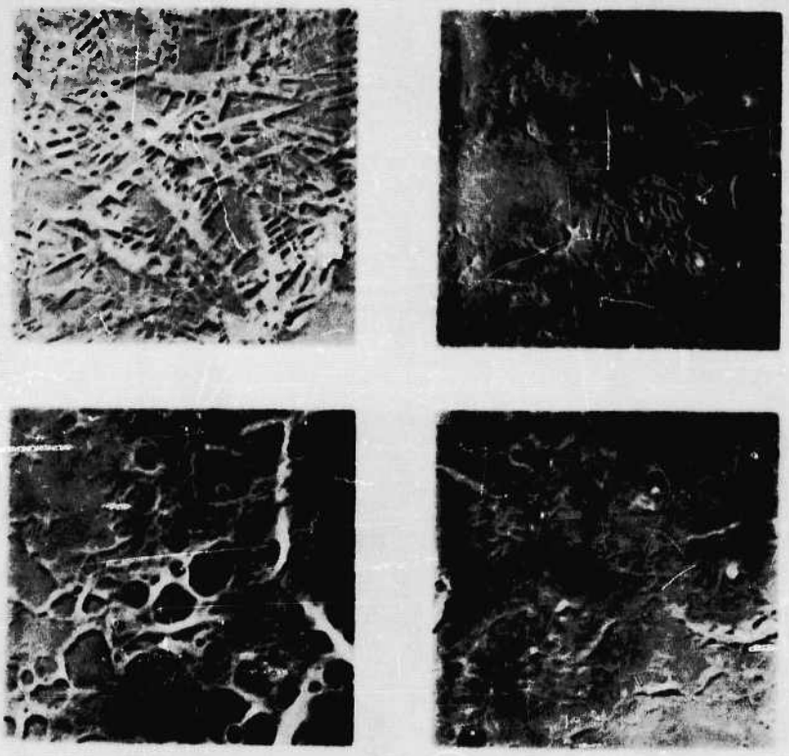
GELLING POWER AND RADIATION RESISTANCE OF MIXED SALTS

1:1 Molar Sodium N-Octadecylterephthalamate:Sodium Salt Mixtures

Grease Number	4669-40		4591-43		4669-27		4669-12		4669-28A	
Composition										
450 SSU Naphthenic Oil, g	431				215		190		207	
NaOH, g	4				4.0		4.0		2.0	
Methyl N-Octadecylterephthalamate[a], g	47				23.5		22.8		23.5	
Na Benzoate			b							
p-Biphenylcarboxylic Acid, g					9.9					
Dibenzyldithiocarbamic Acid (crude), g							12.9			
Na Dibenzyldithiocarbamate (purified), g									8.85	
Total Solids, %	10		15		14		16		14	
Texture	Smooth		Smooth		Smooth		Smooth		Smooth	
ASTM Worked Penetration (P_{60})	267		227		261		281		241	
ASTM Dropping Point, °F	528		580+		580+		456		370	
Radiation Resistance (Co^{60} Source) (Dosage 10^{10} ergs/g C)	Dose[c]	P_{60}	Dose	P_{60}	Dose	P_{60}	Dose	P_{60}	Dose	P_{60}
	0	267	0	227	0	261	0	281	0	241
	0.87	271	0.061	208	0.865	301	0.578	286	0.865	237
	1.74	260	0.784	219	1.72	296	1.01	275	1.47	231
	2.62	264	1.65	215	2.54	298	1.44	267		
	3.48	265	3.48	245	2.98	298	1.71	275		
	4.35	278					2.52	271		

a. Oronite GA-10
b. Na benzoate-terephthalamate grease made in non-Government research
c. Radiations performed at WADC.

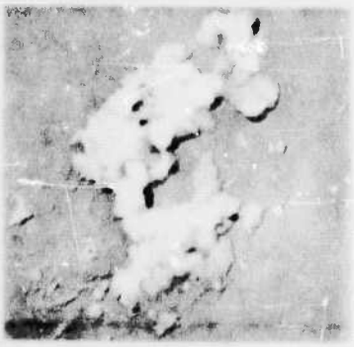
DOSAGE, 10^{10} ERGS/g. C:	0	0.061	0.704
WORKED PENETRATION:	227	208	219



DOSAGE, 10^{10} ERGS/g. C:	1.65	3.48
WORKED PENETRATION:	215 (2 VIEWS)	245 (2 VIEWS)

FIG. 8 - EFFECT OF Co^{60} IRRADIATION ON CRYSTALLITE STRUCTURE OF Na BENZOATE:Na N-OCTADECYLTEREPHTHALAMATE GREASE

8000 X



DOSAGE, 10^{10} ERGS/g. C:	0	0.578	1.01
WORKED PENETRATION:	281	286	275

DOSAGE, 10^{10} ERGS/g. C:	1.44	1.71
WORKED PENETRATION:	267	275

FIG. 9 - EFFECT OF Co^{60} IRRADIATION ON CRYSTALLITE STRUCTURE OF Na N-OCTADECYLTEREPHTHALAMATE:Na DIBENZYLDITHIO-CARBAMATE GREASE

8000 X

Grease 4669-28a contained a purer form of sodium dibenzyldithiocarbamate, which was made as follows:

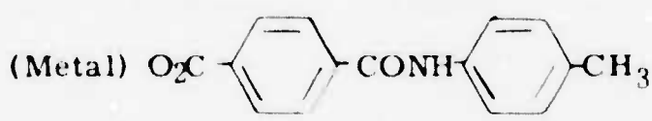
> A mixture of 79 g (0.4 mole) dibenzylamine and 76 g (1 mole) carbon disulfide was stirred in a 500-ml flask. The temperature rose from 77°F to 140°F from the heat of reaction. A solution of 16 g (0.4 mole) sodium hydroxide in an equal amount of water was added slowly. The mixture formed a thick paste, 32-ml water was added to thin it. The mixture was refluxed one hour. The excess carbon disulfide was boiled off. The residue was cooled to room temperature, filtered, and the white crystals obtained were dried: Yield 40 g; sulfated ash, 23% (theor. 24%).

Despite the difference in methods of synthesis, the two dibenzyldithiocarbamate greases responded equally well to irradiation. An attempt to make a grease from sodium dibenzyldithiocarbamate with no terephthalamate failed.

3.3.2 p- Tolylterephthalamate Greases

Another method of achieving higher aromaticity in the solid phase of greases was the use of a more aromatic primary gelling agent in place of aromatic salts added to the N-octadecylterephthalamate. The ester for one such gelling agent was synthesized as follows:

> Two moles (640 g) of methyl terephthaloyl chloride in toluene was added during two hours to a mixtures of 2 moles (214 g) p-toluidine, 2 moles (202 g) triethylamine, and 300 ml toluene at 140-158°F. The cooled suspension was filtered. The filter cake was washed with water until free of chloride and extracted with hot toluene five times. The toluene solution was cooled and filtered. The filter cake was rinsed with ether and dried. This solid amounted to 160 g of light tan crystals - melting point 406°F (previously obtained melting point for methyl N-tolylterephthalamate - 403°F). The residue insoluble in hot toluene weighed 206 g; it was probably terephthaldi-p-toluidide. Salts of the monotoluidide are highly aromatic and should have good radiation resistance:



Three greases made with this amate are described in Table XXIX. Grease 4669-17 (mineral oil) softened about 20 penetration points initially and leveled off in further irradiation (cobalt-60) to 3.36×10^{10} ergs/g C. Its dropping point increased with irradiation.

TABLE XXIX

p-TOLYLTEREPHTHALAMATE GREASES

Composition	4669-17	4669-18-3	4669-19
Methyl N-p-tolylterephthalamate, g	23.5		
NaOH, g	4.0	8.0	
450 SSU Naphthenic Oil, g	150		
C_{10-18}-Alkylbiphenyl Oil, g		307	300
Didodecyl Selenide[a], g		18.7	18.7
$LiOH \cdot H_2O$, g			8.4
Gelling Agent Concentration, %	14	13	14
ASTM Worked Penetration (P_{60})	256	254	Fluid mush
ASTM Dropping Point, °F	516	580+	
Radiation Resistance:			
1. (Co^{60} Source) Dosage, 10^{10} ergs/g C			
2. MTR Canal Source, 11.3×10^{10} ergs/g C			
Navy High-Speed Bearing Life, 350°F, Hours		P_{60} 282 Dropping Point 580+	
		204, 89, 233	

Dose	P_{60}	ASTM Dropping Point
0	256	516
0.80	280	526
1.49	282	
1.78	288	580+
3.36	275	580+

[a] Oronite "OLOA 250."

Grease 4669-18-3 (alkylbiphenyl oil) softened only about 30 points even after the very high dosage of 11.3×10^{10} ergs/g C in the MTR Canal Source. Its bearing life at 350° F[1] was good in two runs out of three. An attempt to use lithium hydroxide in place of sodium hydroxide as the saponifying agent in Grease 4669-19 failed to yield a useful gel structure.

3.3.3 Nonmetallic Gelling Agents

Several attempts to prepare effective nonmetallic gelling agents from isocyanates were made. In each experiment the amine was dissolved in half of the base oil and the isocyanate in the other half. The two portions were then mixed and heated to about 400° F. These agents had inadequate gelling power at about 20% concentration in an alkylbiphenyl oil, as shown in Table XXX.

Table XXX

Exploratory Isocyanate Derivatives as Gelling Agents

Grease No.	4669-19a	4669-20	4669-20a	4669-21a
p-Biphenylyl Isocyanate, g	19.5			
p-Phenylene Diisocyanate, g		16	16	
n-Octadecyl Isocyanate, g				29.5
p-Toluidine, g	21.3	21.3		
p-Aminoacetanilide, g			30	
p-Biphenylcarboxylic Acid, g				19.8
C_{16-18}-sec-alkylbiphenyl Oil, g	204	204	184	180
Consistency	mushy	mushy	mushy	mushy

N, N'-Bis(dibenzyl)terephthaldiamide was also synthesized from terephthaloyl chloride and dibenzylamine for trial as a gelling agent. Its melting point of 320° F was too low for use in bearings at 350° F. (Other metal-free gelling agents are mentioned in Tables XXXI, page 67 and Table XXXIV, page 71.)

[1] MIL G-3278A specification bearings.

3.3.4 Comparison of Radiation Resistance

The effect of cobalt-60 irradiation on consistency of greases containing the new gelling agents is summarized graphically in Figure 10. All the experimental greases tested are much more stable than the sodium stearate grease shown for comparison. The exact quantitative effect of added salts on radiation resistance of N-octadecylterephthalamate greases is uncertain, because the two base greases, A (Expt. 2490-24A) and B (Expt. 4669-40), differed in radiation resistance.

3.4 Oil Variation in Greases

3.4.1 Irradiation of Greases at 350° F

A series of greases containing various oils was irradiated at 350° F in the MTR Canal Source. All but one made use of sodium N-octadecylterephthalamate as the gelling agent. Results are in Table XXXI. In general, stability was very good for the severe conditions of about 10^{11} ergs radiation/g C and 18 days heating at 350° F. Grease 2579-48 (CALRESEARCH 159), containing the C_{16-18}-sec-alkylbiphenyl oil, gave the best 350° F bearing life of the group both before and after irradiation. It also had longer bearing life after irradiation at 350° F than after irradiation at room temperature (160 vs 120 hours, see page 56.)

3.4.2 Volatility

As a basis for choosing new oils for greases, oils from the synthesis work were screened for volatility by evaporation of 1-g samples for 24 hours at 350° F. Results are shown in Table XXXII.

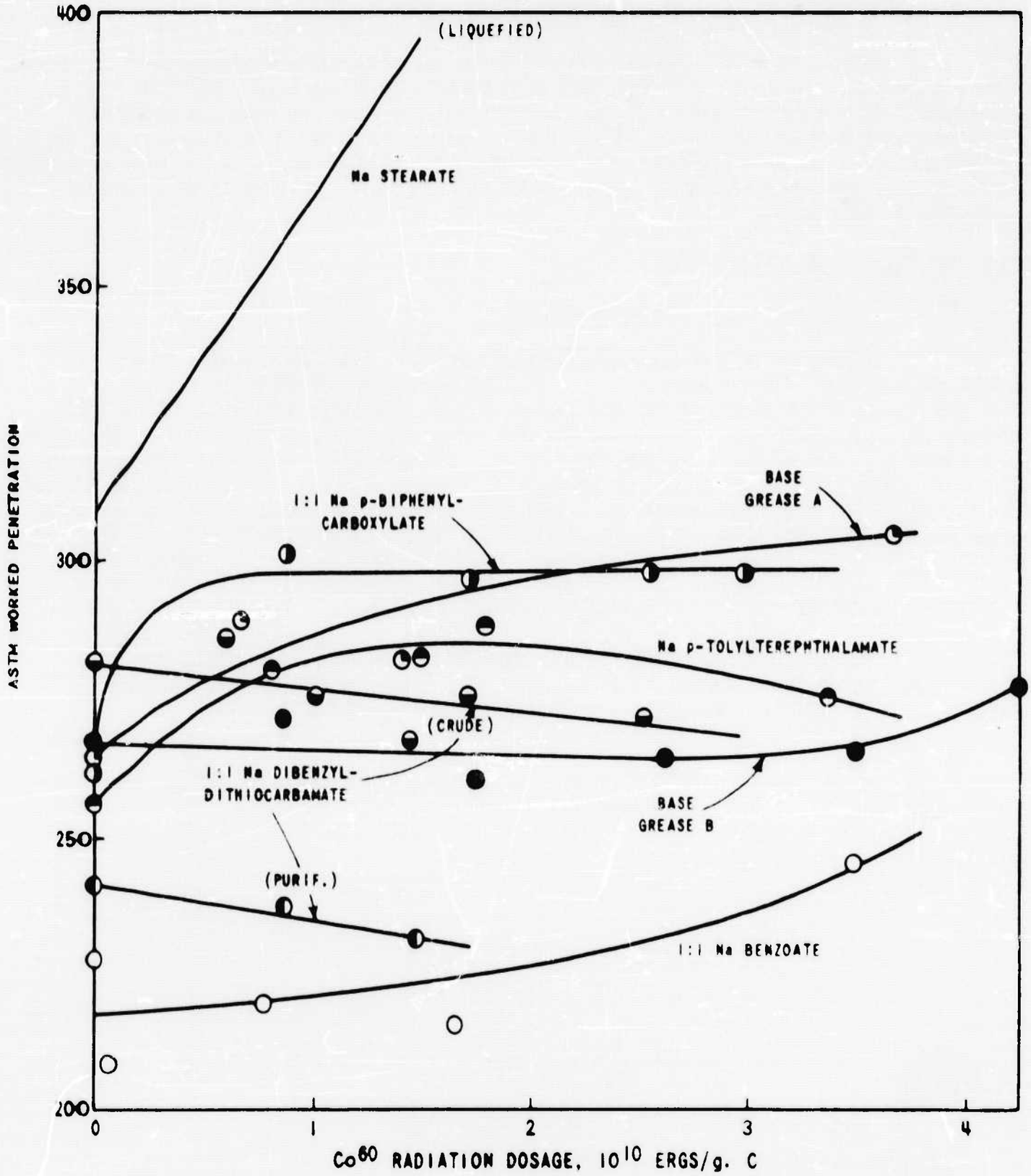


FIG. 10 - EFFECT OF γ-IRRADIATION ON CONSISTENCY OF GREASES

NAPHTHENIC OIL GREASES CONTAINING VARIOUS GELLING AGENTS.
SALTS MARKED 1:1 ARE IN 1:1 MOLAR RATIO WITH SODIUM
N-OCTADECYLTEREPHTHALAMATE

TABLE XXXI

EFFECT OF IRRADIATION[a] AT 350°F ON EXPERIMENTAL GREASES

Various Oils Gelled with a Terephthalamate or a Terephthaldiamide

Grease No.	2579-43		2579-47		2579-48[b]		2579-49A		2579-49B		2579-49C		Chevron Industrial Grease - Heavy	
Radiation Dosage, 10^{10} ergs/g C	0	9.3	0	10.5	0	13.4	0	12.5	0	12.9	0	11.5	0	7.8
ASTM Worked Penetration	241	246	244	297	261	246	260	297	203	270	233	290	239	238
ASTM Dropping Point, °F	580	580+	572	580+	572	580+	-	580+	-	580+	-	580+	580+	580+
Bearing Performance; 350°F, 10,000 rpm - Life in Hours	166 156	185 53	-	74 54	279 188 400	174 147	194 156	23 26	56 147	82 83		111 26 87	137 182 113	153 88
- Geometric Mean Life	161	99		63	276	160	174	24	91	82		63	141	116
Ingredients, Per Cent by Weight														
Sodium N-octadecylterephthalamate	12		13		12		12		13					
N-dodecyl-N'-phenylterephthaldiamide											15			
Didodecyl Selenide	5		5		5		5		5		5			
Quinizarin	0.1		0.1		0.1		0.1		0.1		0.1			
Dioctylbiphenyl	83													
Trioctylbiphenyl			82											
C_{16-18}-Alkylbiphenyl					83									
Didodecyl Diphenyl Ether							83							
Trioctyl Diphenyl Ether									82		83			

[a] In vented tin-plated cans; MTR Canal Source.

[b] Same as CALRESEARCH 159.

Table XXXII

Oil Evaporation at 350° F
1-g Oil in 2-Inch Diameter Dish
After 24 Hours at 350° F

Oil	Reference	Vis at 100° F, cs	Pour, ° F	Evaporation, %
C_{14-16}(50/50)sec-Alkyl diphenyl ether (bottoms)	4896-9	15.7	-75	33
1,9-Bis(n-butylphenyl)nonane	4658-25	47.5	-60	35
C_{14-16}(50/50)sec-Alkyl diphenyl ether (bottoms)	4658-21	67.0	5	18
Poly-sec-dodecyl diphenyl ether (71-88%)	4956-2	135	-44	6
Di-sec-tetradecyl diphenyl ether (77-89%)	4965-2	130	-18	9
Dioctyl m-terphenyl	3470-21B	643	0	10
Polyoctyl m-terphenyl (bottoms)	3470-22	708	-20	5
Tris(carbethoxydecyl)benzene	4965-25	105	-5	18
1,9-Bis(phenoxyphenyl)nonane	4658-27	99.9	-20	13
Tris(p-phenoxyphenyl)-n-dodecylsilane[a]	MLO 56-1066	1807	55	5
Polyoctyl m-terphenyl	4658-38	657	-38	8
Poly-sec-dodecyl diphenyl ether (bottoms)	5051-30	179	-50	2
Tris(carbethoxydecyl) diphenyl ether	5051-38	185	-45	10
1,9-Bis(1,2,3,4-tetrahydronaphthyl)-nonane (bottoms)	4956-37	302	12	2
Poly(n-nonylphenyl)methane	5108-27	187	-	1
Poly-sec-dodecyl diphenyl ether (bottoms)	5158-36	242	-18	1

[a] Sample furnished by WADC.

Greases were made from the available oils that evaporated less than about 10%.

3.4.3 Trial of New Synthetic Oils

Greases made from the most promising oils in the volatility test are listed in Table XXXIII. A mixture of 1:1 molar sodium N-octadecylterephthalamate and sodium benzoate was used as the gelling agent in most of the greases.

Poly-sec-dodecyl diphenyl ether in Grease 4669-32a gave longer bearing life at 350°F than the polyoctyl m-terphenyl in Grease 4669-32. Greases 4669-38 and 4669-38a, both made from a new batch of poly-sec-dodecyl diphenyl ether but one with didodecyl selenide and the other with a different antioxidant, performed equally well on the average. Grease 4669-38a had the best individual life run, 537 hours, Grease 4669-39, containing sodium dibenzyldithiocarbamate in place of sodium benzoate had somewhat shorter bearing life.

Greases 4669-30 and 4669-39a (Table XXXIII) were made from tris(phenoxyphenyl)dodecylsilane. The former lasted about 40 times as long as the alkyl aromatic oil greases in the thin film test for heat stability at 350°F. However, its life in bearings was only 240 hours. This combination of results indicates that the grease had adequate chemical stability for very long life but that its colloidal structure did not provide optimum retention, feed rate, etc., in the bearing. Further research on gelling agents for this and other silane oils should thus be rewarding.

The Navy Gear Wear Test values in Table XXXIII show that the silane oil has much better wear preventive power than silicone oils in greases. The latter seize in the test prior to 1000 cycles, and no comparable wear measurements are possible. One new gelling agent was tried in Grease 4669-39a, a mixture of terephthaldi-p-ditoluidide and sodium N-octadecyl-terephthalamate. This grease gave the longest individual bearing run at 350°F (594 hours) of any grease tested in this project. However, one very short run of 62 hours brought the geometric mean life down to 213 hours (395 hours if the 62-hour run is rejected). The bearing life at 450°F was better than that of mineral oil greases, which last only about 20-40 hours[1].

3.5 Inhibitor Variation in Greases

Didodecyl selenide has been a standby as an oxidation inhibitor in greases for use at high temperatures. However, some of the inhibitors investigated by Professor Cole at the University of Virginia appeared to be interesting alternates. They and other new inhibitors were tested as shown in Table XXXIV. A 1:1 molar mixture of sodium N-octadecylterephthalamate and sodium benzoate was used as the gelling agent in the alkylbiphenyl oil of CALRESEARCH 159 grease. Five per cent of each additive was employed.

[1] Unpublished Cal Research data.

TABLE XXXIII

GREASES CONTAINING NEW SYNTHETIC OILS

Grease Number	4669-32	4669-32a	4669-38	4669-38a	4669-39	4669-50	4669-39a
Composition							
Methyl N-Octadecylterephthalamate[a], g	23.5	23.5	68.0	68.0	11.75	24.0	
Benzoic Acid, g	5.1	5.1	17.8	17.8			
NaOH, g	4.0	4.0	11.6	11.6	1.00	2.0	
Na Dibenzyldithiocarbamate, g					4.43		
Terephthalic Ditoluidide, g							8.0
Na N-Octadecylterephthalamate, g							4.0
Didodecyl Selenide, g	12.0	12.0	28.0		6.00	6.0	2.5
Proprietary Inhibitor T, g				28.0			
Polyoctyl m-terphenyl (4658-38), g	196						
Polydodecyl Diphenyl Ether (50-30), g		196					
Polydodecyl Diphenyl Ether (5158-36), g			485	485	97.5		
Tris(p-phenoxyphenyl)dodecylsilane[b], g						166	34.5
ASTM Worked Penetration	246	239	229	222	244	269	298
ASTM Dropping Point, °F	577	568	580+	580+	424	580+	500+
Thin Film Life, 350°F, Hours	~50	~50				~2000	
ASTM Bomb Oxidation, 250°F, 100 Hours, psi Drop						4	
Navy High Speed Bearing Life,							
350°F, Hours	184, 122	201, 291	116; 346; 350	80; 315; 537	113; 225; 200	233; 186; 320	(62); 594; 263
350°F, Geom. Mean	150	242	242	238	172	240	213(395)
450°F, Hours							109; 65; 65
Navy Gear Wear							
5 lb, mg loss/1000 cycles						2.1	
10 lb, mg loss/1000 cycles						4.9	

a. Oronite GA-10
b. Sample furnished by WADC

TABLE XXXIV

COMPARISON OF ANTIOXIDANTS AT 5% CONCENTRATION IN RADIATION RESISTANT GREASES

Grease Number	4669-33 (Base Grease)	4669-18-1	4669-18-2	4669-22	4669-25	4669-28	4669-33a	4669-37
Composition								
Methyl N-Octadecylterephthalamate[a], g	34.0	34	34	18.55	23.5	23.5	10.7	68.0
Benzoic Acid, g	8.88	8.88	8.88	4.84	6.1	6.1	2.8	17.70
NaOH, g	5.8	5.8	5.8	3.16	4.0	4.0	1.83	11.6
C_{16-18}-Alkylbiphenyl Oil, g (DG 1269)	256	311	284	142	180	180	81	484
Didodecyl Selenides[b], g		18.8						
Proprietary Inhibitor T, g			17					
2-Phenylbenzoselenazole[c], g				8.8				
Goodrite 3110 x 48[d], g					11.1			
2,2'-Dipyridylamine[e], g						11.1		
Proprietary Inhibitor H, g							5	
N,N'-Di-2-naphthyl-p-phenylenediamine[f], g								28.0
ASTM Worked Penetration	241	267	267	254	265	288	321	244
ASTM Dropping Point, °F	580+	580+	580+	580+	580+	580+	580+	532
ASTM Bomb Oxidation								
250°F, 100 Hours, psi Drop	-70	-9.5	-23.5	-44.5	-27	-59	-17	-33
Bomb Cu Corrosion, 212°F, 100 hr	Mottled Green	Very Light Stain	Very Light Stain	Badly Corroded	Light Stain	Blackened	Mottled Black	Two Black Spots
Navy High Speed Bearing Life,								
350°F, Hours	157; 172; 159	288; 247; 474	314; 330; 94	144; 388; 153	266; 169; 412	108; 185; 425	117; 157; 131	439; 184; 396
Geometric Mean Life, Hours	155	323	213	205	265	204	134	317
Radiation Resistance, 11.5 x 10^{10} ergs/g C in MTR Canal Source								
ASTM Worked Penetration			364	307	378	353		
ASTM Dropping Point, °F			580+	506	580+	580+		

a. Oronite GA-10
b. Oronite CIDA 250
c. Furnished by WADC from Peninsula Chemical Company
d. Goodrich Chemical Division
e. Reilly Tar and Chemical Company
f. Eastman Kodak

The inhibitors caused large variations in bomb oxidation rates. All of them showed improvement over the base grease pressure drop of 70 psi. Didodecyl selenide gave the lowest pressure drop, 9.5 psi. Corrosiveness to copper also varied widely. 2-Phenylbenzoselenazole, 2,2'-dipyridylamine, and the proprietary inhibitor H were most corrosive. Didodecyl selenide, proprietary inhibitor T, Goodrite 3110X48, and N,N'-di-2-naphthyl-p-phenylenediamine were only slightly or moderately corrosive.

Life in the Navy High Speed Bearings at 350°F varied less than the bomb oxidation rates did. All but one inhibitor (proprietary inhibitor H) improved upon the base grease geometric mean life of 155 hours. Didodecyl selenide gave the best individual run, 474 hours, and the longest geometric mean of three runs, 323 hours. N,N'-Di-2-naphthyl-p-phenylenediamine gave the second best geometric life, 317 hours. However, the reproducibility of this test is so poor that at least two more runs should be made on the greases that averaged more than 200 hours to permit a conclusive ranking. A graphical picture of the variability of the bearing test and its poor correlation with the bomb oxidation test is in Figure 11.

Radiation resistance of four of the greases to the very high dose of 11.3×10^{10} ergs/g C was measured by the penetration change. Softening varied from 53 points for the 2-phenylbenzoselenazole grease to 113 points for the Goodrite 3110X48 grease. Data on the base grease without additives are not yet available with which to compare the irradiation results. Thus no clear cut answer on the performance of additives after exposure can yet be given.

3.6 Status, Conclusions, and Recommendations

a. A lubricating grease (CALRESEARCH 159) containing sodium N-octadecylterephthalamate as the gelling agent, C_{16-18}-sec-alkylbiphenyl as the oil, and didodecyl selenide as oxidation inhibitor has been developed for use in equipment exposed to radiation. The good work stability makes it useful for both low and high speed equipment. Its useful temperature range is 0-350°F, and its dropping point is 580+°F. It retains good consistency and lubricating properties under such extreme dosages as 7×10^{10} ergs/g C gamma radiation at room temperature, 13×10^{10} ergs/g C gamma radiation at 350°F, and 2×10^{18} slow neutrons[1]/square cm at room temperature. It is recommended for further field trials in all types of equipment exposed to radiation.

b. The following new gelling agents are promising for greases with better radiation resistance than CALRESEARCH 159: sodium N-octadecylterephthalamate-sodium benzoate mixtures; sodium N-p-tolylterephthalamate; and sodium N-octadecylterephthalamate-sodium dibenzyldithiocarbamate mixtures. The dibenzyldithiocarbamate mixtures had the best resistance to softening in preliminary radiation tests of any grease studied. Especially recommended for further study are higher ratios of sodium benzoate and lower ratios of sodium dibenzyldithiocarbamate to the terephthalamate in their mixtures. Chemical relatives of sodium dibenzyldithiocarbamate should also be of interest for study.

[1] See page 56 for discussion of other components of reactor dosage.

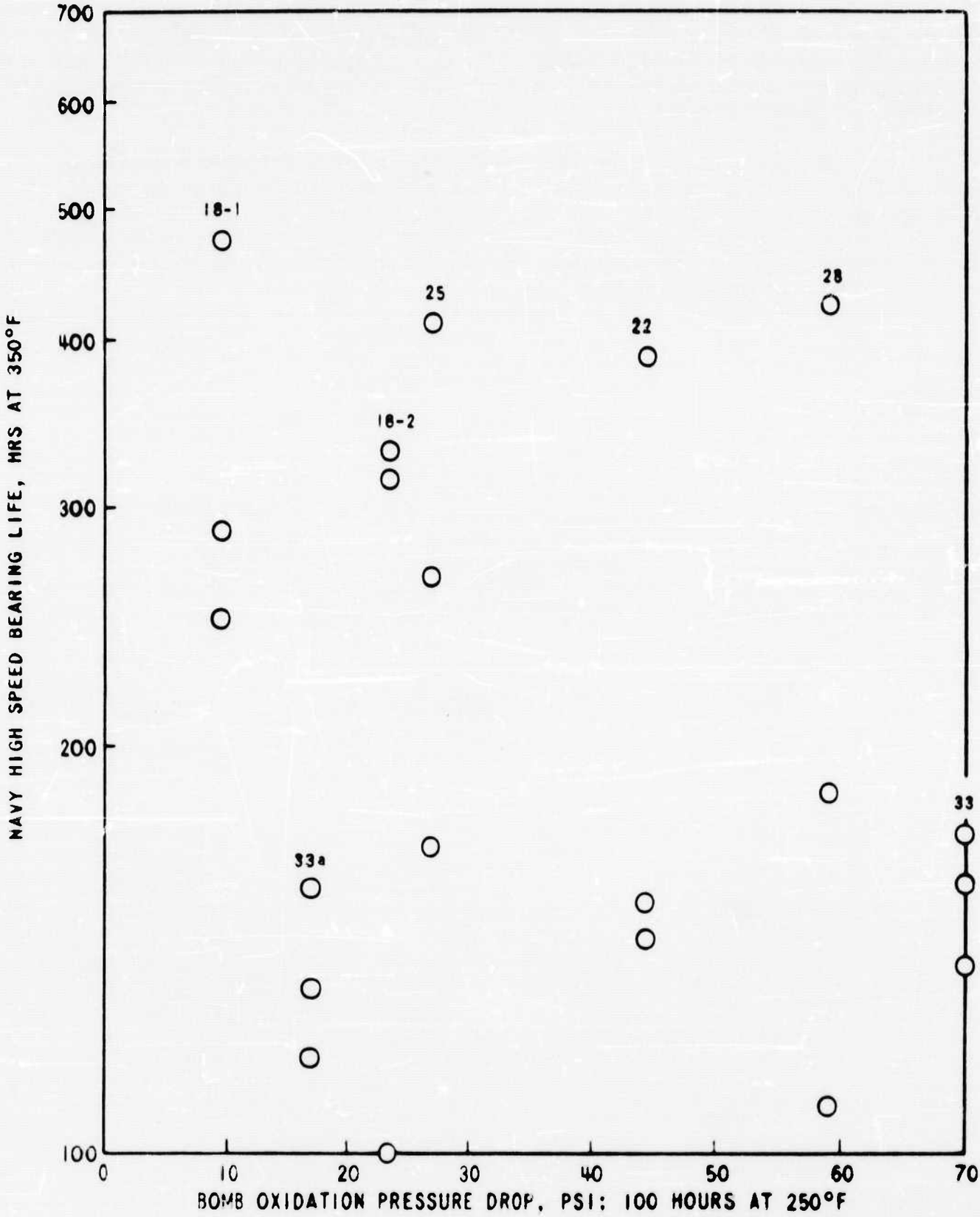


FIG. 11 - CORRELATION BETWEEN ASTM BOMB OXIDATION AND NAVY HIGH SPEED BEARING TESTS

GREASES CONTAIN VARIOUS ANTIOXIDANTS: GREASES ARE CODED BY LAST PART OF GREASE NO IN TABLE XXXIV

c. The most promising new oil for long-range development among those studied for use in heat stable and radiation resistant greases is tris(phenoxyphenyl)dodecylsilane. It and chemically related silanes are recommended for intensive study with a wide variety of existing and specially synthesized gelling agents.

d. Among a group of antioxidants tried in greases containing sodium N-octadecylterephthalamate mixed with sodium benzoate as the gelling agent and the C_{16-18}-sec-alkylbiphenyl as oil, the second most effective after didodecyl selenide in preliminary 350° F bearing tests was N, N'-di-2-naphthyl-p-phenylenediamine. It is recommended for further evaluation as an alternate to didodecyl selenide.

4 HYDRAULIC FLUIDS (R. L. Peeler)

4.1 Introduction

The objective of this research was the development of a radiation resistant fluid capable of operating at temperatures higher than those possible with current fluids. The target fluid specification was similar to MIL-H-8446. The properties desired were thermal stability, low volatility, adequate lubricity, high bulk modulus, good viscosity-temperature properties, hydrolytic stability, oxidation stability, low corrosivity, low flammability, and a low rate of gassing during irradiation.

Previous work[1] showed that alkyl aromatics were most promising as base materials because of their combination of thermal stability and radiation resistance. Disiloxane base fluids, although inferior in these two properties, offered the best chance of combining -65°F operation with medium to high temperature capabilities. Studies on several additional available base stocks were completed. Included were a naphthenic white oil and a polyglycol (UCON DLB 144E). Work here was to determine the most satisfactory lubricant which could be produced from each base stock by means of additives.

In earlier work[2], selenide additives were found particularly effective in reducing radiation damage in base stocks. However, the selenides cause serious corrosion of some nonferrous metals. Therefore, the base stocks of interest were evaluated uninhibited (or neat) and also with didodecyl selenide or di-tert-butyl-p-cresol (DBPC) added. These results are listed in Section 4.2. Additional additives were evaluated, mostly in C_{14-16}-alkyl diphenyl ether, and results are reported in Section 4.3. Finished lubricants are reviewed in Section 4.4, while subsequent sections cover special tests.

In order to minimize repetition of chemical names in the voluminous tables in this section, the names of the additives have been coded. The key to the code names is shown in Table XXXV.

[1] "Effects of Radiation on Aircraft Lubricants and Fuels," (California Research 1956 Summary Report on Contract AF 33(616)-3184) WADC Technical Report 56-646 (CONFIDENTIAL).

[2] "Effects of Fission Radiation on Lubricants and Lubrication," (Final Report on California Research-NEPA Contract), Report No. NEPA 1844, April 30, 1951 (SECRET - RESTRICTED DATA).

TABLE XXXV

KEY TO ADDITIVE CODE

PB 128	Polybutene 128
$C_{13}Se$	Bis(tridecyl) Selenide
C_8Se	Di-2-ethylhexyl Selenide
$C_{12}Se$	Didodecyl Selenide
BzSe	Dibenzyl Selenide
ØSe	Diphenyl Selenide
DC	Dimethyl Silicone of 60,000 cs
S-50	Parapol S-50 (isobutylene-styrene copolymer)
S-60	Parapol S-60 (isobutylene-styrene copolymer)
DBPC	2,6-Di-tert-butyl-4-methylphenol (Di-tert-butyl-para-cresol)
AN-1	Ethyl AN-1 (2, 6-di-tert-butylphenol)
AN-2	Ethyl AN-2 (4, 4'-methylene bis-2,6-di-tert-butylphenol)
AN-3	Ethyl AN-3 (2, 6-di-tert-butyl-4-dimethylaminomethylphenol)
A2246	2,2'-Methylene bis(4-methyl-6-tert-butylphenol)
C_8S_2	Di-tert-octyldisulfide
$ØS_2$	Diphenyl Disulfide
BzS_2	Dibenzyl Disulfide
ØS	Diphenyl Sulfide
BzS	Dibenzyl Sulfide
DNPD	Di-β-naphthyl-p-phenylenediamine
PAN	Phenyl-α-naphthylamine

4.2 Evaluation of Base Stocks

4.2.1 C_{14-16}-Alkyl Diphenyl Ether

Research in 1956[1] showed alkyl diphenyl ethers to be the preferred compounds of the alkyl aromatic types then synthesized. Physical properties were superior to those of the corresponding alkylbiphenyls while radiation stability was equivalent or only slightly inferior. Because of these promising properties, a one-barrel batch of C_{14-16}-alkyl diphenyl ether was prepared for more complete evaluation. This base stock had the best combination of properties of any investigated this year for hydraulic fluid use. It was used extensively as a reference for evaluating additives and in preparing a finished formulation. These blends are discussed in later sections. Pertinent data on the base stock are tabulated in Table XXXVI.

The physical properties of the C_{14-16}-alkyl diphenyl ether indicate a low temperature limit for the hydraulic fluid application of around 0° F, or slightly lower. The high temperature limit can be established by the operating requirements of the system in which the hydraulic fluid is used, being dependent on viscosity, volatility, oxidative and thermal stability. In practice, the limit which cannot be changed significantly by system design is set by thermal stability. The upper limit, on the basis of thermal stability tests to be discussed more fully in Section 4.5, is between 600° F and 700° F for this fluid.

Of the remaining properties, lubricity in Four-Ball Wear tests is low for a neat liquid[2], while the Mean Hertz Load of 13 shows low film strength. Hydrolytic stability at 400° F is good, while oxidation and corrosion characteristics are relatively good at 400° F and 500° F for an uninhibited base stock. Viscosity changes, ranging up to +198% at 210° F in the 500° F test, are high but are relatively good compared to those for more conventional lubricants.

The uninhibited base stock showed moderate radiation resistance with a 100° F viscosity increase of 195% after exposure to 8.7×10^{10} ergs/g C. Selenide and phenolic inhibitors reduced this change to 175% and 155%, respectively. Inhibitors did not affect the gas evolution rate detectably. Lubricity of the base stock was not affected by irradiation. The apparent increase in Mean Hertz Load value for the selenide inhibited fluid may be due to conversion of the selenide to a more active form. The volume of foam increased moderately with radiation dosage, but stability remained low. Vapor pressure of the bulk oil, following evaporation of radiolysis gases and "light ends," is not markedly increased by irradiation.

[1] "Effects of Radiation on Aircraft Lubricants and Fuels," (California Research 1956 Summary Report on Contract AF 33(616)-3184) WADC Technical Report 56-646 (CONFIDENTIAL).

[2] The following are Four-Ball Wear values (mm scar) for neat di(2-ethylhexyl) sebacate, a commonly used synthetic: 2 Hours, 167° F 4-kg load 0.58
10-kg load 0.74
40-kg load 1.06

(R. J. Benzing, WADC TR 57-283, July 1957).

TABLE XXXVI

PROPERTIES OF FLUIDS BASED ON C_{14-18}-ALKYL DIPHENYL ETHER

Sample No.	9276-2-3						947-14C		947-11A		947-8-21	947-10A	
Additives	0.001% DC						0.001% DC		-		-	-	
Radiation Dosage, 10^{10} ergs/g C	0						0.9[a]		0.9[a]		2.5[b]	8.7[a]	
Viscosity, cs, °F													
400	1.26[d]						1.18[c]		1.19[c]		1.21[c]	1.92[c]	
210	4.851						4.11		5.20		6.08	10.0	
100	26.81						25.9		29.9		38.0	79.4	
0	1064						1180		1180		1800	5970	
Pour Point, °F	-25						-25		-25		-20	-30	
Flash Point, COC, °F	450						450		425		440	415	
Spontaneous Ignition Temp., °F	810						820		820		800	820	
Foaming													
Volume, ml	<5						30		15		20	50	
Stability, min	1						0.7		0.2		0.5	0.7	
Gassing During Irradiation, ml/g	-						-		-		-	-	
Density at 68°F	0.925						-		-				
Acid Number, mg KOH/g	nil						nil		nil		0.5	nil	
Vapor Pressure at													
400°F, mm Hg	4.4						3.8		5.0		1.5	4.9	
500°F, mm Hg	16						12		13.5		10	10	
Oxidation Corrosion													
Time, hours	48	48	48	72	48	48	48	48	48	48	48	48	48
Temperature, °F	400	400	400	400	500	500	500	500	400	500	500	400	500
wt. Change, mg/cm²													
Cu	-0.35	-0.13	-0.21	-0.34	-1.47	-0.35	-0.19	-1.2	-4.26	-0.75	-0.16	-0.67	-0.92
Cu-Pb	+0.10	+0.03	-0.24	+0.08	-1.94	0	+1.55	-0.23	-2.88	+0.30	-1.13	-0.45	-0.86
Ag	+0.10	+0.26	-0.06	-0.03	-0.33	-0.6	+0.09	0	-0.06	-0.10	0	-0.10	0
Pb	+0.06	+0.06	-0.05	+0.06	-0.11	0	+0.06	-0.11	-0.03	-0.14	0	-0.03	0
Al	+0.10	+0.19	+0.09	0.03	0	0	+0.06	0	0	-0.03	+0.06	0	0
Insolubles, %	nil	nil	nil	0.1	1.5	3.3	1.3	1.5	nil	0.5	1.3	nil	4.5
Viscosity Change, 100°F, %	+80.4	+59.4	+42.9	+97.3	+229	+274	+54	+264	+200	+125	+580	+368	-
Viscosity Change, 210°F, %	+39.2	+29.8	+23.7	+44.3	+108	+117	+196	+110	+265	+81.1	+162	+220	+810
Neutralization No. Change	11.4	4.0	5.9	11.1	5.9	11.1	7.4	8.1	5.7	9.3	6.2	10.8	8.0
Hydrolytic Stability 100 hours in pressure bomb with 5% water at 400°F													
Viscosity Change, %													
at 210°F	+0.2												
at 100°F, %	-0.5												
Insolubles, %	nil												
Copper wt. Change, mg/cm²	nil												
Four-Ball Wear, mm													
2 hours, 167°F 4 kg	0.40						-		-		-		
10 kg	0.56						-		-		-		
40 kg	0.60						-		-		-		
Mean Hertz load (Screening Test), kg	15						14		15		-	13	

[a] 500 ml irradiated in aluminum container open to air; MTR Canal Source.
[b] 200 ml irradiated in tin-plated container open to air; MTR Canal Source.
[c] At 415°F
[d] At 414°F.
[e] At 413°F.
[f] 10 ml irradiated in 410 stainless steel capsule under helium; MTR Canal Source.
[g] 10 ml irradiated in heated 410 stainless steel capsule at 400°F under helium; MTR Canal Source.
[h] Filter plugged
[i] Copper not present.

TABLE XXXVI (continued)

PROPERTIES OF FLUIDS BASED ON C[illegible]-ALKYL DIPHENYL ETHER

Sample No.	9[illegible]-10D	9[illegible]-1-1	9[illegible]-2-1	9[illegible]-3-1	9[illegible]-4-1	9[illegible]-2-2					9[illegible]-10B		9[illegible]-8-2	9[illegible]-10D		
Additives	0.0016 DC	-	-	-	-	2% C[illegible] + 0.0016 DC										
Radiation Dosage, 10^{18} ergs/g [a]	0.7[e]	0.7[f]	5.0[f]	0.1[g]	5.0[g]	0					0.0[e]		4.8[h]	8.1[e]		
Viscosity, cs, °F																
400	2.616[d]					1.810[e]					1.16[c]		1.42[c]	1.82[c]		
210	9.400	5.055	5.707	5.827	5.715	6.783					5.00		6.41	6.62		
100	71.87	28.80	28.65	28.66	28.57	28.02					28.0		27.1	31.7		
0	5055					5005					1270		2340	5000		
Pour Point, °F	-50					-15					-25		-50	-50		
Flash Point, COC, °F	445					445					440		420	410		
Spontaneous Ignition Temp, °F	850					1050					1040		1040	1020		
Foaming																
Volume, ml	90					<5					50		60	50		
Stability, min	1.4					1					0.7		1.5	1.0		
Gassing During Irradiation, ml/g	-	1.1	2.8	0.9	5.2	-					-		-	-		
Acid Number, mg KOH/g	nil					nil					nil		nil	nil		
Vapor Pressure at																
400°F, mm Hg	8.0										2.8		8.7	6.1		
500°F, mm Hg	15										15		25	25		
Oxidation Corrosion																
Time, hours	48					72	48	48	48	48	48	48	48	48	48	48
Temperature, °F	500					500	500	500	500	500	500	500	500	500	500	500
wt. Change, mg/cm²																
Cu	-0.21					-0.8	-	-	-	-	-	-	-	-	-	-
Cu-Be	+0.06					-0.4	-	-	-	-	-	-	-	-	-	-
Ag	-0.61					-1.2	-	-	-	-	-	-	-	-	-	-
Fe	-0.14					-0.04	-0.01	+0.03	-0.03	-1.16	-0.10	-1.88	-0.48	+0.10	-0.48	-1.48
Al	-0.10					-0.02	0	+0.1	0	0	-0.06	-0.03	+0.03	+0.10	-0.03	-
Insolubles, %	0.2					0.72	0.04	nil	0.4	-	nil	2.1	-	nil	0.4	-
Viscosity Change, 100°F, %	+1.01					+9.0	+11.5	-30.5	+108	+70	+45	+205	+252	+108	+420	-
Viscosity Change, 210°F, %	+1.8					+25.1	+22.7	+28.6	+77	+37	+22.8	+208	+108	+51.7	+152	+406
Neutralization No. Change	7.4					5.6	2.7	5.2	5.8	5.7	4.4	6.3	5.1	4.6	5.5	7.0
Hydrolytic Stability																
100 hours in pressure bomb with 1% water at 400°F																
Viscosity Change, %																
At 210°F													-7.4			
At 100°F													-12.1			
Insolubles, %													0.17			
Copper wt. Change, mg/cm²													[illegible]			
Four-Ball, wear, mm																
2 hours, 100°F, 4 kg																
10 kg																
40 kg																
40 kg	0.77															
Mean Hertz Load (Screening Test), kg	14					14					14		-	14		

[a] 1000 ml irradiated in aluminum container open to air, [illegible] Canal Source.
[b] 2000 ml irradiated in tin-plated container open to air, [illegible] Canal Source.
[c] At 410°F.
[d] At 414°F.
[e] At 413°F.
[f] 10 ml irradiated in 410 stainless steel capsule under helium, [illegible] Canal Source.
[g] 10 ml irradiated in tested 410 stainless steel capsule at 400°F under helium, [illegible] Canal Source.
[h] Filter plugged.
[i] Copper not present.

TABLE XXXVI (continued)

PROPERTIES OF FLUIDS BASED ON [illegible] ALKYL DIPHENYL ETHER

Sample No.	[illegible]					[illegible]		[illegible]	[illegible]		[illegible]	[illegible]	[illegible]	[illegible]
Additives	[illegible]										[illegible]			
Radiation Dosage, 10^{10} ergs/g			0			[illegible][a]		[illegible][b]	[illegible][b]		[illegible][f]	[illegible][f]	[illegible][g]	[illegible][g]
Viscosity, cs, °F														
100			[illegible]			[illegible]		[illegible]	[illegible]					
210			[illegible]			[illegible]		[illegible]	[illegible]		[illegible]	[illegible]	[illegible]	[illegible]
100			[illegible]			[illegible]		[illegible]	[illegible]		[illegible]	[illegible]	[illegible]	[illegible]
0			[illegible]			[illegible]		[illegible]	[illegible]					
Pour Point, °F			-85			-20		-20	-30					
Flash Point, OC, °F			460			425		440	415					
Spontaneous Ignition Temp., °F			820			820		840	820					
Foaming														
Volume, ml			0			90		80	90					
Stability, min			[illegible]			[illegible]		[illegible]	[illegible]					
Dripping Point, Irradiation, °F			-			-		-			[illegible]	[illegible]	[illegible]	[illegible]
Acid Number, mg KOH/g			0.02			0.11		0.11	0.11					
Vapor Pressure at														
400°F, mm Hg						5.0		-	5.5					
500°F, mm Hg						[illegible]		-	[illegible]					
Oxidation Corrosion														
Time, hours	48	72	48	48	48	48	48	48	48	48				
Temperature, °F	450	450	500	500	500	450	500	500	450	500				
wt. Change, mg/cm²														
Cu	-1.03	-1.0	-1.07	-1.14	-0.13	-1.00	-1.77	0	-0.44	-0.90				
Cu-Be	-0.42	-1.0	-1.03	-0.11	-0.20	-1.42	-0.48	-1.12	-0.80	-1.01				
Fe	-0.24	-0.08	0	0	0	-0.17	0	-0.08	-0.02	0				
Pb	-0.01	0	-0.37	-0.51	-0.03	-0.01	-0.03	-0.08	-0.02	0				
Al	-0.05	-0.04	0	0	0	-0.03	0	0	-0.04	0				
Insolubles, %	0.1	0.1	0.3	0.8	0.4	0.1		0.5	0.1	0.4				
Viscosity Change, 100°F, %	+47.3	+[illegible]	-	-	+[illegible]	+[illegible]	+0.19	+[illegible]	+[illegible]	+[illegible]				
Viscosity Change, 210°F, %	+7.4	+[illegible]	+[illegible]	+[illegible]	+[illegible]	+[illegible]		+[illegible]	+[illegible]	+[illegible]				
Neutralization No. Change	5.4	6.7	7.3	8.0	5.4	7.1		4.3	8.6	7.5				
Hydrolytic Stability														
Time, hours to pressure rise with 10 water at 450°F														
Viscosity Change, %														
At 210°F								-[illegible]						
At 100°F								[illegible]						
Insolubles, %								[illegible]						
Copper wt. Change, mg/in²								-[illegible]						
Four Ball Wear, mm														
2 hours, 167°F, 4 kg														
10 kg														
40 kg														
Mean Hertz Load (extending test), kg			13			14		-	16					

[a] 400 ml irradiated in aluminum container open to air, MTR Canal Source.
[b] 200 ml irradiated in tin-plated container open to air, MTR Canal Source.
[c] At 410°F.
[d] At 450°F.
[e] At 410°F.
[f] 10 ml irradiated in 410 stainless steel capsule under helium, MTR Canal Source.
[g] 10 ml irradiated in heated 410 stainless steel capsule at 400°F under helium, MTR Canal Source.
[h] Filter plugged.
[i] Copper not present.

Even the uninhibited fluid remained liquid following 400° F and 500° F oxidation and corrosion tests after the highest radiation dosage used, 9.2×10^{10} ergs/g C. Results of these tests were somewhat erratic, but the didodecyl selenide blends showed the best stability, both before and after irradiation. The selenide inhibitor showed the characteristic corrosivity to copper and silver at 400° F. As a result, most tests with selenides were subsequently run with steel and aluminum specimens only. Irradiated fluids containing DBPC were also superior in oxidation stability to the corresponding irradiated base stock alone.

As a result of these tests, the C_{14-16}-alkyl diphenyl ether showed real promise for use as a high temperature hydraulic fluid. It was, therefore, used for most of the inhibitor evaluation and formulation work during 1957.

4.2.2 Dodecyl and Tetradecyl Diphenyl Ethers

Both dodecyl and tetradecyl diphenyl ethers received limited evaluation prior to the availability of the C_{14-16}-alkyl derivative. The results are shown in Tables XXXVII and XXXVIII. Viscosity at 0° F was 650 cs for the dodecyl and 800 cs for the tetradecyl diphenyl ether. These low values are accompanied by a desirable low pour point but are offset by high volatility and low viscosities at high temperature.

On the balance of all properties, the C_{14-16}-alkyl diphenyl ether appeared slightly preferable to the tetradecyl and considerably better than the dodecyl diphenyl ether.

4.2.3 C_{16-18}-Alkylbiphenyl (Distilled)

Besides the alkyl diphenyl ethers, the alkylbiphenyls appeared promising. The C_{16-18}-alkylbiphenyl was chosen, and two products, a whole stock and a 5% to 60% heart cut, were obtained. The latter was selected for hydraulic fluid evaluation because of its relatively low viscosity and low pour point. Because the viscosity at 0° F was 2297 cs, little V.I. improver could be tolerated, and consequently the biphenyl has been considered primarily as a potential unthickened fluid. The upper temperature limit of application, established by thermal stability tests, was between 600° F and 700° F.

Compared to the C_{14-16}-alkyl diphenyl ether, the biphenyl derivative (see Table XXXIX), before irradiation, had slightly poorer lubricity and viscosity-temperature properties. Other properties were roughly equivalent. The biphenyl showed better resistance to viscosity change on irradiation than the diphenyl ether. However, the biphenyl frequently solidified in 500° F oxidation tests following irradiation, thus indicating substantially poorer oxidation stability than for the diphenyl ether.

As a result of these evaluation tests, the alkylbiphenyls and alkyl aromatics, in general, remained of interest as possible hydraulic fluids. The C_{16-18}-alkylbiphenyl was of less interest than the diphenyl ether because of poorer physical properties.

TABLE XXXVII

PROPERTIES OF FLUIDS BASED ON DODECYL DIPHENYL ETHER

Sample No.	4658-2	4699-17-1	
Additive	-	2% DBPC	
Radiation Dosage, 10^{10} ergs/g C	0	0	
Viscosity, cs, °F			
-40	11,608	-	
0	650	-	
100	18.47	18.52	
210	3.57	3.557	
400	1.00	-	
Pour Point, °F	-75		
Flash Point, °F	405		
Spontaneous Ignition Temp., °F			
Oxidation Corrosion			
Temperature, °F		347	400
Time, hours		72	72
Weight Change, mg/cm²			
Cu		-0.19	-4.54
Cu-Be		-	-
Fe		+0.02	+0.12
Al		+0.06	+0.09
Ag		+0.02[a]	+0.15
Viscosity Change, 100°F, %		+7	+56.8
Viscosity Change, 210°F, %		+4	+26.1
Neutralization Number		0.25	29.8
Insolubles, %		nil	heavy
Vapor Pressure at 400°F, mm	25		

[a] Magnesium: +0.26 mg/cm².

TABLE XXXVIII

PROPERTIES OF FLUIDS BASED ON TETRADECYL DIPHENYL ETHER

Sample No.	4658-3	017-6D	047-1-2	047-2-2	047-3-2	047-4-2
Radiation Dosage, 10^{10} ergs/g C	0	6.5[b]	0.7[a]	3.0[a]	0.1[d]	3.0[d]
Viscosity, cs, °F						
500		1.311[c]				
400	1.12	6.01			4.10	4.72
210	4.135	39.35	4.28	4.80	22.05	27.35
100	22.26	2,156	23.7	28.1		
0	800	50,494				
-40	13,656					
Pour Point, °F	-70	-50				
Flash Point, COC, °F	445	430				
Spontaneous Ignition Temp., °F	820	820				
Bulk Modulus (adiabatic), psi						
At 0 psi and 77°F	269,000	288,000				
Gassing During Irradiation, ml/g			1.1	2.4	1.0	3.9
Density at 68°F	0.932					
Acid Number, mg KOH/g	nil	nil				
Vapor Pressure at						
400°F, mm Hg	1.9					
500°F, mm Hg	14.3					
Oxidation Corrosion						
Time, hours	48	48				
Temperature, °F	400	400				
Weight Change, mg/cm²						
Cu	-2.72	-1.26				
Cu-Be	-1.63	-0.84				
Ag	0	-0.03				
Fe	0	-0.13				
Al	+0.06	-0.10				
Insolubles, %	trace	trace				
Viscosity Change, 100°F, %	+156	+58.9				
Viscosity Change, 210°F, %	+132	+32.0				
Neutralization Number Change	9.2	4.9				
Hydrolytic Stability						
100 hours in pressure bomb with 6% water at 400°F						
Viscosity, cs						
At 210°F, %	+0.7					
At 100°F, %	-0.4					
Insolubles, %	0.003					
Mean Hertz Load (screening test), kg	18	12.5				

[a] 10 ml irradiated in 410 stainless steel capsule under helium; MTR Canal Source.

[b] 500 ml irradiated in aluminum container in air; MTR Canal Source.

[c] At 414°F.

[d] 10 ml irradiated in heated 410 stainless steel capsule at 400°F under helium; MTR Canal Source.

TABLE XXXIV

PROPERTIES OF [illegible] ALKYLDIPHENYL (DISTILLED)

Sample No.	[illegible]-1-1-3	[illegible]-1-N	[illegible]-1-R	[illegible]-1-2	[illegible]-2-2	[illegible]-3-H	[illegible]-4-H	[illegible]-2-2	[illegible]-1-10	[illegible]-7-2
Additive	-	-	-	-	-	-	-	[illegible]		
Radiation Dosage, 10^{10} ergs/g C	0	0.4[b]	8.1[b]	1.5[c]	5.5[c]	0.2[d]	4.4[d]	0	0.4[b]	0.2[c]
Viscosity, cs, °F										
400	[illegible]	[illegible][e]	[illegible][e]	-	-	-	-	-	[illegible][e]	[illegible][e]
210	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
100	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
0	[illegible]	[illegible]	[illegible]	-	-	-	-	-	[illegible]	[illegible]
-40	[illegible]	-	-	-	-	-	-	-	-	-
Pour Point, °F	-[illegible]	-[illegible]	-[illegible]					-10	-10	-[illegible]
Flash Point, °F	[illegible]	[illegible]	[illegible]					[illegible]	[illegible]	[illegible]
Spontaneous Ignition Temp., °F	[illegible]	[illegible]	[illegible]					[illegible]	[illegible]	[illegible]
Bulk Modulus (adiabatic), psi[f]										
At 0 psi and 77°F	[illegible][g]		[illegible][g]							
Foaming										
Volume, ml	[illegible][h]	[illegible]	-					[illegible]	[illegible]	[illegible]
Stability, min	[illegible][h]	[illegible]	-					[illegible]	[illegible]	[illegible]
Gassing During Irradiation, ml/g	-	-	-	1.0	4.0	1.0	4.2	-	-	-
Acid Number, mg KOH/g	0.02	nil	nil						nil	nil
Vapor Pressure at										
400°F, mm Hg	[illegible]	[illegible]	[illegible]						[illegible]	
100°F, mm Hg	[illegible]	[illegible]	[illegible]						[illegible]	
Oxidation Corrosion										
Time, hours	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]			[illegible]	[illegible]	[illegible]
Temperature, °F	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]			[illegible]	[illegible]	[illegible]
Weight Change, mg/cm²										
Cu	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]			-	-	-
Cu-Pb	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]			-	-	-
Ag	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]			-	-	-
Fe	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]			[illegible]	[illegible]	[illegible]
Al	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]			[illegible]	[illegible]	[illegible]
Insolubles, %	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]			[illegible]	nil	[illegible]
Viscosity Change, 100°F, %	[illegible]	[illegible]	nil	[illegible]	nil			[illegible]	[illegible]	[illegible]
Viscosity Change, 210°F, %	[illegible]	[illegible]		[illegible]				[illegible]	[illegible]	[illegible]
Neutralization Number Change	[illegible]	[illegible]		[illegible]				[illegible]	[illegible]	[illegible]
Mean Hertz Load										
Screening Test, kg	[illegible]	[illegible]	[illegible]						[illegible]	[illegible]

[a] Of neutrons product.

[b] [illegible] irradiated in aluminum container open to air, NTS Gamma Facility.

[c] [illegible] irradiated in 316 stainless steel capsule [illegible] air, NTS Gamma Facility.

[d] [illegible] irradiated in heated 316 stainless steel capsule at [illegible] psig under helium, NTS Gamma Facility.

[e] At 4.0°F.

[f] [illegible] irradiated in tin-plated can open to air, NTS Gamma Facility.

[g] Data unclear.

[h] Density at [illegible]°F = [illegible] g/ml.

[i] Minimum Stability (130 hours at 400°F in presence of [illegible] ml of water)

[illegible]

[illegible]

[illegible]

[illegible]

TABLE XXXIX (continued)

PROPERTIES OF FLUIDS BASED ON C_{18}-$_{22}$-ALKYLTRIPHENYL (DISTILLED)

Sample No.	91T-1B-7	91T-1C	94T-1-1	4B98-9-1	94T-1-1C	91T-1B-6	91T-1B-5	91T-4B	94T-1-1B	94T-2-1B
Additive	2% DRPC + 0.001% DC									
Radiation Dosage, 10^{10} ergs/g C	7.9[f]	9.2[b]	1.3[c]	0	0.9[b]	1.9[f]	4.0[f]	9.2[b]	1.3[c]	5.4[c]
Viscosity, cs, °F										
400	1.22[e]	1.4[e]			1.18[e]	1.215[e]	1.24[e]	1.400[e]		
210	5.184	5.475	5.471	5.19	5.47	5.47	5.44	7.78[e]	5.542	5.341
100	45.08	54.74	48.00	50.3	54.2	44.78	51.70	58.53	45.28	47.51
0	3173	4447			2750	3105	4345	6572		
Pour Point, °F	-45	-50		-50	-50	-40	-45	-40		
Flash Point, °F	440	440		440	455	425	450	450		
Spontaneous Ignition Temp., °F	920	1000		800	770	770	770	770		
Foaming										
Volume, ml	50			5	50	5	40	60		
Stability, min	3			0.5	0.8	0.8	0.0	1.8		
Gassing During Irradiation, ml/g	-	-	1.8	-					-	1.2
Acid Number, mg KOH/g	0.04	nil		0.05	nil	nil	0.04	nil		
Vapor Pressure at										
400°F, mm Hg		4.5			3.0			5.3		
500°F, mm Hg		12.1			11.5			24		
Oxidation Corrosion										
Time, hours	48			48 / 72	48 / 48	48	48	48		
Temperature, °F	400			400 / 347	400 / 500	400	400	500		
Weight Change, mg/cm²										
Cu	-			-0.07 / -0.13	-0.34 / 0	-1.36	-1.55	-0.07		
Cu-Be	-			+0.52 / -	-0.40 / -0.04	-0.14	-0.71	+1.54		
Ag	-			+0.48 / 0	-0.22 / 0	0	-0.32	-0.17		
Fe	-0.48			+0.57 / -0.02	-0.03 / -0.58	-0.10	-0.14	-0.03		
Al	-0.14			+0.04 / +0.03	-0.15 / +1.4	-0.14	-0.64	-0.03		
Insolubles, %	trace			2.5 / nil	nil /	1.4	trace	0.5		
Viscosity Change, 100°F, %	-4.50			+.4 / +.1	+.204 / solid	+.047	-	+.250		
Viscosity Change, 210°F, %	+14.7			+29.5 / +10.5	+.150	+.144	+.132	+.124		
Neutralization Number Change	3.5			4.1 / 3.0	7.1	7.5	7.5	4.8		
Mean Hertz Load (screening test), kg	14	14			10	10	10	12		

[a] Of bottoms product.

[b] 600 ml irradiated in aluminum container open to air, MTR Gamma Facility.

[c] 10 ml irradiated in 410 stainless steel capsule under helium, MTR Gamma Facility.

[d] 10 ml irradiated in heated 410 stainless steel capsule at 500°F under helium, MTR Gamma Facility.

[e] at 210°F.

[f] 200 ml irradiated in tin-plated can open to air, MTR Gamma Facility.

[g] Tube broken.

[h] Density at 68°F = 0.91 g/ml.

[i] Hydrolytic Stability (100 hours at 400°F in pressure bomb with 1% water)
Viscosity Change = -0.2% at 100°F and +0.3% at 210°F.
Insolubles = 0; Weight Change of Copper = 0.

[j] Four-ball wear: wear diameter in mm after 1 hours at 167°F
0.47 mm at 5 kg load, 0.55 mm at 15 kg load, [illegible] mm at 40 kg load.

4.2.4 Naphthenic White Oil

Naphthenic white oil was carried along in the work as a reference fluid representing petroleum oil refined as highly as practicable. A secondary objective was to determine the extent to which radiation resistance of such a material could be improved through the use of inhibitors. Test results are shown in Table XL.

The white oil was inferior to the alkyl aromatics discussed in previous sections in two respects: (1) poorer viscosity-temperature properties and (2) poorer oxidation stability when uninhibited. The addition of inhibitors, either selenide or phenolic, allowed satisfactory 400° F oxidation results, but all blends solidified in 500° F tests.

On irradiation, the white oil thickened much faster than the alkyl aromatics and evolved gas at approximately five times the rate. The irradiated fluids solidified in 500° F oxidation tests; 400° F results were less discouraging.

Because of the limited radiation resistance and poor 500° F oxidation stability, naphthenic white oil was not suitable for use as a radiation resistant high temperature hydraulic fluid.

4.2.5 UCON DLB 144E

This polypropylene glycol diether was also evaluated as a possible hydraulic fluid base stock. Work with inhibitors was confined to didodecyl selenide (plus silicone) because polyglycols generally have poor response to phenolic inhibitors[1]. Results are shown in Table XLI.

UCON DLB 144E had excellent viscosity-temperature properties and good lubricity. In oxidation tests, it decreased in viscosity because of depolymerization. Selenide inhibitors increased both radiation and oxidation resistance, allowing an irradiated fluid to pass a 500° F oxidation test without solidification.

However, thermal stability proved to be a major problem. Even at 600° F a marked viscosity decrease was noted; while at 700° F, 10-ml volumes of the irradiated fluids developed very high pressures (in excess of 1000 psi) so that the stainless steel capsules in which the test was being run were ruptured. As a result of this instability, the planned high temperature work was not completed on the polyglycol. Although it had many desirable properties, thermal instability after irradiation eliminates UCON DLB 144E from further consideration as a high temperature hydraulic fluid.

[1] R. G. Larsen and A. Bondi, Ind Eng Chem 42, 2426 (1950).

TABLE VI

PROPERTIES OF FLUIDS BASED ON NAPHTHENIC WHITE OIL

Sample No.	D01259[f]		047-11B		047-6A	047-1-11	047-2-11	047-3-6	047-4-6
Additive	-		-		-	-	-	-	-
Radiation Dosage, 10^{10} ergs/g C	0		0.9[a]		9.2[a]	1.2[b]	6.4[b]	0.12[c]	4.0[c]
Viscosity, cs, °F									
400	1.51		1.44[e]		1.72[e]				
210	7.44		8.59		41.20	9.01	15.73	7.483	18.58
100	70.46		88.5		1010	92.23	232.7	69.97	290.6
0	14,519		17,900		-				
Pour Point, °F	-30		-30		-5				
Flash Point, °F	435		400		395				
Spontaneous Ignition Temp., °F	735		720		740				
Foaming									
Volume, ml			40		680				
Stability, min			0.5		6.5				
Gassing During Irradiation, ml/g	-		-		-	6.4	6.0	0.5	25.2
Acid Number, mg KOH/g	nil		nil		nil				
Vapor Pressure at									
400°F, mm Hg	2.1		7.7		10				
500°F, mm Hg	25		15		20				
Oxidation Corrosion									
Time, hours	48	48	48	48	48				
Temperature, °F	400	500	400	500	500				
Weight Change, mg/cm²									
Cu	-1.22	-1.61	-0.38	-0.11	-0.14				
Cu-Be	-0.10	-0.10	+0.19	0	-0.10				
Fe	-0.26	-0.10	-0.06	0	-0.10				
Pb	-0.03	0	+0.06	0	0				
Al	-0.03	-0.06	-0.03	0	-0.14				
Insolubles, %			0.2						
Viscosity Change, 100°F, %	solid	solid	+502	solid	solid				
Viscosity Change, 210°F, %			+175						
Neutralization Number Change			10.8						
Hydrolytic Stability									
100 hours in pressure bomb with 5% water at 400°F									
Viscosity Change									
At 210°F, %	-0.1				-9.2				
At 100°F, %	-0.2				-9.6				
Insolubles, %	nil				nil				
Copper Wt. Change, mg/cm²	-0.1				0				
Mean Hertz Load (screening test), kg	14		12						

[a] 500 ml irradiated in aluminum container open to air; MTR Canal Source.

[b] 10 ml irradiated in 410 stainless steel capsule under helium; MTR Canal Source.

[c] 10 ml irradiated in heated 410 stainless steel capsule at 400°F under helium; MTR Canal Source.

[d] 200 ml irradiated in tin-plated can open to air; MTR Canal Source.

[e] At 415°F.

[f] Density at 68°F = 0.887.

TABLE XL (continued)

PROPERTIES OF FLUIDS BASED ON NAPHTHENIC WHITE OIL

Sample No.	G14809				G47-11D		G17-7A-5	G17-6B	G47-1-15	G47-2-13	G47-3-7	G47-4-7
Additive							2% $C_{12}Se$					
Radiation Dosage, 10^{10} ergs/g C	0				0.9[a]		4.4[d]	0.5[a]	1.2[b]	4.9[b]	0.16[c]	4.9[c]
Viscosity, cs, °F												
400					1.43[e]		2.10[e]	1.84[e]				
210	7.41				7.87		15.5	12.10	7.99	12.01	7.19	12.57
100	72.0				74.75		221	150	70.44	145.2	64.75	149.5
0					29,600		79,000	43,610				
Pour Point, °F	0				-20		-15	-20				
Flash Point, °F	595				595		400	595				
Spontaneous Ignition Temp., °F	840				840		840	850				
Foaming												
Volume, ml	55				50		85					
Stability, min	0.6				0.8		4					
Gassing During Irradiation, ml/g	-				-		-		8.6	24.1	2.0	21.8
Acid Number, mg KOH/g	nil				nil		0.04	nil				
Vapor Pressure at												
400°F, mm Hg					6.0		9.5					
500°F, mm Hg					18		19					
Oxidation Corrosion												
Time, hours	48	48	48	48	48	48	48	48				
Temperature, °F	400	400	400	500	400	500	400	400				
Weight Change, mg/cm²												
Cu	-	-	-	-	-	-	-	-				
Cu-Be	-	-	-	-	-	-	-	-				
Ag	-	-	-	-	-	-	-	-				
Fe	+0.55	+0.10	+0.03	-0.65	+0.10	-0.55	-0.06	+0.10				
Al	+0.61	+0.15	+0.02	+5.45	+0.26	0	+0.05	-0.15				
Insolubles, %	0.48	0.23	0.09		nil		trace	trace				
Viscosity Change, 100°F, %	+28.5	-	+2.7	solid	+105	solid	+240	+210				
Viscosity Change, 210°F, %	+9.5	+14	+2.0		+87		+100	+86.8				
Neutralization Number Change	12.3	0.6	0.05		4.6		4.0	5.2				
Mean Hertz Load (screening test), kg	18				14		25	14				

[a] 600 ml irradiated in aluminum container open to air; MTR Canal Source.

[b] 10 ml irradiated in 410 stainless steel capsule under helium, MTR Canal Source.

[c] 10 ml irradiated in heated 410 stainless steel capsule at 400°F under helium; MTR Canal Source.

[d] 200 ml irradiated in tin-plated can open to air; MTR Canal Source.

[e] At 415°F.

[f] Density at 68°F = 0.887.

TABLE XL (continued)

PROPERTIES OF FLUIDS BASED ON NAPHTHENIC WHITE OIL

Sample No.	G14810				G47-11C	G17-7A-6	G17-6C	G47-1-12	G47-2-12
Additive					2% DBPC				
Radiation Dosage, 10^{10} ergs/g C	0				0.9[a]	2.1[a]	6.5[a]	1.2[b]	4.9[b]
Viscosity, cs, °F									
400						1.76[e]	1.82[e]		
210	7.41				8.46	11.29	12.58	10.51	12.55
100	72.2				89.3	116.7	165.9	82.55	162.0
0	14,551				22,100	49,600	623.9		
Pour Point, °F	-25				-15	-15	-15		
Flash Point, °F	580				410	395	380		
Spontaneous Ignition Temp., °F	700				710	710	740		
Foaming									
Volume, ml	10				70	50	80		
Stability, min	2.8				1.5	1.5	1.1		
Gassing During Irradiation, ml/g								9.2	25.5
Acid Number, mg KOH/g	nil				nil	0.10	nil		
Vapor Pressure at									
400°F, mm Hg					8.0	8.4	6.0		
500 °F, mm Hg					18	35	13		
Oxidation Corrosion									
Time, hours	48	48	48	48	48	48	48		
Temperature, °F	400	400	400	500	400	400	400		
Weight Change, mg/cm²									
Cu	+0.03	+0.15	+0.35	-0.52	-1.02	-0.87	-0.68		
Cu-Be	+0.03	+0.48	+0.68	0	-0.22	+0.03	+0.03		
Ag	-0.01	+0.71	+0.77	0	-0.35	0	0		
Fe	-0.01	+0.32	+0.58	0	-0.16	+0.10	+0.03		
Al	-0.02	+0.48	+0.68	-0.06	+0.03	+0.03	0		
Insolubles, %	nil	1.7	-		nil	trace	trace		
Viscosity Change, 100°F, %	-	+27.6	+36.7	solid	+2500	+241	+258		
Viscosity Change, 210°F, %	+4.6	+11.5	+9.1		+1300	+83.3	+108		
Neutralization Number Change	0.03	3.3	20.2		15.8	6.2	6.5		
Mean Hertz Load (screening test), kg					14	22	23		

[a] 600 ml irradiated in aluminum container open to air; MTR Canal Source.

[b] 10 ml irradiated in 410 stainless steel capsule under helium, MTR Canal Source.

[c] 10 ml irradiated in heated 410 stainless steel capsule at 400°F under helium; MTR Canal Source.

[d] 200 ml irradiated in tin-plated can open to air; MTR Canal Source.

[e] At 415°F.

[f] Density at 68°F = 0.887.

TABLE XLI

PROPERTIES OF FLUIDS BASED ON UCON DLB 144E

Sample No.	014580[f]		047-12D	047-1-14	047-2-14	4898-9-3		047-13A	017-7A-8	017-6A	017-7A-7	047-1-15	047-2-15
Additive	None					2% $C_{18}Se$ + 0.001% DC							
Radiation Dosage, 10^{10} ergs/g C	0		0.9[a]	1.2[b]	4.9[b]	0		0.9[b]	5.0[c]	6.4[a]	7.1[c]	1.2[b]	4.9[b]
Viscosity, cs, °F													
400	2.12							1.93[d]	3.58[e]				
210	7.098		8.34	8.457	17.48	7.00		7.37	8.62	14.63	11.20	7.77	10.75
100	30.50		39.2	40.24	112.5	29.9		35.0	42.92	90.61	62.24	35.36	63.28
0	766		1210						1841	4775	2695		
-40	16,550		23,000						solid	145,330	72,113		
Pour Point, °F	-65		<-60			+30		-35	-50	-40	-50		
Flash Point, COC, °F	455		390			475		380	370	310	375		
Spontaneous Ignition Temp., °F	770		730			930		960	920	920	920		
Bulk Modulus (adiabatic), psi													
at 0 psi and 77°F	232,000									249,000			
Foaming													
Volume, ml			40			15		65	80	-	95		
Stability, min			0.5			0.3		1.1	3.5	-	3.3		
Gassing During Irradiation, ml/g				1.0	16.1							5.2	14.4
Acid Number, mg KOH/g	0.10		nil			0.04		nil	0.23	nil	0.17		
Vapor Pressure at													
400°F, mm Hg	7.8							5.2	7.1	-			
500°F, mm Hg	-							15	17	-			
Oxidation Corrosion													
Time, hours	48	48	48			48	48	48	48	48	48		
Temperature, °F	400	500	500			400	500	500	400	400	400		
Weight Change, mg/cm²													
Cu	-0.03	+0.06	0										
Cu-Be	0	+0.10	0										
Ag	0.10	-0.03	0										
Fe	-0.16	-1.54	0			+0.02	-0.20	-1.54	-0.22	+0.26	0		
Al	-0.19	0	0			0	0	0	-0.13	0	-0.03		
Insolubles, %	trace	0.4				0.12	0.9	1.6	trace	trace	trace		
Viscosity Change, 100°F, %	-19.4	-18.0	solid			-0.9	+33.0	-39.8	-28.8	-49.9	-39.4		
Viscosity Change, 210°F, %	-34.8	-24.2				-5.9	+3.0	-33.6	-33.3	-50.2	+36.5		
Neutralization Number Change	15.4	3.2				1.7	8.6	0.4	5.9	6.2	6.3		
Hydrolytic Stability													
100 hours in pressure bomb with 6% water at 400°F													
Viscosity Change,													
At 210°F, %	-2.8								-29.9		-49.9		
At 100°F, %	+3.0								-		-		
Insolubles, %	0.01								0.02		0.06		
Copper Weight Change, mg/cm²	-0.1								-		-		
Four-Ball Wear, mm													
2 Hours, 160°F, 4 Load	0.30												
10 Load	0.34												
40 Load	0.52												
Mean Hertz Load (screening test), kg	24		23			27		32	30	31	30		

[a] 600 ml irradiated in aluminum container open to air, MTR Canal Source.

[b] 10 ml irradiated in sealed 410 stainless steel capsule under helium; MTR Canal Source.

[c] 200 ml irradiated in tin-plated can open to air, MTR Canal Source.

[d] At 415°F

[e] At 414°F

[f] Density at 68°F = 0.973 g/ml.

4.2.6 Silicones

Silicone fluids combine excellent viscosity-temperature properties with low volatility and good oxidation resistance. They are among the organic compounds which are least resistant to radiation[1]. Aromatic rings impart radiation resistance to silicones as well as to hydrocarbons[2]. A series of nine silicones of varying phenyl content was irradiated in the MTR Gamma Source to investigate this further. Results are shown in Table XLII.

The Dow Corning 200, 4209, and the three Linde silicones were aliphatic. DC 703, 550, 710, and XF-4320 were increasingly aromatic. The experimental XF-4320 fluid remained fluid and showed low gassing (2.4 ml/g) at 9×10^{10} ergs/g C. This stability was above that of previously tested silicones. The large viscosity decrease of DC 4209 was reported previously and was probably due to depolymerization of a high molecular weight component.

4.3 Evaluation of Additives

4.3.1 Oxidation Inhibitors

As the C_{14-16}-alkyl diphenyl ether was the most promising base stock available, most evaluations of oxidation inhibitors were carried out in it. Results of a series of 400°F oxidation and corrosion tests with sulfide and selenide inhibitors are shown in Table XLIII and with amine and phenolic inhibitors in Table XLIV.

Although experience has indicated that results from this test are rather erratic, the inhibitors most effective in preventing viscosity change can be placed in the following order of decreasing effectiveness in the alkyl aromatic base oil:

Morpholine diselenide

Di-β-naphthyl-p-phenylenediamine

Phenothiazine

Dioctyl selenide

Bis(tridecyl) selenide

Dibenzyl selenide

Didodecyl selenide

Phenyl-α-naphthylamine

Phenolic inhibitors and aryl selenides, which are relatively ineffective, are not listed.

[1] R. O. Bolt and J. G. Carroll, "The Radiolysis and Radiolytic Oxidation of Lubricants," Ind Eng Chem 50, No. 2, February 1958.

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

TABLE XLII

INSPECTIONS OF IRRADIATED[a] SILICONES

Identity	Capsule No. G-100-	Gamma[a] Dosage, 10^{10} ergs/g C	Viscosity, cs 100°F	Viscosity, cs 210°F	Gas Evolved psi	Gas Evolved ml of Gas/g sample (STP)	Color	Texture	Reference
Dow Corning 200/50 cs	-		39.01	15.92					AA2895
	13	0.2[b]			-	-	Clear white	Rubbery	
	16	4.5			155	10	Clear white	Rubbery	
	15	5.1			300	22	Clear white	Rubbery	
	14	8.5			-	-	Clear white	Brittle	
Dow Corning 550	-		68.48	17.41			Clear		BB170
	36	0.5	110.3	26.2	27	0.9	Lt amber		
	35	4.5	190.2	44.88	36	1.5	Lt amber		
	34	5.1			46	2.1	Amber	Gel	
	33	8.5			73	4.2	Amber	Rubbery	
Dow Corning 703			25.81	5.44					FF1116
	17	0.5[b]	218.4	34.96	36	1.5			
	20	5.1	288.9	44.4	35	1.9	Amber		
	19	8.5			37	2.1	Amber	Rubbery	
	18	9.0			54	2.7	Amber	Rubbery	
Dow Corning 710	-		247.3	34.95					HH94
	44	0.5	397.3	57.64	27	0.8	Lt amber		
	43	4.5	626.4	74.73	22	0.5	Lt amber		
	42	8.5			41	1.7	Amber	(Soft) Rubbery	
	41	9.0			59	3	Amber	(Hard) Rubbery	
Dow Corning 4209			72.55	30.05					BB170
	40	4.5	11.87	4.45	173	14	Clear white		
	39	5.1	29.08	9.35	287	23	Clear white		
	38	8.5			365	29	Lt amber	Gel	
	33	8.5			593	59	Amber	Rubbery	
Dow Corning XF-4320			44.84	10.47					A585-25
	48	4.5	73.85	16.03	32	1.2			
	47	5.1	118.0	23.49	38	1.7			
	46	8.5	292.9	52.26	50	2.4	Amber		
	45	9.0			62	3.2	Brown	Rubbery	
Linde-X-520			477.1	77.38					1
	24	0.5			82	5	Clear white	Rubbery; "froth" on top	
	21	3.4			292	19	Clear white	Rubbery; white crystals on top	
	22	5.8			383	26	Clear white	Rubbery; white crystals on top	
	23	9.0			328	22	Clear white	Rubbery; white crystals on top	
Linde-X-522			50.07	13.01					1
	28	0.5	113.6	22.28	76	4.6			
	25	3.4			283	20	Clear white	Rubbery; "froth" on top	
	26	5.8			346	24	Amber	Rubbery	
	27	9.0			375	26	Clear white	Rubbery	
Linde-X-525			69.38	15.57					1
	32	0.5	150.0	30.07	73	4.2			
	29	3.4			255	18	Amber	Rubbery; "froth" on top	
	30	5.8			336	24	OK amber	Rubbery	
	31	9.0			346	24	OK amber	Rubbery	

[a] In 10-ml quantities in 410 stainless steel capsule sealed under helium; MTR Canal Source - Series G-100 (17-1)

[b] Approximate; other dosages ± 10% with 95% confidence limits.

TABLE XLIII

FLUIDS BASED ON C_{14+16}-ALKYL DIPHENYL ETHER
WITH SELENIDE AND SULFIDE INHIBITORS

Sample No.	4946-5-30	4946-4-31	4946-4-32	4946-4-33	4946-4-34	4946-5-38	4946-6-47	4946-6-48
Additive	3.86 C_8Se	5.26 $C_{12}Se$	3.30 BzSe	2.95 ØSe	2.09 Morpholine Diselenide	5.63 $C_{13}Se$	0.53 $C_{12}Se$	0.30 ØSe
Viscosity, cs, °F								
210	5.541	4.666	4.639	4.606	4.801	4.712	4.796	4.801
100	24.11	24.88	25.16	24.76	26.95	25.81	26.52	26.86
Spontaneous Ignition Temp., °F				1020	890		920	860
Oxidation Corrosion								
Time, hours	48	48	48	48	48	48	48	48
Temperature, °F	400	400	400	400	400	400	400	400
Weight Change, mg/cm²								
Cu	-	-	-	-1.42				-3.45
Cu-Be	-	-	-	+0.58				-1.58
Ag	-	-	-	+1.19				-0.10
Fe	-	-	+0.16	+0.45	-2.9	0	+0.07	-0.10
Al	+0.19	+0.16	+0.16	+0.55	+0.32	0	+0.10	-0.48
Insolubles, %	+0.13	+0.10	0.82	1.5	0.64	2.3	0.1	3.1
Viscosity Change, 100°F, %	0.59	0.29	+24.8	+36.5	+6.5	+23.2	+44.8	-
Viscosity Change, 210°F, %	+20.3	+29.4	+12.7	+19.8	+3.7	+11.2	+23.9	-
Neutralization Number Change	+11.4	+15.7	3.7	6.9	0.36	2.59	3.78	-
	0.63	3.1						

Sample No.	-	-	4946-4-35	4946-4-25	4946-5-36	4946-5-37
Additive	2 $C_{12}Se$	2 ØSe	Sat. Phenoselenazine	3.41 $ØS_2$	2.35 ØS	2.71 BzS
Viscosity, cs, °F						
210	4.763	4.658	4.855	4.599	4.004	4.647
100	26.02	25.11	27.02	24.70	24.81	25.22
0	3965					
Spontaneous Ignition Temp., °F	1030		950			
Oxidation Corrosion						
Time, hours	48	48 | 48	48	48	48	48
Temperature, °F	400	400 | 400	400	400	400	400
Weight Change, mg/cm²						
Cu	-	+6.42 | -	-4.0	-	-4.35	-
Cu-Be	-	-0.62 | -	+2.9	-	-4.70	-
Ag	-	+0.67 | -	+2.1	-	0	-
Fe	-0.01	+0.34 | -0.10	+0.52	+0.13	-1.13	+0.32
Al	0	+0.46 | -0.13	+0.80	+0.10	+0.06	+0.16
Insolubles, %	0.04	2.20	2.20	0.61	-	5.8
Viscosity Change, 100°F, %	+11.5	+32.1	-32.1	+83.4	+27.3	+38.3
Viscosity Change, 210°F, %	+22.7	+18.4	+18.4	+46.4	+29.0	+20.5
Neutralization Number Change	1.74	4.1	4.1	3.32	3.21	1.42

TABLE XLIV

FLUIDS BASED ON C_{14-18}-ALKYL DIPHENYL ETHER WITH AMINE AND PHENOLIC INHIBITORS

Sample No.	4946-6-49	4946-6-50	4946-6-51	4946-12-1
Additive	1% Phenyl-α-naphthylamine	1% Phenothiazine	1% Di-β-naphthyl-p-phenylenediamine	1% Triphenylamine
Viscosity, cs, °F				
210	4.807	4.832	4.826	5.049
100	26.86	26.96	26.87	26.90
Spontaneous Ignition Temp., °F	840			
Oxidation Corrosion				
Time, hours	48	48	48	48
Temperature, °F	400	400	400	400
Weight Change, mg/cm²				
Cu	-0.61	+0.48	-2.1	-0.58
Cu-Be	+0.16	+0.52	-0.74	-0.26
Ag	+0.19	+0.94	0	-0.06
Fe	+0.10	+0.68	0	-0.06
Al	+0.16	+0.87	0	0
Insolubles, %	1.92	2.55	5.62	nil
Viscosity Change, 100°F, %	+29.6	+15.0	+12.0	+110
Viscosity Change, 210°F, %	+15.3	+10.0	-2.6	+47.8
Neutralization Number Change	5.3	7.2	4.81	12.1

Sample No.	4946-2-11	4946-3-12	4946-3-14	4946-3-15	-	4946-3-13	4946-12-7
Additive	2 AN-1	2 AN-2	2 DBPC	2 A2246	2 DBPC	2 AN-3	2 DBPC + 1 ØSe
Viscosity, cs, °F							
210	4.726	4.931	4.245	4.928	4.737	4.811	4.689
100	26.09	28.17	26.55	28.50	26.48	27.12	25.69
Spontaneous Ignition Temp., °F					810	820	
Oxidation Corrosion							
Time, hours	48	48		48	48	48	48
Temperature, °F	400	400		400	400	400	400
Weight Change, mg/cm²							
Cu	-4.0	-3.54		+0.39	-1.69	-1.4	-3.59
Cu-Be	-1.0	-1.3		-0.23	-0.49	-0.10	-1.94
Ag	-0.03	-0.23		+0.13	-0.06	+0.90	-0.23
Fe	+0.26	0		+0.13	+0.03	+0.77	-0.7
Al	0	-0.06		+0.06	-0.05	+0.71	+0.7
Insolubles, %	0.075	1.47		2.59	nil	5.2	0.17
Viscosity Change, 100°F, %	+80.2	+374.0		+47.0	+47.3	+46.8	+56.9
Viscosity Change, 210°F, %	+41.7	+84.6		+22.2	+27.4	+23.9	+32.9
Neutralization Number Change	3.0			8.5	3.4	8.5	5.5

No additive yielded a completely satisfactory oxidation test result; insolubles and neutralization number were generally high. Copper and silver alloys were omitted from most of the tests containing selenide inhibitors. It was observed that the insolubles from many of the tests with selenide inhibitors had the characteristic reddish color of selenium. To determine the extent to which the inhibitor was producing insolubles, the solids from several oxidation and corrosion tests with selenide inhibitors were analyzed for selenium. Results are in Table XLV.

Table XLV

Analysis of Insolubles from Corrosion Tests

% Inhibitor	Inhibitor	% Selenium in Insolubles
5.63[a]	Bis(tridecyl) Selenide	67
5.26	Didodecyl Selenide	68
2.09	Dimorpholine Diselenide	51
3.86	Dioctyl Selenide	85
Sat. *	Phenoselenazine	3.27
2.55	Diphenyl Selenide	1.06
0.26*	Diphenyl Selenide	0.15

[a] All blends but those asterisked (*) were made to have 1% selenium content; this resulted in different inhibitor concentrations.

The insolubles thus tended to have a high selenium content where the selenium is attached to nitrogen or to an aliphatic carbon atom, the value was much lower if the selenium was part of an aromatic heterocyclic system or was connected to a benzene ring. The former were unfortunately the more effective, and the latter the less effective oxidation inhibitors.

Tables XLIII and XLIV (pages 93 and 94) also show the effect of selenide inhibitors in increasing the spontaneous ignition temperatures of an organic liquid. The 800° F value of the base stock was raised to 1000° F by using alkyl or aryl selenides. Typical phenolic and amine inhibitors had no such effect.

A few additional 400° F oxidation and corrosion tests were performed in other base stocks as shown in Table XLVI. Here a selenide was superior to phenolic inhibitors in naphthenic white oil, as it was in the dipnenyl ether. Both the C_{16-18}-alkyldiphenylmethane and distilled C_{14-16}-alkyl diphenyl ether showed good oxidation stability at 400° F. Dibenzyl selenide preserved the oxidation stability of a polyglycol diether at 347° F following irradiation to 12.5×10^{10} ergs/g C.

TABLE XLVI

MISCELLANEOUS OXIDATION AND CORROSION TESTS

Base Stock	Dodecyl Diphenyl Ether	Naphthenic White Oil					C_{16}-$_{18}$-Alkyl Diphenyl Ether (Dist.)	C_{16}-$_{18}$-Alkyl Diphenylmethane	Polyglycol Diether (144)	Same as 5581-6-5[a]
Additive	2% AN-3	2% $C_{16}Se$	2% AN-1	2% AN-2	2% AN-3	2% A2246	2% DBPC	2% DBPC	5% H_2Se	-
Sample No.	4P50-55-3	4946-3-17	4946-3-18	4946-3-19	4946-3-20	4946-3-21	5468-56-1	5468-56-2	5581-6-5	2111A
Temperature, °F	400	400	400	400	400	400	400	400	347	347
Time, hours	48	48	48	48	48	48	48	48	72	72
Metal Weight Change, mg/cm²										
Cu	-2.03	-	+0.03	+0.84	+0.19	+0.28	-0.01	-0.02	-	-
Pb-Cu	+0.02	-	+0.45	+1.16	+0.45	+0.45	+0.00	+0.00	-	-
Ag	+0.43	-	+0.58	+1.26	+0.42	+0.59	+0.03	-0.05	b	c
Fe	+0.40	-0.13	+0.03	+1.20	+0.42	+0.81	+0.03	+0.03	+0.19	+0.05
Al	+0.59	-0.10	+0.52	+1.29	+0.05	+0.42	0	-0.02	+0.14	+0.05
Insolubles, %	0.16	1.0	2.65	5.0	3.55	0.62	nil	nil	nil	nil
Viscosity Change, %										
At 100°F	+45.6	+12.8	+24.9	+57.0	+13.9	+102	+2.5	+5.2	+10.8	-3.6
At 210°F	+23.7	+5.6	+11.3	+24.2	+10.2	+31.5	+1.7	+3.3	-	-
Neutralization Number Change	6.6	1.3	2.9	4.3	3.1	5.1	0.26	0.03	8.4	3.8

[a] Irradiated to 12.5 x 10^{10} ergs/g C.

[b] Magnesium +0.10 mg/cm²

[c] Magnesium: +0.02 mg/cm²

Although didodecyl selenide is commercially available, its relatively high melting point often causes high pour points in blends containing it. Therefore, bis(tridecyl) selenide (see Appendix V) was extensively used. A blend of C_{14-16}-alkyl diphenyl ether with Polybutene 128 and oxidation inhibitor was one of the more interesting fluids. Varying concentrations of bis(tridecyl) selenide were added and the nonirradiated blends tested in the 500°F oxidation and corrosion test. Results are shown in Table XLVII.

No advantage was gained by increasing selenide concentration above 0.5%. The apparent anomaly at 2% probably resulted from use of a different batch of bis(tridecyl) selenide for this blend. Results are considered good in view of the severity of the test.

Several other oxidation inhibitors which had been tested previously in the C_{14-16}-alkyl diphenyl ether base stock were also tested in the ether-polybutene blends. A comparison was made between bis(tridecyl) selenide, DBPC, phenothiazine, di-β-naphthyl-p-phenylenediamine, and a mixture of the latter with diphenyl selenide. Results are given in Table XLVIII.

The bis(tridecyl) selenide appeared superior to the other inhibitors in ability to maintain a fluid condition during high temperature oxidation tests. DBPC was the next most effective single inhibitor while DNPD and phenothiazine were much less effective. The phenothiazine samples solidified in all 500°F tests. Addition of diphenyl selenide with DNPD to the blend gave stability comparable to DBPC. However, the blends are highly corrosive to copper and silver despite the aromatic attachment of the selenium.

The extent to which oxidation inhibitors retain their beneficial effect following irradiation may determine their usefulness in radiation resistant formulations. Table XLIX shows the effect of irradiation at two dosage levels on oxidation life in a Dornte-type[1] test at 400°F of four base oils with and without inhibitors. Neither C_{16-18}-alkylbiphenyl, C_{14-16}-alkyl diphenyl ether, nor naphthenic white oil had significant oxidation life without inhibitors. With didodecyl selenide or DBPC marked increases in stable life were shown. This increase was retained to varing degrees after irradiation to 10^{10} ergs/g C. The C_{16-18}-alkylbiphenyl retained most of its initial stability, C_{14-16}-alkyl diphenyl ether slightly less than half, and the white oil considerably less.

Even after irradiation to 10×10^{10} ergs/g C, the inhibited oils still had greater stability than did the unirradiated base stock. The UCON DLB 144E, which contained phenyl-α-naphthylamine as manufactured, showed a reduction in stability after irradiation to 10^{10} ergs/g C. With didodecyl selenide added, sensitivity to irradiation was reduced. These data are highly significant. They show that inhibitors are beneficial to oxidation stability, both before and after exposure to nuclear radiation.

[1] G. H. Denison and P. C. Condit, Ind Eng Chem 41, 944 (1949).

TABLE XLVII

EFFECT OF SELENIDE CONCENTRATION ON 500°F OXIDATION AND CORROSION TESTS
86% C_{14-18}-ALKYL DIPHENYL ETHER +14% PB 128 WITH VARYING SELENIDE CONCENTRATIONS

Sample No.	5263-5-7	5263-5-6	5263-5-5	5263-5-4	4946-16	5263-5-3
% Bis(tridecyl) Selenide	nil	0.1	0.5	1.0	2.0	5.0
Metal Weight Change, mg/cm²						
Steel	-0.26	-0.10	0	0	+0.13	+0.10
Aluminum	0	0	-0.10	-0.06	+0.06	0
Viscosity Change, %						
At 100°F	+322	+148	+43	+39	+78	+47
At 210°F	+97	+48	+9.9	+8.0	+20.5	+9.5
Insolubles, %	4.6	2.8	0.4	0.4	0.4	0.4
Neutralization No.	6.30	6.13	4.57	4.88	5.34	4.48

TABLE XLVIII

PROPERTIES OF FLUIDS BASED ON C_{14-18}-ALKYL DIPHENYL ETHER, 1% POLYBUTENE 128, AND 0.001% DIMETHYL SILICONE

Sample No.	4946-2-4		G117-1D		947-8-24	947-1-38	947-2-38	4946-23-1		947-4-1			947-1-17	947-2-17	4946-23-13	947-3-7
Oxidation Inhibitor	2% $C_{13}Se$							2% DHPC							0.5% Phenothiazine	
Radiation Dosage, 10^{10} ergs x C	0		1.0[d]		5.5[a]	0.6[b]	2.6[b]	0		0.7[a]	3.1[a]		1.7[b]	5.7[b]	0	0.6[a]
Viscosity, cs, °F																
210	12.06		9.84		10.26	9.70	9.12	12.07		9.624	9.454		9.057	9.503	12.28	9.75
100	74.29		70.18		82.6	69.7	67.2	96.54		69.87	74.94		70.12	72.50	89.75	62.49
0	4867		4155		6280					4476	4602					4804
Pour Point, °F	-20		-25		-35			-25		-30	-30				-25	-20
Flash Point, COC, °F	480		450		450			400		465	465				470	470
Spontaneous Ignition Temp., °F	1000		990		1010			820		780	780				840	840
Foaming																
Volume, ml	175		180		250			25							25	
Stability, min	1		0.0		5			0.7							0.5	
Gassing During Irradiation, ml/g						1.7	4.0						1.7	4.7		
Density at 68°F, g/ml								0.910							0.901	
Acid Number, mg KOH/g	0.17		0.01		nil			0.54		nil	nil				0.27	nil
Vapor Pressure at																
400°F, mm Hg	5.8		5.1					8.7								
500°F, mm Hg	14.2		25					23								
Oxidation Corrosion																
Time, hours	48	48	48	48	48			48	48	48	48	48			48	48
Temperature, °F	400	500	400	500	500			400	500	400	400	500			500	400
Wt. Change, mg/cm²																
Cu					-			-1.57							-0.16	-0.46
Cu-Be					-			-0.29							+0.16	-0.10
Ag					-			-0.07							-0.16	-0.13
Fe	-0.61	+0.13	0	-0.52	-0.43			0	-0.15	-0.15	+0.22	0			-1.68	+0.29
Al	-0.19	+0.04	+0.16	+0.13	+0.32			-0.18	+0.24	+0.24	+0.14	-0.04			-0.15	+0.38
Insolubles, %	nil	0.5	nil	1.0	2.5			trace	0.5	nil	nil	2.5				nil
Viscosity Change, 100°F, %	+9.0	+78.0	+44.0	+44.0	+17			+40.4	+154	+42.1	+115	+114			+116	+42.5
Viscosity Change, 210°F, %	-0.8	+20.5	+14.5	+38	+41			+24.4	+25	+42.4	+50.4	+129				+7.5
Neut. Number Change	2.5	5.5	0.0	5.0	3.4			5.54	5.5	78	6.07	6.6				1.2

[a] 200 ml irradiated in tin-plated can open to air, MTR Canal Source.

[b] 10 ml irradiated in stainless steel capsule under helium, MTR Canal Source.

[c] Solubility less than 1%.

[d] 500 ml irradiated in aluminum container open to air, MTR Canal Source.

TABLE XLVIII (continued)

PROPERTIES OF FLUIDS BASED ON C_{14-18}-ALKYL DIPHENYL ETHER, 14% POLYBUTENE 128, AND 0.001% DIMETHYL SILICONE

Sample No.	G67-4-7		G67-1-23	G67-2-23	4946-23-6	G67-3-5	G67-4-5		G67-1-21	G67-2-21	4946-23-7	G67-3-6	G67-4-6		G67-1-22	G67-2-22
Oxidation Inhibitor	0.5% Phenothiazine				Sat. DNPD						Sat. DNPD + 2% ØSe					
Radiation Dosage, 10^{10} ergs/g C	2.7[a]		1.3[b]	5.7[b]	0	1.1[a]	4.9[a]		1.3[b]	5.7[b]	0	1.0[a]	4.0[a]		1.3[b]	5.7[b]
Viscosity, cs, °F																
210	9.611		9.689	9.763	12.22	10.05	10.96		9.950	10.43	12.30	10.41	8.987		9.695	8.726
100	69.48		70.46	75.71	87.41	72.97	81.45		72.99	81.81	87.14		64.90		69.20	64.44
0	4351					4479	6010					4493	4295			
Pour Point, °F	-25				-20	-30	-30				-30	-20	-30			
Flash Point, COC, °F	475				455	460	440				450	430	460			
Spontaneous Ignition Temp., °F	800				820	780	800				920	980	980			
Foaming																
Volume, ml					50						65					
Stability, min					0.5						0.7					
Gassing During Irradiation, ml/g			1.7	1.8					1.8	4.6					1.7	4.5
Density at 68°F, g/ml					0.9305						0.935					
Acid Number, mg KOH/g	nil				0.20	nil	nil				0.23	nil	nil			
Vapor Pressure at																
400°F, mm Hg					8.1						7.2					
500°F, mm Hg					25						27					
Oxidation Corrosion																
Time, hours	48	48			48	48	48	48			48	48	48	48		
Temperature, °F	400	500			500	400	400	500			500	400	400	500		
Wt. Change, mg/cm²																
Cu	-2.72	-1.0			-0.78	-2.50	-1.02	-0.29			-	-8.56	-16.94	-		
Cu-Be	-1.44	-1.74			+1.16	+1.94	-0.67	+0.93			-	-1.50	-0.10	-		
Ag	-0.32	-0.23			-0.23	+0.79	-0.32	-0.13			-	-1.06	-2.27	-		
Fe	-0.13	-0.61			-0.54	+0.13	-0.19	-0.13			-0.10	+0.19	-0.03	-0.06		
Al	-0.03	-0.06			-0.06	+0.29	-0.06	-0.03			-0.06	+0.42	-0.26	-0.13		
Insolubles, %	nil					nil	nil	2.3			2.7	nil	nil	3.6		
Viscosity Change, 100°F, %	+147	solid			solid	+168	+157	+243			+109	-	+101	+305		
Viscosity Change, 210°F, %	+79.9					+12	+79.2	+107			+35	+21.3	+49.2	+122		
Neut. Number Change	5.4					6.6	7.2	5.9			5.9	0.66	6.1	5.7		

[a] 200 ml irradiated in tin-plated can open to air, MTR Canal Source.

[b] 10 ml irradiated in stainless steel capsule under helium, MTR Canal Source.

[c] Solubility less than 1%.

[d] 600 ml irradiated in aluminum container open to air, MTR Canal Source.

TABLE XLIX

EFFECT OF IRRADIATION ON OXIDATION STABILITY
DORNTE TEST - UNCATALYZED OXYGEN ABSORPTION AT 400°F

Base Stock	Additives	Hours to Absorb 1000 ml O_2/100 g Oil After Radiation Dosage of		
		0	10^{10}	10×10^{10} ergs/g C
C_{18-18}-Alkylbiphenyl (dist)	None	0.2	-	0.2
	2% $C_{12}Se$	3.7	4.0	1.3
	2% DBPC	2.2	1.8	0.6
C_{14-18}-Alkyl Diphenyl Ether	None	0.2	-	0.2
	2% $C_{12}Se$	6.0	2.9	0.8
	2% DBPC	4.0	1.6	0.3
Ucon DLB 144E[a]	None	1.7	0.3	-
	2% $C_{12}Se$	1.1	0.8	-
Naphthenic White Oil	None	0.1	-	0.1
	2% $C_{12}Se$	6.1	1.2	0.4

[a] Contains phenyl-α-naphthylamine as manufactured.

4.3.2 Viscosity Index Improvers

Because of the wide temperature range over which an hydraulic fluid is intended to operate, a flat viscosity-temperature curve is desirable, i.e., minimum change of viscosity with temperature. Although alkyl aromatics have viscosity-temperature properties comparable to the best petroleum oils, they are considerably poorer than the best synthetics in this respect. Since the target properties are based on the latter, V.I. improvers may be necessary in the alkyl aromatics to obtain an adequate range of operating temperatures. Previous data[1] showed that Polybutene 128, a low molecular weight polyisobutylene, possessed better radiation stability than other V.I. improvers tested.

In 1957 several additional commercially available V.I. improvers were investigated, e.g., polybutenes such as Vistanex LM-MH and LM-MS and Paratone N and the "Parapols" (styrene-isobutylene copolymers). (The APAMS and APEMS discussed in Section 2, page 39, were developed late in the contract year. They were not available in time for formulation and testing of hydraulic fluids.) Relative shear stability tests were performed by the sonic oscillator method (see Appendix I) on inhibited alkyl diphenyl ether-polymer blends having the same initial viscosities at 210° F. Results are shown in Figure 12. The low molecular weight Polybutene 128 was the most stable polymer in this test. The high molecular weight Parapols, which were not originally intended for V.I. improver use, were severely degraded.

Several similar blends were evaluated before and after irradiation. Results are shown in Table L. The higher molecular weight polybutenes, Vistanex and Paratone N, produced blends with better viscosity-temperature properties than Polybutene 128. However, blends with the latter retained much more of their initial viscosity as shown in Figure 13. The Parapols were about as radiation stable as were the higher molecular weight polybutenes. The comparative stability of the Parapols to radiation was much better than their resistance to shear. The presence of aromatics in these doubtlessly enhanced radiation stability. Within the reproducibility of the test, the type of V.I. improver used, whether polybutene or Parapol, did not appear to affect the 400° F oxidation stability following irradiation as shown in Table L.

4.3.3 Radiation Damage Inhibitors

Effects of inhibitors on radiation stability were investigated in at least two base stocks, C_{14-16}-alkyl diphenyl ether and an aliphatic material, e.g., naphthenic white oil, 10-C insulating oil, or hexa(2-ethylbutoxy)-disiloxane. Results for selenide inhibitors are shown in Table LI and for sulfur, phenolic, and amine inhibitors in Table LII.

[1] "Effects of Radiation on Aircraft Lubricants and Fuels," (California Research 1956 Summary Report on Contract AF 33(616)-3184) WADC Technical Report 56-646.

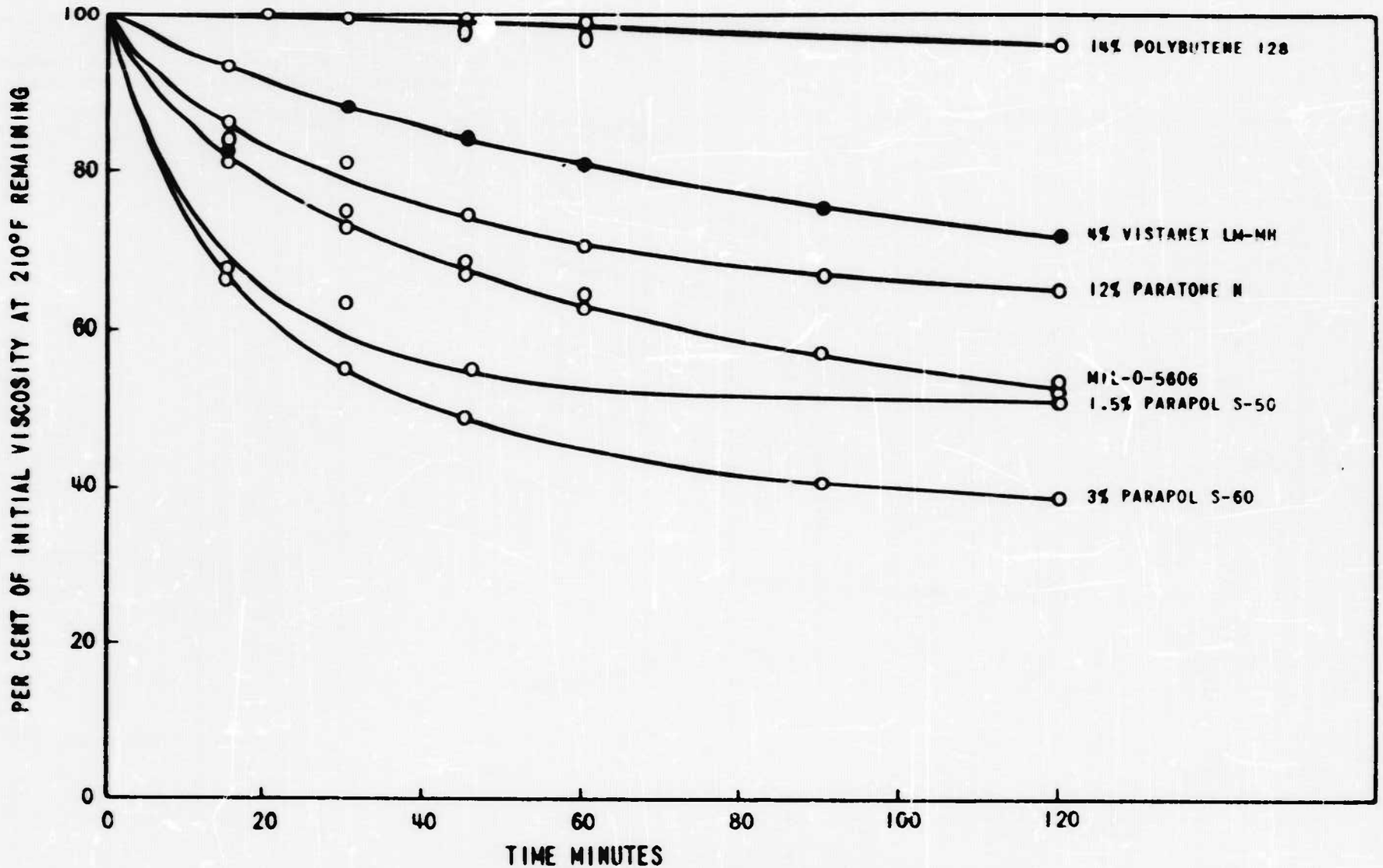


FIG. 12 - SHEAR STABILITY IN SONIC OSCILLATOR TEST

C_{14-16}-ALKYL DIPHENYL ETHER CONTAINING 2% BIS(TRIDECYL) SELENIDE AND 0.001% DIMETHYL SILICONE

TABLE 1

PROPERTIES OF FLUIDS BASED ON C_{14-18}-ALKYL DIPHENYL ETHER
2% BIS(TRIDECYL) SELENIDE, AND 0.001% DIMETHYL SILICONE

Sample No.	4946-2-4		G117-1D		G47-8-44	G47-1-38	G47-2-38	4946-23-3	G67-3-2	G67-4-2	G67-1-18	G67-2-18	4946-2-9	G47-5-1	G47-6-1
VI Improver	14% PH 128							5% Viatanex LM-MS					4% Viatanex LM-ML		
Radiation Dosage, 10^{10} ergs/g C	0		1.0[d]		5.3[a]	0.6[b]	2.6[b]	0	1.0[a]	4.4[a]	1.3[b]	5.7[b]	0	0.7[b]	3.0[b]
Viscosity, cs, °F															
400	2.38[c]		2.01[c]		1.96[c]								2.67[c]		
210	12.00		9.80		10.20	9.70	9.12	12.37	7.10	7.95	7.26	7.50	11.85	7.51	6.95
100	85.26		70.18		82.6	69.7	67.2	75.97	44.38	52.2	45.23	50.81	70.80	45.15	45.16
0	4857		4153		6280				1975	3158			2946		
Pour Point, °F	-20		-25		-35			-20	-20	-30					
Flash Point, COC, °F	480		460		430			465	465	430					
Spontaneous Ignition Temp., °F	1000		980		1010			1020	1020	990			1020		
Foaming															
Volume, ml	170		180		250			150							
Stability, min	1		0.9		5			0.75							
Gassing During Irradiation, ml/ml						1.7	4.0				1.7	4.2		1.0	2.1
Density at 68°F, g/ml								0.932							
Acid Number, mg KOH/g	0.17		0.01		nil			0.20	nil	nil					
Vapor Pressure at															
400°F, mm Hg	3.8		3.1					9.7							
500°F, mm Hg	14.2		25					21							
Oxidation Corrosion															
Time, hours	48	48	48	48	48				48	48					
Temperature, °F	400	500	400	500	500				400	400					
Wt. Change, mg/cm²															
Cu	-								-	-					
Cu-Be	-								-	-					
Ag	-								-	-					
Fe	-0.61	+0.13	0	+0.39	-0.48				+0.06	-0.06					
Al	-0.10	+0.06	+0.10	+0.13	+0.32				+0.26	-0.22					
Insolubles, %	nil	0.5	nil	1.0	0.5				nil	nil					
Viscosity Change, 100°F, %	+5.0	+78	+44.0	+84	+172				+44.5	+71.6					
Viscosity Change, 210°F, %	-0.8	+20.5	+19.5	+38	+61				+18.6	+31.6					
Neut. Number Change	2.3	5.3	0.6	5.0	3.4				4.8	28					

[a] 200 ml irradiated in tin-lined cans open to air, MTR Canal Source.
[b] 10 ml irradiated in stainless steel capsules under helium, MTR Canal Source.
[c] At 415°F.
[d] 600 ml irradiated in aluminum container open to air, MTR Canal Source.

TABLE I (continued)

PROPERTIES OF FLUIDS BASED ON C_{14}-$_{18}$-ALKYL DIPHENYL ETHER, 2% BIS(TRIDECYL) SELENIDE, AND 0.00.% DIMETHYL SILICONE

Sample No.	4946-2-10	067-5-2	067-6-2	4946-12-4	067-3-3	067-4-3	067-1-19	067-2-19	4946-23-5	067-3-4	067-4-4	067-1-20	067-2-20
VI Improver	12% Paratone N			1.5% S-50						2.6% S-60			
Radiation Dosage, 10^{10} ergs/g C	0	0.7[b]	3.0[b]	0	1.2[a]	5.2[a]	1.3[b]	5.7[b]	0	1.3[a]	5.7[a]	1.3[b]	5.7[b]
Viscosity, cs, °F													
400	2.47[c]			2.57[c]									
210	12.58	6.43	6.49	11.89	6.335	7.747	6.298	6.978	15.18	7.334	8.262	7.424	7.831
100	51.28	37.52	40.53	70.73	58.14	53.41	58.00	45.61	92.45	45.12	57.47	45.79	52.80
0	2571			2880	1559	3031				2013	3322		
Pour Point, °F				-20	-25	-25			-20	-20	-25		
Flash Point, COC, °F				465	440	455			475	445	450		
Spontaneous Ignition Temp., °F	1000			1020	1010	990			1000	980	1000		
Foaming													
Volume, ml				190					220				
Stability, min				0.5					0.75				
Dessing During Irradiation, ml/ml	1.5	3.8			[illegible]		1.8	3.9				1.6	4.2
Density at 68°F, g/ml				0.933					0.929				
Acid Number, mg KOH/g				0.22	nil	nil			0.26	nil	nil		
Vapor Pressure at													
400°F, mm Hg				7.2					6.2				
500°F, mm Hg				16.2					16.0				
Oxidation Corrosion													
Time, hours					48	48				48	48		
Temperature, °F					400	400				400	400		
Wt. Change, mg/cm²													
Cu													
Cu-Fe													
Ag													
Fe					+0.32	-0.10				+0.32	-0.13		
Al					+0.35	-0.05				+0.51	-0.10		
Insolubles, %					nil	nil				nil	nil		
Viscosity Change, 100°F, %					+24.4	+11.1				+22.8	+244		
Viscosity Change, 210°F, %					+10.5	+34.2				+7.5	+101		
Neut. Number Change					3.3	5.0				0.40	10.2		

[a] 200 ml irradiated in tin-lined cans open to air; MTR Canal Source.

[b] 10 ml irradiated in stainless steel capsules under helium; MTR Canal Source.

[c] at 415°F.

[d] 500 ml irradiated in aluminum container open to air; MTR Canal Source.

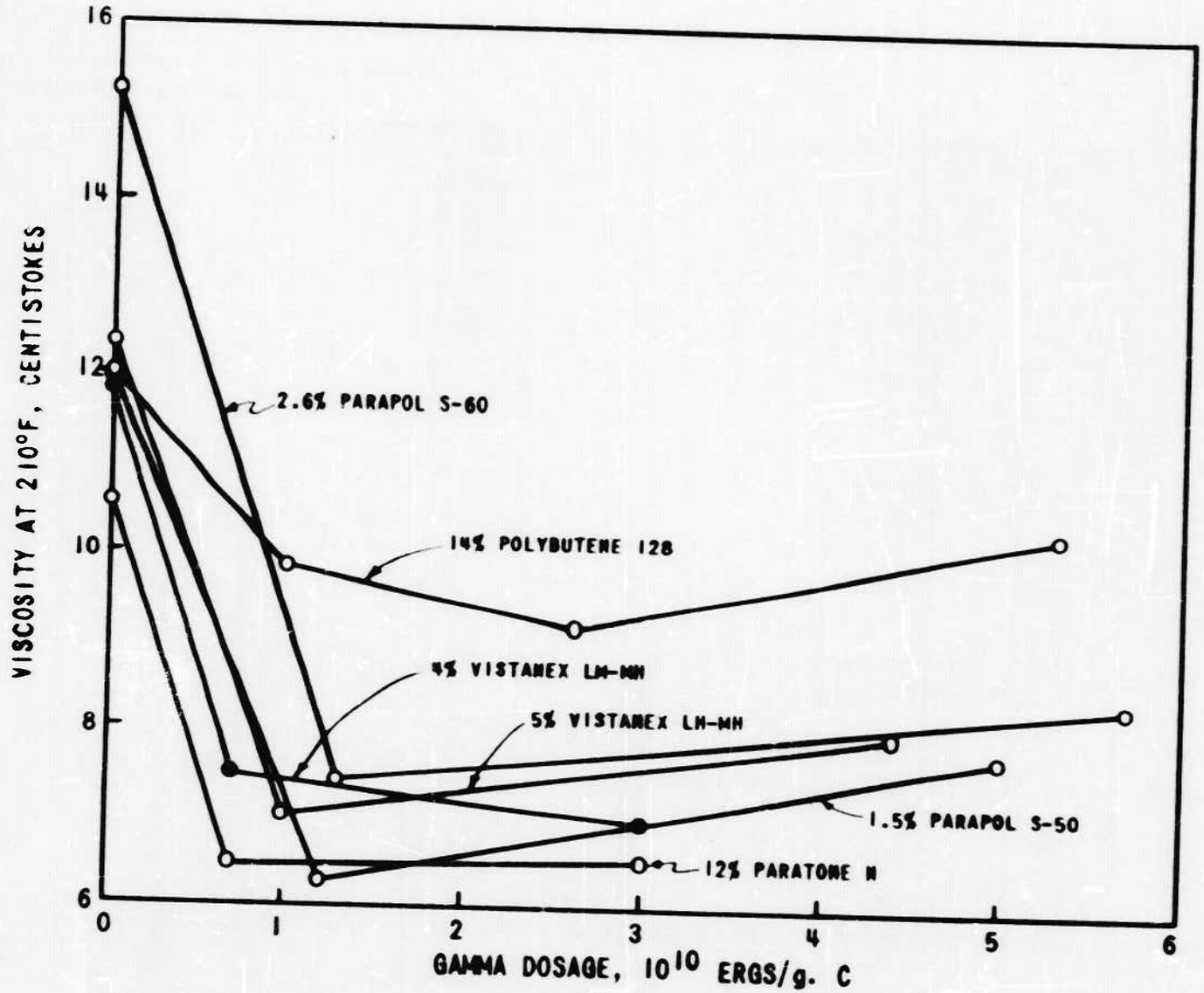


FIG. 13 - RADIATION STABILITY OF THICKENED C_{14-18}-ALKYL DIPHENYL ETHER BLENDS

TABLE LI

EFFECT OF SELENIDE INHIBITORS ON RADIATION STABILITY
410 STAINLESS STEEL CAPSULES UNDER HELIUM

Additive	C_{18}-$_{20}$-Alkyl Diphenyl Ether					10-C Insulating Oil				
	Sample No.	Dosage, 10^{18} ergs/g C	Viscosity, cs, at 100°F	Viscosity, cs, at 210°F	Gas Evolved, ml/g	Sample No.	Dosage, 10^{18} ergs/g C	Viscosity, cs, at 100°F	Viscosity, cs, at 210°F	Gas Evolved, ml/g
None	4948-41-1	0	26.83	4.85	-	G14147	0	8.205	2.166	-
	G47-1-1	0.7	28.80	5.055	1.2	G47-1-10	1.0	9.083	2.324	4.8
	G47-2-1	3.0	34.65	5.707	2.8	G47-2-10	4.0	13.0	2.91	15.5
3.8% C_8Se	4946-4-50	0	24.11	4.541	-	4830-40-16	0	7.859	2.120	-
	G47-5-17	1.3	26.06	4.770	1.7	G47-7-6	1.2	8.508	2.192	4.8
	G47-6-17	5.4	38.95	6.271	5.3	G47-8-6	4.9	10.67	2.57	14.2
5.2% $C_{12}Se$	4946-4-51	0	24.88	4.660	-	4946-6-40	0	8.318	2.200	-
	G47-5-18	1.3	26.94	4.904	2.1	G47-5-35	1.0	8.754	2.291	4.9
	G47-6-18	5.4	40.1	6.30	5.6	G47-6-35	3.9	10.7	2.56	15.1
5.6% $C_{16}Se$	4946-5-38	0	25.81	4.712	-	4946-3-22	0	8.427	2.208	-
	G47-5-25	1.3	27.17	4.873	2.1	G47-5-12	1.2	8.775	2.251	4.5
	G47-6-25	5.4	39.22	6.202	5.3	G47-6-12	4.9	11.74	2.747	18.9
3.5% BzSe	4946-4-52	0	25.16	4.639	-	4830-40-18	0	7.969	2.500	-
	G47-5-19	1.3	26.94	4.848	1.4	G47-7-7	1.2	8.414	2.188	3.4
	G47-6-19	5.4	36.6	5.98	3.5	G47-8-7	4.9	10.09	2.475	13.6
2.0% dSe	4946-5-33	0	24.76	4.606	-	4830-40-19	0	7.796	2.118	-
	G47-5-20	1.3	26.96	4.848	1.7	G47-7-8	1.2	8.219	2.169	3.3
	G47-6-20	5.4	34.7	5.65	4.7	G47-8-8	4.9	9.161	2.330	14.7
2.0% Morpholine Diselenide	4946-5-34	0	26.95	4.801	-	4830-40-20	0	8.273	2.168	-
	G47-5-21	1.3	30.14	5.163	2.0	G47-7-9	1.2	9.043	2.300	4.9
	G47-6-21	5.4	48.76	7.121	5.2	G47-8-9	4.9	12.615	2.808	17.9
3.12% Phenoselenazine	4946-5-35	0	27.02	4.855	-					
	G47-5-22	1.3	29.60	5.111	1.7					
	G47-6-22	5.4	40.9	6.28	5.3					
0.38 C_8Se	4946-6-48	0	26.57	4.801	-					
	G47-5-32	1.0	28.93	5.071	1.7					
	G47-6-32	3.9	38.1	6.11	4.1					
0.53 $C_{12}Se$	4946-6-47	0	28.52	4.796	-					
	G47-5-31	1.0	29.38	5.175	1.7					
	G47-6-31	3.9	39.96	6.313	4.0					

TABLE LII

EFFECT OF INHIBITORS ON RADIATION STABILITY
410 STAINLESS STEEL CAPSULES UNDER HELIUM

Additive	Sec-Bu-Alkyl Diphenyl Ether					10-C Insulating Oil					Naphthenic White Oil				
	Sample No.	Dosage, 10^{10} ergs/g C	Viscosity, cs at 100°F	Viscosity, cs at 210°F	Gas Evolved ml/g	Sample No.	Dosage, 10^{10} ergs/g C	Viscosity, cs at 100°F	Viscosity, cs at 210°F	Gas Evolved ml/g	Sample No.	Dosage, 10^{10} ergs/g C	Viscosity, cs at 100°F	Viscosity, cs at 210°F	Gas Evolved ml/g
None	5868-41-1	0	26.85	4.85	-	Q14147	0	8.205	2.166	-	DO 1259	0	70.46	7.441	-
	Q47-1-1	7	28.80	5.055	1.2	Q47-1-10	1.0	9.083	2.324	4.8	Q47-1-11	1.2	96.23	9.009	6.4
	Q47-2-1	3.0	34.65	5.707	2.8	Q47-2-10	4.0	13.0	2.91	15.5	Q47-2-11	4.9	232.7	15.74	8.0
2.35 Phenyl Sulfide	4946-5-36	0	24.81	4.605	-										
	Q47-5-23	1.5	27.66	4.844	1.7										
	Q47-6-23	5.4	38.5	6.14	5.0										
2.71 Benzyl Sulfide	4946-5-37	0	25.22	4.647	-										
	Q47-5-24	1.5	26.78	4.866	2.0										
	Q47-6-24	5.4	36.6	5.95	5.3										
5.40% Phenyl Disulfide	4946-4-25	0	24.70	4.599	-	4850-40-22[b]	0	7.790	2.118	-					
	Q47-5-15	1.2	-	-	1.3	Q47-7-10	1.2	8.345	2.197	5.9					
	Q47-6-15	4.9	34.1	5.56	4.4	Q47-8-10	4.9	11.02	2.562	15.1					
5.84% Benzyl Disulfide	4946-4-26	0	25.33	4.659	-	4850-40-23[c]	0	7.977	2.145	-					
	Q47-5-16	1.5	26.75	4.822	1.6	Q47-1-32	1.0	8.83	2.28	5.0					
	Q47-6-16	5.4	34.5	5.71	5.3	Q47-2-32	3.9	11.0	2.63	12.1					
4.53% Octyl Disulfide	4946-4-24	0	25.55	4.610	-	4946-4-23	0	8.297	2.196	-					
	Q47-5-14	1.2	25.62	4.712	1.7	Q47-5-13	1.2			4.1					
	Q47-6-14	4.9	30.6	5.32	5.4	Q47-6-13	4.9	30.6	5.32	17.5					
5% Santolube 395X	4946-5-41	0	28.46	4.975	-										
	Q47-5-26	1.2	31.04	5.283	1.7										
	Q47-6-26	4.9	42.3	6.51	5.0										
5% Sinclair RD 107	4946-5-42	0	28.21	4.957	-										
	Q47-5-27	1.2	30.60	5.220	2.0										
	Q47-6-27	4.9	40.6	6.30	5.1										
2% DRPC	4946-5-14	0	26.55	4.745	-										
	Q47-5-5	0.7	27.34	4.848	1.4										
	Q47-6-5	3.0	40.6	6.30	3.9										
2% AN-1	4946-2-11	0	26.09	4.726	-						4946-3-18	0	66.52	7.181	-
	Q47-1-39	0.6	29.30	5.090	1.9						Q47-5-8	1.0	75.50	7.714	5.5
	Q47-2-39	2.0	35.5	5.75	2.3						Q47-6-8	4.0	157.2	12.22	22.8
2% AN-2	4946-3-12	0	28.17	4.931	-						4946-3-19	0	74.43	7.558	-
	Q47-5-3	0.7	29.18	5.035	1.3						Q47-5-9	1.0	82.19	8.066	5.1
	Q47-6-3	3.0	37.66	5.902	3.9						Q47-6-9	4.0	159.0	12.3	23.8
2% AN-3	4946-3-13	0	27.12	4.811	-						4946-3-20	0	70.05	7.307	-
	Q47-5-4	0.7	28.50	4.962	1.0						Q47-5-10	1.0	77.59	7.860	4.5
	Q47-6-4	3.0	38.03	5.988	3.8						Q47-6-10	4.0	170.0	13.06	23.5
2% A2246	4946-3-15	0	28.30	4.928	-						4946-3-21	0	74.29	7.560	-
	Q47-5-6	1.0	30.32	5.156	1.0						Q47-5-11	1.2	85.71	8.280	6.5
	Q47-6-6	4.0	43.96	6.624	4.5						Q47-6-11	4.9	172.73	13.16	25.7
1% PAN	4946-6-49	0	26.86	4.807	-										
	Q47-7-19	0.7	27.88	4.930	1.0										
	Q47-8-19	2.7	34.59	5.693	17.0										
Sat. Phenothiazine (<1%)	4946-6-50	0	26.96	4.832	-										
	Q47-5-38	1.0	29.16	5.093	1.4										
	Q47-6-38	3.9	37.41	5.926	3.9										
Sat. DNPD	4946-5-51	0	26.87	4.826	-										
	Q47-7-20	0.7	27.90	4.944	1.0										
	Q47-8-20	2.7	33.14	5.555	2.4										

[a] Approximate.

[b] 2.35% phenyl disulfide.

[c] 2.71% benzyl disulfide.

The selenide blends were prepared to contain either 1% or 0.1% selenium. Dibenzyl selenide and diphenyl selenide were slightly more effective than the dialkyl selenides in reducing viscosity change on irradiation. In addition, they appeared to reduce gas evolution slightly in the diphenyl ether and in 10-C insulating oil. None of the sulfur, phenolic, or amine inhibitors had a demonstrably significant effect on gas evolution rate. Sulfide inhibitors as a class appeared to mitigate viscosity change with results comparable to selenide inhibitors.

Several irradiations were carried out at 400° F to compare with the usual ambient temperature (about 60° F) exposures. Results are shown in Table LIII. Surprisingly, both viscosity change and gas evolution were lower for the 400° F than for the lower temperature condition. While this result may be considered tentative until confirmed by further work, the failure of 400° F temperature to accelerate radiolysis is encouraging.

Irradiations were also carried out with unsaturated or ketonic aromatic compounds as additives. This was to determine if radiolytic gassing could be cut down by providing easily reduced materials to take up evolved hydrogen. The data of Table LIV fail to show a significant lowering of gas evolution rate by this method.

Table LV contains results of a series of high dosage irradiations of dodecyl diphenyl ether-inhibitor blends in comparison with other alkyl aromatics and conventional base stocks. None of the conventional materials remained liquid after irradiations above 10×10^{10} ergs/g C, although data were sufficiently scattered that the exact solidification dosages could not be established. At the highest dosage, 69×10^{10} ergs/g C, some alkyl aromatics were still liquid, including octylbiphenyl and di-p-tolylisodecane. Dodecyl diphenyl ether blends containing dibenzyl selenide, dibenzyl sulfide, diphenyl selenide, diphenyl sulfide, and phenoselenazine were still fluid at dosages greater than 40×10^{10} ergs/g C.

Silicate base fluids (8200 and 8515) are being widely used in the -65° F to 400° F temperature range (Specification MIL-H-8446A). The limited radiation resistance of these materials is typical of aliphatic materials. The effect of adding aromatic compounds to 8200 fluid was investigated, and results are reported in Table LVI. As is normal for viscosity index-improved fluids, viscosity at first decreased on irradiation (due to scission of the polymer) and then increased. The presence of considerable volatile material in many cases prevented viscosity measurement at 210° F.

The addition of diphenyl ether, C_{16-18}-alkylbiphenyl, dibutyl phthalate, or tetradecyl diphenyl ether to 8200 fluid reduced both the viscosity change and the rate of gas evolution on irradiation. This latter effect is shown in Figure 14. The data are very scattered but indicate that increasing aromatic content resulted in decreasing gas evolution during irradiation. This plot also shows that gas evolution per unit dosage is not independent of total dosage but decreases at the higher levels. The effect of added aromatics is further illustrated in Figure 15. The DC 710 fluid [also Kenflex L (naphthalene-formaldehyde polymer)] reduced gas evolution while having an adverse effect on viscosity stability (see Table LVI).

TABLE LIII

EFFECT OF INHIBITORS ON RADIATION STABILITY OF C_{14-16}-ALKYL DIPHENYL ETHER
UNDER HELIUM IN 410 STAINLESS STEEL CAPSULES AT 400°F

Additive	Sample No.	Gamma Dosage, 10^{10} ergs/g C	Viscosity, cs, at 100°F	Viscosity, cs, at 210°F	Gas Evolved, ml/g
None	3468-41-1	0	26.83	4.85	-
	G47-3-1	0.09	26.66	4.827	0.9
	G47-4-1	3.0	34.57	5.715	3.2
2% DBPC	4946-3-14	0	26.55	4.745	-
	G47-3-15	0.17	26.72	4.761	1.0
	G47-4-15	5.4	33.07	5.478	5.9
5.26% C_{12}Se	4946-4-31	0	24.88	4.666	-
	G47-3-16	0.16	24.71	4.650	0.3
	G47-4-16	4.9	24.93	4.695	3.8
3.30% BzSe	4946-4-32	0	25.16	4.639	-
	G47-3-17	0.16	25.07	4.643	0.6
	G47-4-17	4.9	26.34	4.835	3.3
2.95% ØSe	4946-5-33	0	24.76	4.606	-
	G47-3-18	0.16	25.08	4.648	1.0
	G47-4-18	4.9	28.58	5.032	3.9
2.35% ØS	4946-5-36	0	24.81	4.604	-
	G47-3-19	0.13	24.77	4.623	0.6
	G47-4-19	3.9	28.78	4.783	4.2
2.75% BzS	4946-5-37	0	25.22	4.647	-
	G47-3-20	0.13	24.95	4.637	0.8
	G47-4-20	3.9	26.14	4.775	3.9
5% Benzophenone	4946-6-46	0	24.28	4.412	-
	G47-3-21	0.13	24.42	4.521	0.4
	G47-4-21	3.9	27.81	4.846	3.8
0.53% C_{12}Se	4946-6-47	0	26.52	4.796	-
	G47-3-22	0.09	26.56	4.800	0.4
	G47-4-22	2.6	25.75	4.677	0.3
0.30% ØSe	4946-6-48	0	26.57	4.801	-
	G47-3-23	0.09	26.57	4.823	0.8
	G47-4-23	2.6	26.03	4.738	2.8
None (heart cut of base stock used)	4658-21 OV	0	22.96	4.28	-
	G47-3-24	0.09	23.01	4.272	0.3
	G47-4-24	2.6	22.59	4.198	3.2

TABLE LIV

EFFECT OF HYDROGEN ACCEPTORS ON RADIATION STABILITY
410 STAINLESS STEEL CAPSULES UNDER HELIUM

Additive	C_{14-18}-Alkyl Diphenyl Ether					Hexa(2-ethylbutoxy)disiloxane				
	Sample No.	Dosage, 10^{10} ergs/g C	Viscosity, cs, at 100°F	Viscosity, cs, at 210°F	Gas Evolved ml/g	Sample No.	Dosage, 10^{10} ergs/g C	Viscosity, cs, at 100°F	Viscosity, cs, at 210°F	Gas Evolved ml/g
None	3468-41-1	0	26.83	4.85	-	DC 1231	0	11.17	3.999	-
	G47-1-1	0.7	28.80	5.055	1.2	G59-13	0.3	11.90	3.788	2.9
	G47-2-1	3.0	34.65	5.707	2.8	G60-13	3.0	26.72	8.110	13.0
5% Azobenzene	4946-6-44	0	23.64	4.58	-	4830-39-9	0	10.09	3.333	-
	G47-5-28	1.2	27.94	4.893	1.6	G47-7-3	1.3	14.91	4.579	2.4
	G47-6-28	4.9	43.2	6.36	4.5	G47-8-3	5.3	43.57	10.47	16.1
5% Benzophenone	4946-6-46	0	24.28	4.412	-	4830-39-15	0	10.37	3.570	-
	G47-5-30	1.2	30.07	5.113	1.6	G47-7-5	1.3	Two Phase		4.8
	G47-6-30	4.9	43.6	6.32	4.4	G47-8-5	5.3	83.28	17.73	18.2
5% Stilbene	4946-6-45	0	25.34	4.636	-					
	G47-5-29	1.2	31.29	5.283	1.7					
	G47-6-29	4.9	47.5	7.01	4.6					
5% UV Absorber 9	4946-23-10	0	27.12	4.781	-					
	G67-1-28	0.6	28.56	4.926	1.0					
	G67-2-26	2.8	33.37	5.501	2.4					
5% UV Absorber 24	4946-23-11	0	27.12	4.781	-					
	G67-1-28	0.6	28.56	4.926	1.0					
	G67-2-26	2.8	33.37	5.501	2.4					
5% UV Absorber 24	4946-23-11	0	27.94	4.861	-					
	G67-1-29	1.3	30.43	5.087	1.5					
	G67-2-27	5.7	39.10	5.931	4.0					

TABLE LV

EFFECTS OF HIGH GAMMA DOSAGE[a] ON BASE STOCKS AND BLENDS

Base Stock	Additives	Sample No.	Gamma Dosage, 10^{10} ergs/g C	Viscosity, cs, at 100°F	Viscosity, cs, at 210°F	Gas Evolved ml/g
Dodecyl Diphenyl Ether	-	4658-2	0	18.48	3.568	-
		G101-57	50	119.15	12.38	11.8
		G100-53	7	35.11	5.447	(96.0)
		G101-35	69	solid-rubbery		34.8
Dodecyl Diphenyl Ether	5% $C_{12}Se$	4752-18-1		16.62	3.62	
		G100-54	7	35.80	5.542	6.0
		G101-23	50	solid-rubbery		41.9
Dodecyl Diphenyl Ether	5% C_8Se	4752-18-2	0	16.50	3.50	
		G101-25	10	liquid-lost sample		1.84
		G101-24	50	10,350	324.41	32.5
Dodecyl Diphenyl Ether	5% BzSe	4752-18-3	0	17.06	3.42	
		G100-56	7	23.59	4.226	4.8
		G101-26	50	1372	58.85	27.8
	5% $ØS_2$	4752-18-4	0	16.78	3.40	
		G101-51	63	159.5	14.08	23.8
Dodecyl Diphenyl Ether	5% BzS	4752-18-5	0	16.92	3.42	
		G100-57	7	23.47	4.255	5.25
		G101-42	69	1529	70.8	15.0
Dodecyl Diphenyl Ether	5% ØSe	4752-18-8	0	16.56	3.35	
		G100-58	9	23.74	4.189	5.30
		G100-27	50	599.8	31.91	26.7
Dodecyl Diphenyl Ether	5% ØS	4752-18-7	0	16.12	3.33	
		G101-43	68	612.8	37.11	1.34
Dodecyl Diphenyl Ether	5% Santopoid 395X	4752-18-9	0	19.92	3.12	
		G101-9	10	39.17	5.851	7.46
		G101-10	37	890.1	46.12	27.7
Dodecyl Diphenyl Ether	5% RD 107	4752-18-10	0	19.76	3.71	-
		G101-11	10	35.29	5.44	7.38
		G101-12	37	1153	52.25	30.1
Dodecyl Diphenyl Ether	5% Sulfasan R	4752-19-2		18.76	3.54	
		G101-22	37	519.5	29.25	25.9
Dodecyl Diphenyl Ether	5% Benzophenone	4752-19-4	0	19.24	3.38	-
		G101-45	10	44.38	6.08	7.30
		G101-44	63	2019	73.89	-
Dodecyl Diphenyl Ether	5% Anthraquinone	4752-19-7	0	15.62	3.25	-
		G101-49	10	42.45	6.37	8.63
		G101-48	63	soft-solid-tacky		29.0
Dodecyl Diphenyl Ether	5% Dimorpholine Diselenide	4752-19-9	0	18.82	3.57	-
		G100-55	7	34.08	5.119	5.61
		G101-28	50	solid-soft-tacky		-
Dodecyl Diphenyl Ether	Sat. Phenoselenazine	4752-19-10	0	18.69	3.590	-
		G101-38	10	37.16	5.45	3.53
		G101-37	68	2809	90.7	32.0
60% Ucon DLB 144E + 40% DLB 62E	-	4752-19-3	0	20.3	5.13	
		G100-59	9	75.23	12.39	23.1
		G100-60	9	69.07	9.81	23.2
50% Cetane + 50% m-Terphenyl	-	4752-19-8	0	18.7	3.50	
		G101-39	68	solid-rubbery		28.5

[a] 10 ml samples in capsules of 410 stainless steel sealed under helium; series G-100 and G-101, MTR Canal Source.

TABLE LV (continued)

EFFECTS OF HIGH GAMMA DOSAGE[a] ON BASE STOCKS AND BLENDS

Base Stock	Additives	Sample No.	Gamma Dosage, 10^{10} ergs/g C	Viscosity, cs, at 100°F	Viscosity, cs, at 210°F	Gas Evolved ml/g
Tetradecyl Diphenyl Ether	-	4658-5	0	22.26	4.130	-
		G101-58	36	174.97	16.86	14.9
OS-45	-	G14541	0	11.95	3.932	-
		G101-13	2	206.9	35.40	42.1
Tetradecyl Diphenyl Ether	-	3470-42HC	0	19.77	3.849	-
		G101-14	9	224.8	20.20	3.55
Hexyl Diphenyl Ether	-	3470-25HC	0	16.17	2.977	-
		G101-15	9	70.38	7.36	9.32
		G101-16	21	216.5	14.59	14.3
Dioctyl Diphenyl Ether	-	3470-153	0	50.9	6.57	-
		G101-17	9	267.7	19.69	17.0
Didodecylbiphenyl	-	3470-41 bot	0	134.8	13.15	-
		G101-18	21	584.4	108.8	28.0
OS-45-1	-	G14357	0	12.21	3.951	-
		G101-19	21	solid-hard		-
Bis(1,1,3,3-tetramethylbutyl)diphenyl Ether	-	G14370	0	1014	14.98	-
		G101-20	21	5662	49.50	16.1
10-C Insulating Oil	-	G14147	0	8.205	2.166	
		G101-21	21	solid-soft-tacky		(92.6)
1-Phenyldodecane	-	EK 6816	0	4.181	1.569	
		G101-29	64	solid-hard		70.4
2-Phenyldodecane	-	2580-45	0	4.331	1.551	
		G101-30	64	solid-rubbery		8.40
Alkylbenzene (MW 250)	-	SL 541	0	6.212	1.727	
		G101-31	64	2668	78.16	52.2
1,3,3,6-Tetramethyl-1-p-tolylindan	-	1983-26	0	88.9	4.50	
		G101-32	69	87,860	69.37	13.8
1,9-Diphenylnonane	-	4658-8	0	8.04	2.35	
		G101-33	69	solid-rubbery		24.6
Octylbiphenyl	-	4658-6	0	15.05	2.742	
		G101-34	69	242.6	14.44	17.5
α,ω-Ditolylisodecane	-	4658-16	0	23.12	3.641	
		G101-36	69	27,627	643.2	28.8
C_{16-18}-Alkylbiphenyl (bot)	-	DG 1269		55.03	7.08	
		G101-41	36	291.5	22.05	14.8
		G101-40	68	solid-rubbery		37.7
Di-n-butyl Phthalate	-	G14194		9.639	2.292	
		G101-47	10	53.84	7.28	7.83
		G101-46	63	solid-rubbery		27.5
88.5 Fluid	-	G14476		24.23	8.197	
		G101-50	63	solid-hard		-
Diisooctyl Terephthalate	-	DG 1264		31.70	5.09	
		G101-52	52	solid-rubbery		31.3
8200 Fluid	-	G14566		31.62	11.04	
		G101-53	52	solid-hard		90.0
1-Phenyltetradecane	-	2364-5		5.80	1.942	
		G101-54	52	solid-rubbery		46.6
Dioctylbenzene	-	863-25		12.02	2.531	
		G101-55	52	88.96	9.27	29.8
Trioctylbiphenyl	-	3470-442		171.4	12.86	
		G101-56	52	2118	65.42	20.0
C_{16-18}-Alkylbiphenyl (distilled)	-	G14754		36.54	5.209	
		G101-59	36	160.2	14.20	2.82
Tetradecylbiphenyl	-	3470-43HC		33.16	4.80	
		G101-60	36	117.1	10.87	-

[a] 10 ml samples in capsules of 410 stainless steel sealed under helium; series G-100 and G-101, MTR Canal Source.

TABLE LVI

EFFECT OF ADDITIVES ON THE RADIATION STABILITY OF ORONITE 8200 FLUID
IRRADIATIONS IN TIN-PLATED CANS - 200-ML SAMPLES OPEN TO AIR
AND IN CAPSULES SEALED UNDER HELIUM - 10 ML SAMPLES

Additives	Sample No.	Dosage, 10^{10} ergs/g C	Viscosity, cs, at °F 100	210	-65	Neut. No.	Micro-flash Point, °F	Spontaneous Ignition Temp., °F	Pour Point, °F	Vapor Pressure, mm, at °F 400	500	Capsule Irradiation - 10-ml Sample Sealed Under Helium: Sample No.	10^{10} ergs/g C	Viscosity, cs, at °F 100	210	Gas Evolved ml/g
None	014566	0	51.76	11.14	2116	0.05	410	720	<-80	1.0	14					
	G37-1-1	0.55	50.86	9.074	2633	nil	420	720	<-80			G47-1-18	1.5	52.26	10.54	7.5
	G37-3-1	2.7	63.97	18.82	15,806	0.66	150	790	-80	82	216	G47-2-18	5.4	141.1	34.05	20.9
10% Diphenyl Ether	4850-42-9	0	21.88	8.068	too viscous		550	780	<-80							
	G37-1-2	0.77	19.46	6.59	1880	nil	290	760	<-80			G47-1-26	1.2	21.8	7.39	4.5
	G37-3-2	3.7	42.50	11.77	10,400	1.5	350	800	-80			G47-2-26	4.9	50.2	13.9	6.0
25% Diphenyl Ether	4850-42-10	0	13.00	5.147	too viscous		280	830	50							
	G37-1-3	1.0	12.74	4.59	too viscous	nil	250	800	-50			G47-1-27	1.2	13.8	4.94	2.8
	G37-3-3	4.4	20.63	6.508	4486	1.0	150	840	<-80	220	600	G47-2-27	4.9	21.84	7.04	7.1
5% Kenflex L	4850-42-11	0	52.16	10.76	5075		410	740	<-80							
	G37-1-4	1.0	59.84	11.65	5232	nil	450	740	<-80			G47-1-28	1.2	42.70	12.65	5.3
	G37-3-4	4.8	184.6	boils	too viscous	0.67	440	850	-80			G47-2-28	4.9	210.4	70.15	17.0
10% Kenflex L	4850-42-12	0	52.62	10.44	too viscous		410	740	<-80							
	G37-1-5	0.9	56.16	10.47	6450	nil	420	740	<-80			G47-1-29	1.2	44.0	11.7	5.3
	G37-3-5	4.4	98.37	boils	48,866	0.52	405	780	-80			G47-2-29	4.9	226.2	50.4	14.7
10% C_{16-18}-Alkylbiphenyl	4850-42-13	0	50.48	9.960	too viscous		400	740	-80							
	G37-1-6	0.8	28.56	8.90	too viscous	nil	415	750	<-80			G47-1-30	1.2	36.5	10.6	5.1
	G37-3-6	3.6	44.06	12.06	14,829	0.51	425	760	<-80			G47-2-30	4.9	158.2	34.95	14.6
25% C_{16-18}-Alkylbiphenyl	4850-42-14	0	29.57	8.613	too viscous		415	740	-55							
	G37-1-7	0.4	28.47	8.217	too viscous	nil	430	740	-40			G47-1-31	1.0	32.67	8.022	4.5
	G37-3-7	2.0	29.27	boils	too viscous	0.59	415	770	-70	52	102	G47-2-31	3.9	63.37	14.11	9.6
5% Tetradecyl Diphenyl Ether	4850-42-2	0	30.32	10.32	4423		420	760	<-80							
	G37-2-1	0.6	27.25	8.667	5004	0.55	425	760	<-80			G47-1-19	1.3	32.37	9.890	3.2
	G37-4-1	3.0	55.81	boils	19,519	0.66	190	790	<-80			G47-2-19	5.4	118.7	27.84	19.2
10% Tetradecyl Diphenyl Ether	4850-42-3	0	29.21	10.04	too viscous		425	760	-65							
	G37-2-2	0.9	26.64	8.201	too viscous	0.50	420	760	-80			G47-1-20	1.3	28.84	8.651	5.3
	G37-4-2	1.5	78.98	boils	45,775	0.67	170	780	-80			G47-2-20	5.4	98.8	24.34	17.0
25% Tetradecyl Diphenyl Ether	4850-42-4	0	25.74	8.028	too viscous		400	780	-40							
	G37-2-3	1.0	24.52	6.941	too viscous	0.70	435	760	-45			G47-1-21	1.3	27.02	7.501	5.1
	G37-4-3	14.2	53.43	boils	too viscous	0.75	420	780	-60	90	175	G47-2-21	5.4	63.40	14.67	13.4
10% Dibutyl Phthalate	4850-42-5	0	25.88	8.987	2307		400	760	<-80							
	G37-2-4	1.0	31.84	9.734	4368	1.4	200	780	<-80			G47-1-22	1.3	44.40	12.76	5.5
	G37-4-4	15.0	169.5	boils	too viscous	3.1	180	800	-75			G47-2-22	5.4	244.2	51.0	16.1
25% Dibutyl Phthalate	4850-42-6	0	19.12	6.510	too viscous		370	760	<-80							
	G37-2-5	1.0	24.15	7.258	5146	1.5	380	780	<-80			G47-1-23	1.3	33.6	9.37	4.4
	G37-4-5	14.6	74.79	boils	54,989	3.8	500	800	<-80	151	390	G47-2-23	5.4	134.8	26.29	9.4
10% DC 710 Fluid	4850-42-7	0	33.51	11.46	too viscous		430	740	-80							
	G37-2-6	0.9	34.81	11.20	4500	0.46	435	800	<-80			G47-1-24	1.3	57.18	16.90	-
	G37-4-6	12.8	128.9	boils	40,261	0.56	195	840	-80			G47-2-24	5.4	rubbery		13.8
18% DC 710 Fluid	4850-42-8B	0	31.00	12.87	-											
	G37-2-7	0.6	35.30	11.55	too viscous	0.44	420	820	-80			G47-1-25	1.3	68.3	19.0	4.5
	G37-4-7	7.8	57.43	16.32	20,367	0.44	445	820	-80			G47-2-25	5.4	rubbery		12.8

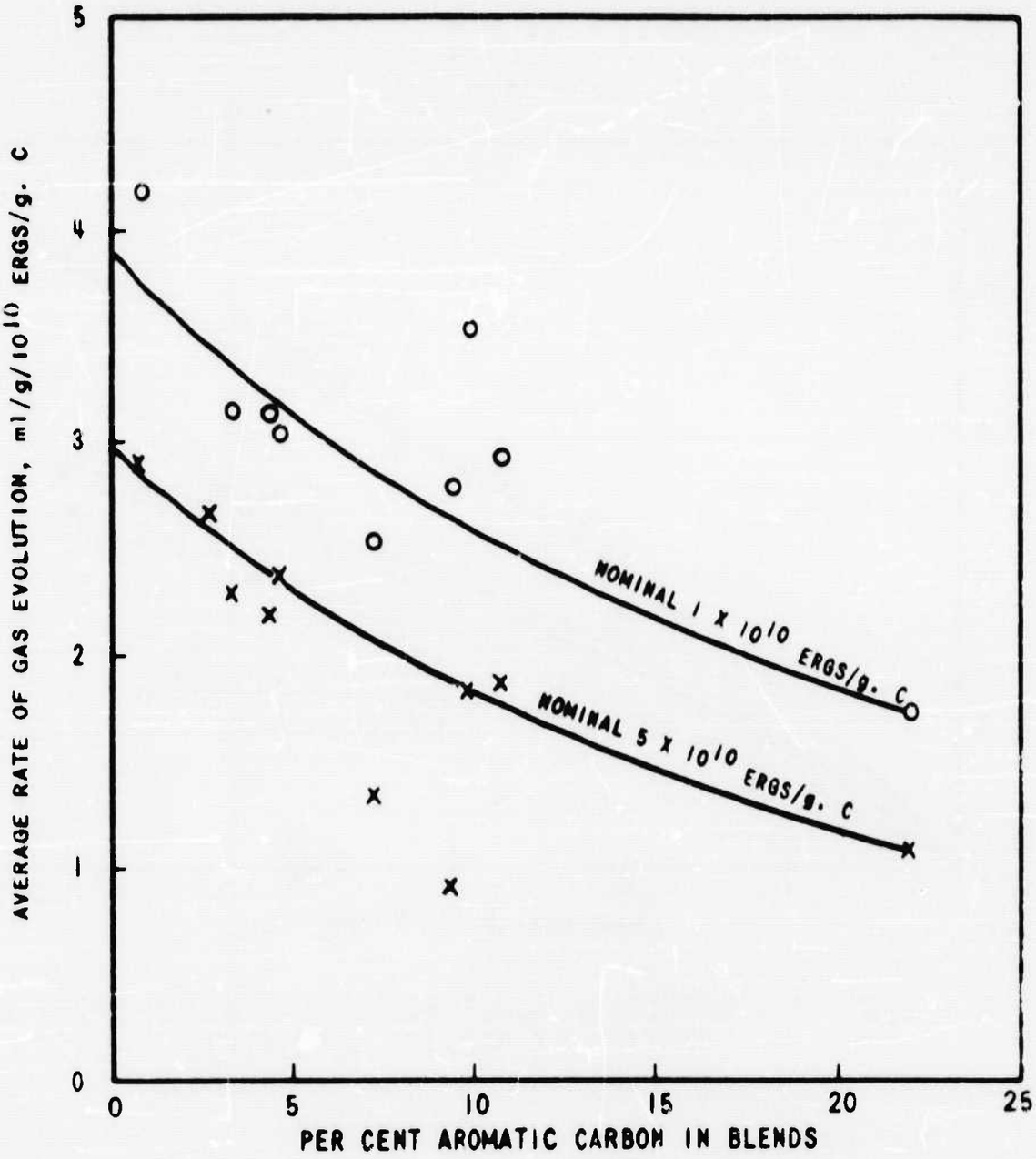


FIG. 14 - EFFECT OF AROMATIC ADDITIVES ON GAS EVOLUTION OF ORONITE 8200 FLUID

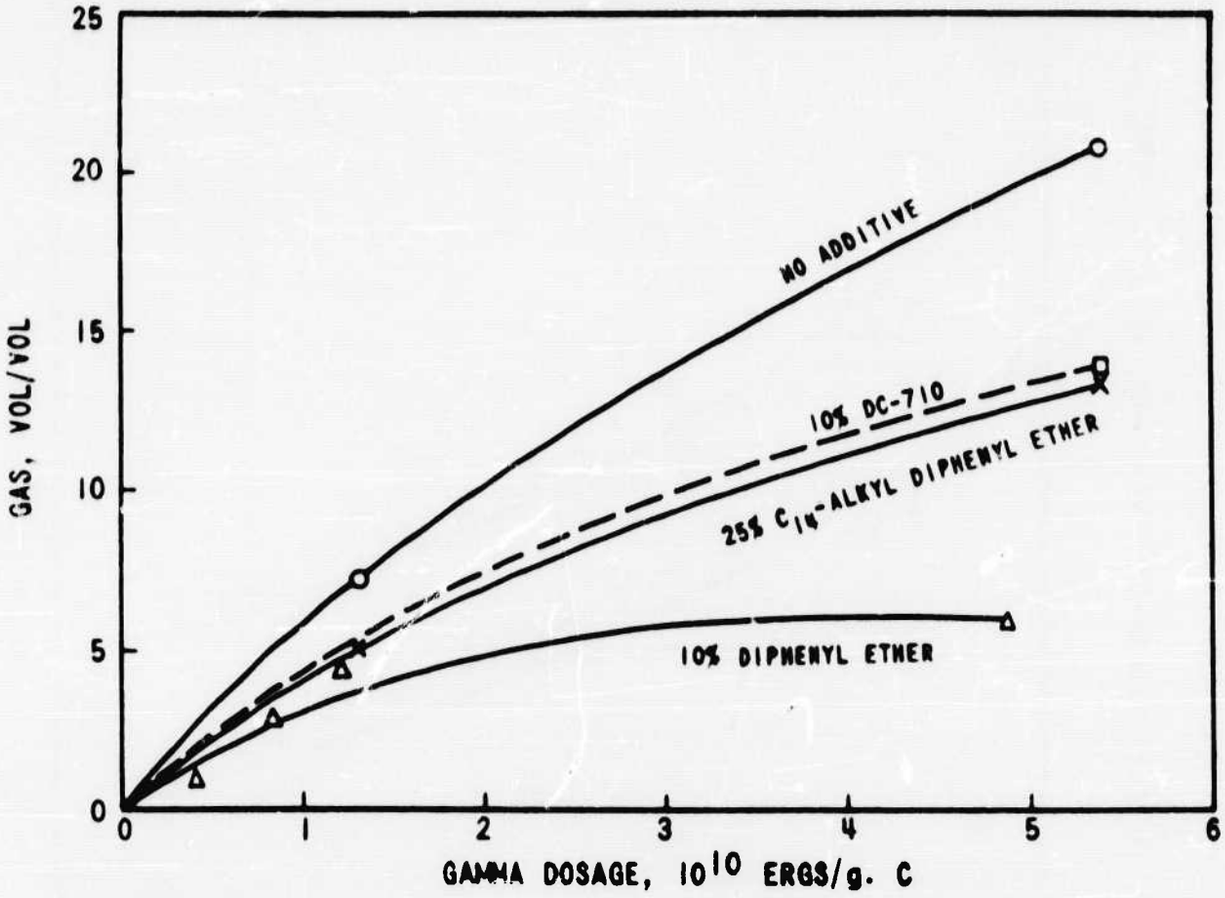


FIG. 18 - EFFECT OF ADDITIVES ON RADIATION-INDUCED GASSING OF ORONITE 8200 FLUID

The blend containing 25% diphenyl ether had the highest percentage of aromatic carbon atoms and, consequently, showed the least radiation damage. Several additional stability tests were performed on this fluid before and after irradiation. Results are shown in Table LVII. The irradiated blend was more stable in the 400° F oxidation test than was the 8200 fluid itself after irradiation. No improvement in hydrolytic stability of the blend over 8200 fluid was evident after irradiation.

4.4 Evaluation of Formulations

4.4.1 CALRESEARCH 216

A formulation based on C_{14-16}-alkyl diphenyl ether was the most promising radiation-resistant high temperature hydraulic fluid developed. It was designated CALRESEARCH 216 and had the following composition:

C_{14-16}-Alkyl diphenyl ether, wt %	84.0
Polybutene 128	14.0
Bis(tridecyl) selenide	2.0
	100.0
1% solution of 60,000 cs dimethyl silicone in kerosene, wt % added	0.1

Properties of this fluid before and after irradiation were summarized in Table II, page vii. All available data on CALRESEARCH 216 are shown in Table LVIII. A viscosity of 2.5 cs at 400° F, as required by Specification MIL-H-8446A, resulted in a viscosity near 5000 cs at 0° F for the fluid. Volatility was low with a vapor pressure at 500° F of less than 15 mm Hg. Spontaneous ignition temperature was around 1000° F, due in part to the selenide inhibitor. Oxidation stability appeared relatively good at both 400° F and 500° F. Copper and silver alloys were omitted from the test because of the known activity of selenides. The apparent high corrosion to steel shown in two of the earliest 500° F runs performed was not confirmed by subsequent tests (see Table XLVII).

Hydrolytic stability tests were run for 100 hours at 400° F with 6% water in a nickel (94%) Parr 22-ml flame ignition peroxide bomb. The base stock alone was unaffected by this test. CALRESEARCH 216 had a small viscosity decrease and left a greenish deposit in the range of several tenths per cent by weight on the walls of the bomb. Apparently in the presence of water, some corrosion by the selenide had occurred. Lubricity, as measured by the Four-Ball Wear test, was good, particularly at high loads. The Mean Hertz Load results showed "average" film strength.

TABLE LVII

EFFECT OF AROMATICS ON OXIDATION STABILITY OF ORONITE 8200 FLUID OXIDATION AND CORROSION TESTS, 48 HOURS AT 500°F

Additive	None		25% Diphenyl Ether	
Sample No.	G14566	G-61	4830-42-10	G37-3-3
Gamma Dosage, 10^{10} ergs/g C	0	6.7	0	4.4
48-Hour 500°F Oxidation and Corrosion Test				
Metal Weight Change, mg/cm^2				
Cu	-0.74	0	-3.52	-1.42
Be-Cu	-0.19	+0.32	-3.13	-1.19
Ag	0	-0.10	-0.40	-0.23
Fe	0	-0.10	-0.13	-1.16
Al	0	-0.10	-0.06	-0.16
Viscosity Change at 100°F, %	-36.6	-	-40.2	+147
Viscosity Change at 210°F, %	-45.5	-	-49	+66.7
Insolubles, %	2.8	a	0.4	0
Neutralization No.		-	0.53	0.72
48-Hour 200°F Hydrolytic Stability Test				
Insolubles, %	0.05	0.84	0.02	6.8
Viscosity Change at 100°F, %	+2.1	+28.1	+0.1	gel
Viscosity Change at 210°F, %	+1.0	-12.2	-0.4	

[a] Filter plugged.

TABLE LVIII

PROPERTIES OF CALNE EARCH 210

Sample No.	[illegible]-1D					C107-4-1		C107-4-2		G117-1D		[illegible]
Radiation Dosage, 10^{10} ergs/g C			0			0.009[f]		0.09[f]		1.9[g]		3.0[h]
Viscosity, cs, °F												
400			2.[illegible][e]			2.[illegible][e]		2.[illegible][e]		2.01[e]		
210			12.00			11.[illegible]		11.[illegible]		[illegible]		10.12
100			[illegible]			[illegible]		[illegible]		70.1[illegible]		80.7[illegible]
0			4857			4[illegible]		4[illegible]		4[illegible]		
Pour Point, °F			-20			-20		-30		-25		-25
Flash Point, °F			480			485		4[illegible]		410		455
Spontaneous Ignition Temp., °F			1000			1000		1000		950		
Bulk Modulus (adiabatic), psi												
At 0 psi and 77°F			290,000									
Foaming												
Volume, ml			170			75		280		190		
Stability, min			1			0.5		1.5		0.9		
Gassing During Irradiation, ml/ml			-			-		-		-		
Density at 68°F, g/ml			0.885									
Acid Number, mg KOH/g			0.17			1.54		1.07		0.81		0.83
Vapor Pressure at												
400°F, mm Hg			3.8			4.4		4.4		3.1		
500°F, mm Hg			14.2			41		35		25		
Oxidation Corrosion												
Time, hours	48	48	48	48	48	48	48	48	48	48	48	
Temperature, °F	400	400	500	500	500	400	500	400	500	400	500	
Weight Change, mg/cm²												
Fe	-0.01	-0.03	-1.28	-1.16	+0.11	+0.16	0	+0.16	-0.06	0	-0.54	
Al	-0.10	+0.01	0	0	+0.06	+0.22	-0.03	+0.19	0	+0.10	+0.15	
Insolubles, %	nil	nil	1.0	2.8	0.5	nil	1.2	nil	1.1	nil	1.0	
Viscosity Change, 100°F, %	+5.0	+6.6	-	-	+78.2	+[illegible]	+[illegible]	+52.4	+72.0	+44.0	+[illegible]	
Viscosity Change, 210°F, %	-0.8	+4.6	+16.5	-	+30.5	+8.8	+12.0	+11.2	+23.5	+19.5	+[illegible]	
Neutralization Number Change	2.1	2.1	5.0	0.8	5.1	5.8	5.0	4.0	5.1	0.4	5.0	
Hydrolytic Stability												
100 hours in pressure bomb with 5% water at 400°F												
Viscosity Change												
At 100°F, %	-4.2	-0.4	-5.2			-1.8		-1.4		-5.5		
At 210°F, %	-2.4	-3.1	-1.8			-1.4		-1.8		-4.0		
Insolubles, %	-	0.02	0.58			0.15		0.13		0.13		
Four-Ball Wear, mm												
2 hours, 167°F, 4 Load			0.64									
10 Load			0.67									
40 Load			0.78			0.84		0.90		0.96		0.72
Mean Hertz Load (screening test), kg	18	20	17.5									

[a] 600 ml irradiated in aluminum container open to air, MTR Canal Source.

[b] 200 ml irradiated in tin-plated can open to air, MTR Canal Source.

[c] 1 gallons irradiated in stainless steel can open to air, MTR Canal Source.

[d] 10 ml irradiated in 4.0 stainless steel capsule under helium.

[e] 10 ml irradiated in heated 4.0 stainless steel capsule at 400°F under helium, MTR Canal Source.

[f] 200 ml irradiated in aluminum can open to air, Cal Research cobalt-60 source.

[g] at 4.0°F.

TABLE LVIII (continued)

PROPERTIES OF CALRESEARCH 216

Sample No.	G67-7	G47-8-24	G87-3-6	C107-4-2	C107-4-4	G47-1-38	G47-2-38	G87-3-7	G47-3-14	G47-4-1
Radiation Dosage, 10^{10} ergs/g C	4.4[c]	5.3[b]	11.7[b]	0.009[d]	0.09[d]	0.6[d]	2.6[d]	11.7[d]	0.17[e]	5.4[e]
Viscosity, cs, °F										
400	1.76[g]	1.96[g]	2.25[g]							
210	9.425	10.2	13.35	11.96	11.61	9.70	9.12	14.06	72.19	26.89
100	71.54	82.6	121.8	84.22	82.23	69.7	67.23	131.0	10.45	5.42
0	4750	6280	12,006							
Pour Point, °F	-30	-35	-35							
Flash Point, °F	370	430	280							
Spontaneous Ignition Temp., °F	1000	1010	960							
Bulk Modulus (adiabatic), psi										
At 0 psi and 77°F	290,000									
Foaming										
Volume, ml	740	250	330							
Stability, min	3.7	5	2.5							
Gassing During Irradiation, ml/ml	-	-	-	0.6	0.6	1.7	4.0	11.4	-	7.5
Density at 68°F, g/ml	0.926									
Acid Number, mg KOH/g	0.36	nil	1.34							
Vapor Pressure at										
400°F, mm Hg	12.4		6.5							
500°F, mm Hg	21		23							
Oxidation Corrosion										
Time, hours	48	48	48	48	48	48	48			
Temperature, °F	400	400	500	500	500	400	500			
Weight Change, mg/cm²										
Fe	+0.10	0	-0.29	-0.39	-0.48	-0.06	-0.61			
Al	+0.13	-0.02	0	+0.03	+0.03	+0.03	0			
Insolubles, %	nil	nil	1.2	0.9	0.5	nil	0.4			
Viscosity Change, 100°F, %	+98	+66	+296	+115	+142	+232	+562			
Viscosity Change, 210°F, %	+50	+31	+128	+51	+61	+100	+184			
Neutralization Number Change	4.8	3.5	5.3	4.2	3.4	5.6	5.2			
Hydrolytic Stability										
100 hours in pressure bomb with 6% water at 400°F										
Viscosity Change										
At 100°F, %	-10.2		-12.4	-13.2						
At 210°F, %	-7.2		-8.3	-						
Insolubles, %	0.41		0.23	0.17						
Four-Ball Wear, mm										
2 hours, 167°F 4 Load	0.34									
10 Load	0.45									
40 Load	0.54			0.51						
Mean Hertz Load (screening test), kg	17.5									

[a] 600 ml irradiated in aluminum container open to air; MTR Canal Source.

[b] 200 ml irradiated in tin-plated can open to air; MTR Canal Source.

[c] 3 gallons irradiated in stainless steel can open to air; MTR Canal Source.

[d] 10 ml irradiated in 410 stainless steel capsule under helium.

[e] 10 ml irradiated in heated 410 stainless steel capsule at 400°F under helium, MTR Canal Source.

[f] 200 ml irradiated in aluminum can open to air; Cal Research cobalt-60 source.

[g] At 415°F.

Thermal stability, as measured in capsule-type tests, will be discussed in the next section. Vapor pressure measurements by the isoteniscope method were made on both CALRESEARCH 216 and the C_{14-16}-alkyl diphenyl ether base stock. Results are shown in Figure 16. At low temperatures, the vapor pressure of CALRESEARCH 216 was probably higher than that of the base stock because of the presence of a small amount of low boiling material in the additives. At high pressures, the deviation was presumably due to thermal decomposition of the additives, which apparently occurred around 500° F.

On irradiation, the first detectable effect on CALRESEARCH 216 was a viscosity loss as a result of a partial depolymerization of the V.I. improver. The viscosity as a function of dosage is plotted in Figure 17. For irradiations carried out at 80° F under an inert atmosphere, the viscosity at 210° F dropped from 12 cs to about 9.0 cs and then rose, reaching only 14 cs at a dosage beyond 10×10^{10} ergs/g C. In 400° F irradiations, the viscosity fell much faster and further, one point below 6 cs being reached. This effect was probably due to the thermal instability of the polybutene additive.

Spontaneous ignition temperature was not adversely affected by irradiation. The flash point gradually fell due to the accumulation of volatile products. Vapor pressure increased for a similar reason. The volume of foam gradually increased, but its stability remained low. Gas evolution, at the higher dosages, was at the rate of 1 to 2 ml gas/ml fluid/ 10^{10} ergs/g C. Acid number depended in considerable part upon the degree of exposure to air during the irradiation. The smaller samples tended to have larger acid numbers.

Oxidation stability gradually decreased as dosage increased, but no solidification occurred at the highest dosages, even in the 500° F test. This result was surprisingly good. As 1020 steel is unlikely to be encountered in high temperature hydraulic systems, 500° F oxidation tests were run with more likely structural materials before and after irradiation of the fluid. Results are shown in Table LIX. Both 304 stainless and M-10 tool steel were unaffected, while 410 stainless, 4140 steel, and titanium were affected to some extent.

Hydrolytic stability, as measured by viscosity change, gradually decreased with dosage (see Table LVIII). The formation of insolubles remained unchanged. At the highest dosages, wear decreased, although no enhancement of end point properties was detected. Results of successful pump tests are described in a later section.

CALRESEARCH 216 was the first complete hydraulic fluid to come from this contract. It had good radiation resistance, oxidation stability, volatility, lubricity, and spontaneous ignition characteristics. Thermal stability of the fluid was better than with most currently used fluids but was inferior to the diphenyl ether base stock. As a first attempt, the properties are encouraging, but this fluid is by no means considered to be the ultimate available from alkyl aromatics.

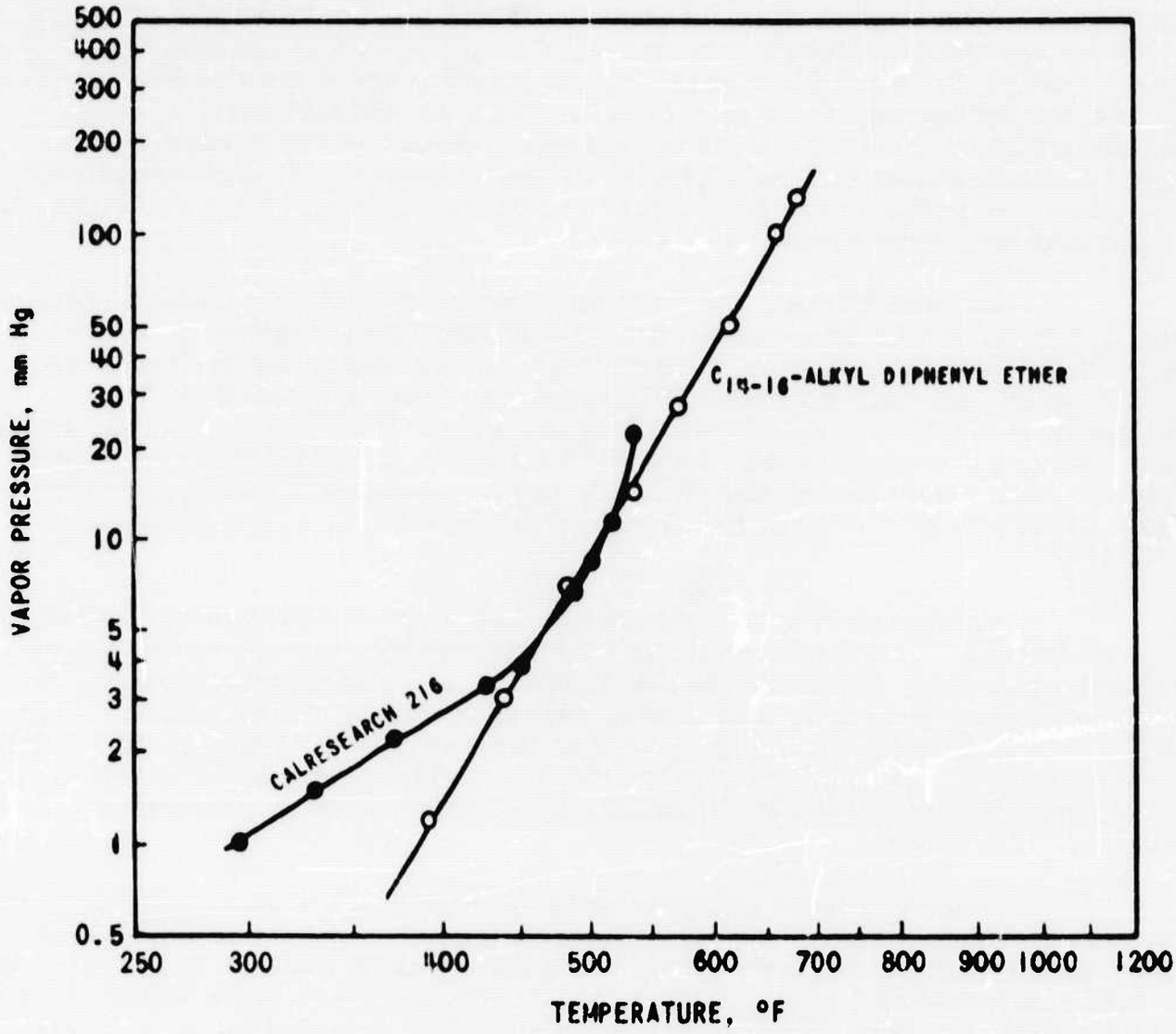


FIG. 18 - VAPOR PRESSURES OF HYDRAULIC FLUIDS USING THE ISOTENISCOPE METHOD

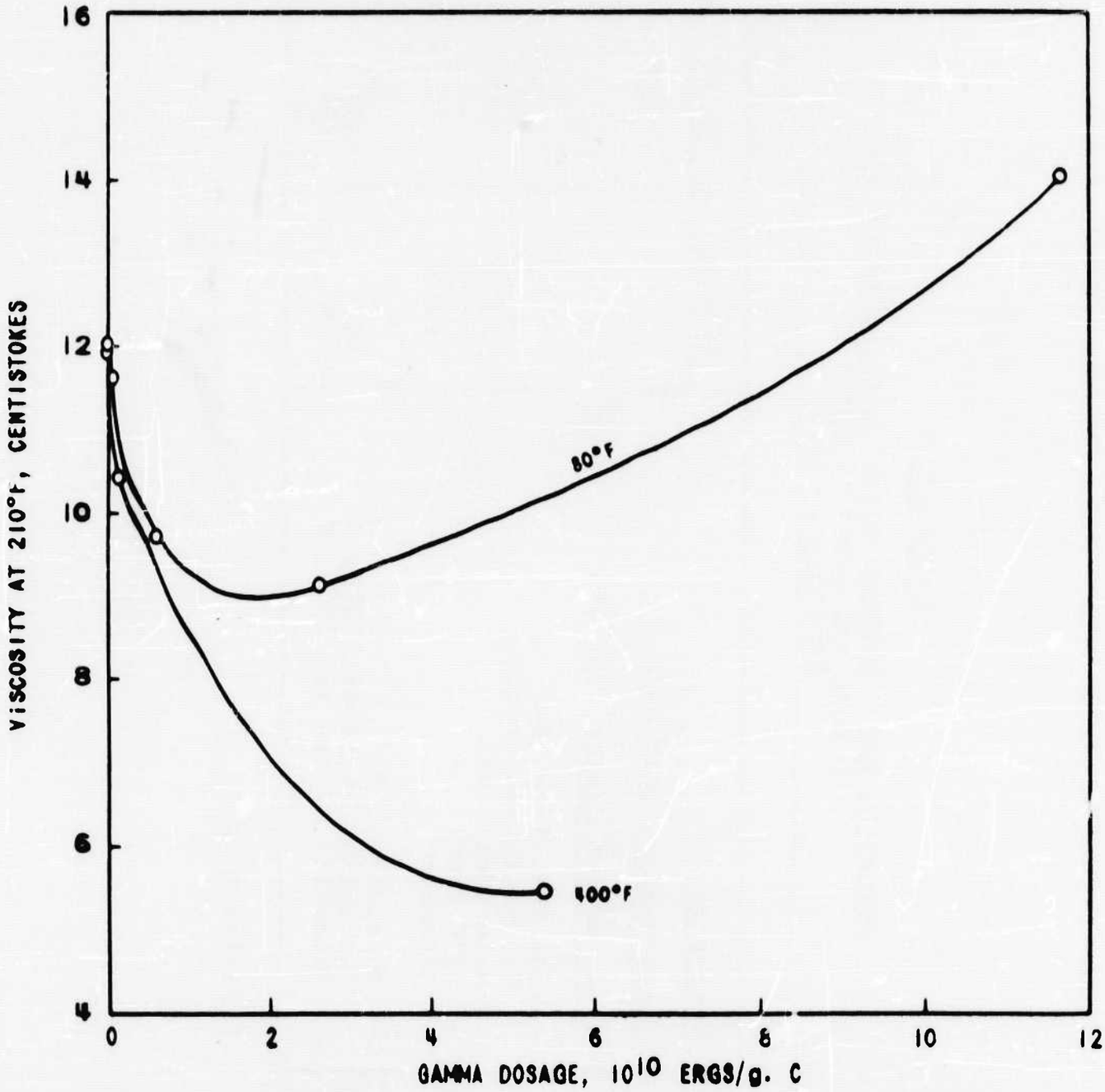


FIG. 17 - RADIATION-INDUCED VISCOSITY CHANGE OF CALRESEARCH 218
IRRADIATED UNDER HELIUM IN SEALED STAINLESS STEEL CAPSULES;
MTR CANAL SOURCE

TABLE LIX

OXIDATION AND CORROSION TESTS ON CALRESEARCH 216
BEFORE AND AFTER IRRADIATION
48 HOURS AT 500°F

Sample No.	4946-16	067-7
Gamma Dosage, 10^{10} ergs/g C	0	4.4
Metal Weight Change, mg/cm²		
304 Stainless Steel	0	-0.06
410 Stainless Steel	+0.29	+0.23
M-10 Tool Steel	+0.06	+0.06
4140 Steel	-0.58	-0.61
Titanium	+0.06	-0.52
Insolubles, %	[a]	3.2
Viscosity Change at 100°F, %	+96	+348
Viscosity Change at 210°F, %	+34	+144

[a] Filter plugged.

4.4.2 n-Nonyl Diphenyl Ether

This new compound was of brief interest as a base stock for thickened hydraulic fluids. With 18% Polybutene 128, 2% bis(tridecyl) selenide, and 0.001% dimethyl silicone, the properties listed in Table LX were obtained. On storage at -20°F, the base stock crystallized in one day. The blend, although stable for one month at this temperature, also crystallized in one day if seeded with frozen base stock. As the main advantage desired from this blend was better low temperature properties than CALRESEARCH 216, its high solidification temperature excluded it from further consideration.

4.4.3 Oronite 8200 Fluid

Because of the widespread use of silicate base hydraulic fluids, an evaluation was made of the ability of Oronite 8200 fluid to withstand nuclear radiation. Results are shown in Table LXI in comparison with some of the properties of its base stock, hexa(2-ethylbutoxy)disiloxane.

Oronite 8200 fluid is intended for continuous operation over the temperature range from -65°F to 400°F, with shorter life at higher temperatures. It is characterized by excellent viscosity-temperature properties and low temperature fluidity. On irradiation, the viscosity first decreased, reaching a minimum near 10^{10} ergs/g C and then increased rather rapidly at higher dosages. Volatile products were formed, but flash point and vapor pressure remained relatively unchanged below 10^{10} ergs/g C.

In oxidation and corrosion tests at 400°F or 500°F, the original fluid typically lost, rather than gained, viscosity. Irradiation increased the viscosity loss and at the higher dosages caused some copper corrosion. Hydrolytic stability is one of the borderline properties of silicate fluids and one that was adversely affected by irradiation as shown in Table LXI. Thus, it is necessary to exclude liquid water from all high temperature hydraulic systems, and especially so for those containing silicate fluids exposed to nuclear radiation. Lubricity of 8200 fluid was improved by a large radiation dosage (greater than 5×10^{10} ergs/g C), the effect on this property at intermediate dosages was not determined. Increasing the temperature of irradiation to 400°F appeared to increase the gas evolution rate but did not produce any other detectable effect.

Several other commercially available silicate base hydraulic fluids were briefly evaluated to determine whether their resistance to irradiation differed markedly from that of 8200 fluid. These data are presented in Table LXII. The usable limit for 8515 fluid, like 8200 fluid, appeared to be about 10^{10} ergs/g C.

4.5 Evaluation of Thermal Stability

Most thermal stability measurements were made by the same technique used for irradiations. The liquid was introduced under a helium atmosphere into a 410 stainless steel capsule, which was then welded shut. After exposure in a muffle furnace for the required time and temperature, the capsules were opened, gas evolved was measured, and viscosity determinations made on the fluid. Results are shown in Table XLIII.

TABLE LX

PROPERTIES OF n-NONYL DIPHENYL ETHER BLEND
ADDITIVES: 18% PB 128 + 2% C_1-Se + 0.001% DC

Sample No.	4946-28	G67-1-30	G67-2-28
Dosage, 10^{10} ergs/g C	0	1.3[b]	5.7[b]
Viscosity, cs, °F			
-40	solid		
0	1163		
100	41.6	30.74	28.46
210	8.54	6.382	5.569
400	2.3[a]		
Pour Point, °F	-50		
Spontaneous Ignition Temperature, °F	1110		
Gas, ml/g	-	1.3	4.1

[a] Extrapolated.

[b] 10 ml irradiated in 410 stainless steel capsules under helium; MTR Canal Source.

TABLE LXI

PROPERTIES OF DROMITE 8200 FLUID AND MEXA(2-ETHYLBUTOXY)DISILOXANE BASE STOCK

Sample No.	8200 Fluid													
	818564[a]		C107-5-1	C107-5-3	017-5	007-1-25	007-1-58	9-61			C107-5-2	C107-5-4	059-2	059-11
Radiation Dosage, 10^{10} ergs/g C	0		0.009[e]	0.09[e]	0.4[e]	0.9[b]	1.1[c]	6.8[d]			0.009[f]	0.09[f]	0.19[f]	0.90[f]
Viscosity, cs, °F														
800	3.67		3.32[h]	3.13[h]	2.85[h]		2.64[h]							
210	11.04		10.99	10.98	9.89	9.61	9.41	37.15			11.04	10.50	10.62	10.18
100	31.62		31.55	29.94	29.61	31.20	29.0	131.6			31.72	30.58	30.79	29.86
0						233	223							
-40	720						904	9,680						
-65	21.6		2093	1988	2029	3446	3169	97,363						
Pour Point, °F	(-80		(-80	(-80	(-80	(-80	(-80	(-80						
Flash Point, °F	400		450	450	425	410	425	415						
Spontaneous Ignition Temp., °F	720		740	730	750	740	740	840						
Specific Heat, Btu/lb/°F at 77°F	0.39													
Thermal Conductivity, Btu/hr-ft²-°F/ft at 77°F	0.082													
Bulk Modulus (adiabatic), psi														
At 0 psi and 77°F	209,000							221,000						
Foaming														
Volume, ml	650				110		25							
Stability, min	15				10		11							
Gassing During Irradiation, ml/g											0.6	1.0	1.0	2.0
Acid Number, mg KOH/g	0.07		0.13	0.16	0.12	0.06	nil	0.08						
Vapor Pressure at														
400°F, mm Hg	1.2		3.6		6.0		19	55						
500°F, mm Hg	17		24		50		62	-						
Oxidation Corrosion														
Time, hours	72	72	68	68	68	68	68	68	72	72	68			
Temperature, °F	347	400	400	450	400	500	400	500	347	400	500			
Weight Change, mg/cm²														
Cu	+0.05	+0.04	-0.13	-0.06	-0.67	-2.48	-0.93	-0.82	-2.06	-0.88	0			
Cu-Be	-	-	+0.05	-0.50	-0.26	-0.82	-0.16	+0.29	-	-	+0.52			
Ag	0	-0.08	0	-0.32	0	0	0	+0.07	+0.08	-0.18	-0.10			
Pb	0	-0.06	0	0	-0.03	0	+0.06	+0.10	+0.08	+0.04	-0.10			
Al	0	-0.02	0	-0.03	-0.08	0	+0.06	-0.06	+0.10	-0.08	-0.10			
Insolubles, %	nil	nil	nil	nil	nil	2.3	nil	nil	nil	nil				
Viscosity Change, 100°F, %	+8.0	-20.0	-30.4	-30.5	32.1	-22.1	-25.9	-34.2	-85.1	-38.8[i]				
Viscosity Change, 210°F, %	-6.5	-28.0	-28.1	-28.8	8.4	-33.0	-30.5	-30.5	-87.7	-41.2				
Neutralization Number Change	0.47	0.50	0.25	0.21	4.2	-	0.23	0.38	2.7	1.2				
Hydrolytic Stability 48 hours [illegible] test at 200°F														
Viscosity Change														
At 100°F, %	+2.1						-0.4		+20.1	+50.1				
At 210°F, %	+1.0			601			-8.5		-6.9	-15.8				
Insolubles, %	0.06		0.10				0.08		0.38	1.33				
Four-Ball Wear, mm														
2 Hours, 167°F, 4 kg Load	0.61	0.79								0.37				
10 kg Load	0.71	0.79								0.35				
40 kg Load	1.50	1.14								0.52				
Mean Hertz Load (screening test), kg	27	40			20	19		41						

[a] 200 ml irradiated in aluminum container open to air, Cal Research cobalt-60 source.
[b] 200 ml irradiated in tin-plated can open to air, WPB Canal Source.
[c] 200 ml irradiated in aluminum container open to air, WPB Canal Source.
[d] 1½ gallons irradiated in aluminum container open to air, WPB Canal Source.
[e] 1000 ml irradiated in heated aluminum container under nitrogen, WPB Canal Source.
[f] 10 ml irradiated in 410 stainless steel capsule under helium, WPB Canal Source.
[g] 410 ml irradiated in heated 410 stainless steel capsule at 400°F under helium, WPB Canal Source.
[h] At 41°F.
[i] Filter plugged.
[j] Density at 68°F = 0.911 g/cc.

TABLE LXI (continued)

PROPERTIES OF ORONITE 2000 FLUID AND HEXA(2-ETHYLBUTOXY)DISILOXANE BASE STOCK

Sample No.	Oronite Fluid						Hexa(2-ethylbutoxy)disiloxane								
	2K0-2	2K7-1-18	2K0-11	2K7-2-18	2K7-1-9	2K7-4-9	2K7-1-1	2K7-1-13	2K7-1-2K	2K7-2-40	2K7-6-20	2K0-1-3	2K7-1-25	2K7-3-10	2K7-4-10
Radiation Dosage, 10^{10} ergs/g C	1.0[f]	1.0[f]	2.0[f]	5.4[f]	10.0[g]	4.0[h]	0	0.24[f]	0.6[f]	1.2[f]	2.0[f]	3.0[f]	5.0[f]	0.1[g]	5.0[g]
Viscosity, cs. °F															
210	9.26	10.34	14.08	14.08	11.02	13.41	4.00	3.14	4.84	4.84	8.44	6.11	16.30	4.07	-
100	40.29	52.29	49.00	141.1	28.88	14.10	11.17	11.40	14.35	14.80	27.4	26.72	61.88	31.28	40.8
Gassing During Irradiation, ml/g	5.2	7.3	12.0	20.4	-	25.0	-	3.8	5.5	5.3	2.8	25.8	26.5	2.1	33.4

[a] 200 ml irradiated in aluminum container open to air, Lal Research cobalt-60 source.
[b] 200 ml irradiated in tin-plated can open to air, MTR Canal Source.
[c] 500 ml irradiated in aluminum container open to air, MTR Canal Source.
[d] 1 gallons irradiated in aluminum container open to air, MTR Canal Source.
[e] 1000 ml irradiated in heated aluminum container under nitrogen, MTR Canal Source.
[f] 10 ml irradiated in 41[illegible] stainless steel capsule under helium.
[g] 10 ml irradiated in heated 410 stainless steel capsule at 400°F under helium, MTR Canal Source.
[h] At 415°F.
[i] Filter plugged.
[j] Density at 68°F = 0.931 g/ml.

TABLE LXII

PROPERTIES OF COMMERCIAL SILICATE ESTER HYDRAULIC FLUIDS

Sample No.	G14838	G47-7-23	G67-1-27	G67-1-26	G59-1	G59-10	G67-1-26	G60-1	G60-10	G67-2-24	G14541	G47-7-24	G14357	G47-7-22	G59-3	G59-12	G60-3	G60-12
Fluid	8515										OS-45		OS-45-1					
Radiation Dosage, 10^{10} ergs/g C	0	1.1[a]	1.1[a]	5.1[a]	0.19[b]	0.30[b]	0.63[b]	1.0[b]	2.6[b]	2.8[b]	0	1.3[a]	0	1.0[a]	0.19[b]	0.30[b]	1.0[b]	2.6[b]
Viscosity, cs, °F																		
400	2.64		2.38[c]									1.09[c]		1.03[c]				
210	8.07	8.11	8.88	23.31	7.96	7.71	7.42	7.72	9.63	10.92	3.93	3.49	3.95	3.39	3.21	2.97	3.10	3.87
100	23.88	27.44	32.6	108.3	23.78	23.37	23.53	25.68	33.97	40.82	11.95	13.2	11.21	12.4	10.32	9.68	10.56	13.58
0	-	231	351	1889								178		159				
-40	-		1920									1140		1000				
-65	2285	4882		78,917							2609		2674					
Pour Point, °F	<-80	<-80	<-80	<-80								<-60	<-80	<-70				
Flash Point, °F	405	240	415	260							370	260	380	385				
Spontaneous Ignition Temp., °F	760	750	720	780								720		740				
Gassing During Irradiation, ml/ml					1.0	2.0	2.1	6.6	14.5	11.8					0.7	1.8	5.5	14.5
Acid Number, mg KOH/g	0.05	0.91	3.3	2.89								4.0	0.05	3.0				
Vapor Pressure at																		
400°F, mm Hg	2.0		165										10	44				
Oxidation Corrosion																		
Time, hours	72	48	48	48									72	48				
Temperature, °F	400	400	500	400									400	500				
Weight Change, mg/cm²																		
Cu	-0.05	-1.25	-0.10	-0.16									-0.87	-3.87				
Cu-Be	-	+0.06	+0.09	+0.03									-	-1.62				
Ag	-0.06	+0.13	+0.03	+0.06									-4.12	-2.10				
Fe	+0.04	0	-0.26	-0.29									0	-0.48				
Al	-0.04	+0.16	+0.06	+0.06									0	+0.06				
Insolubles, %	nil	nil	nil	nil									-	nil				
Viscosity Change, 100°F, %	-	-28.2	-58.9	-57.2									+1.6	+30.2				
Viscosity Change, 210°F, %	-28	-39.6	-56.2	-63.5									+21.9	+10.1				
Neutralization Number Change	0.50	0.24	0.46	0.57									0.08	0.9				

[a] 200 ml irradiated in tin-plated can open to air; MTR Canal Source.

[b] 10 ml irradiated in 410 stainless steel capsule under helium; MTR Canal Source.

[c] At 415°F.

TABLE [illegible]

THERMAL STABILITY TESTS
UNDER [illegible] IN [illegible] STAINLESS STEEL CAPSULES

Base Fluid	Additives	Neutron Dosage, 10^{18} n/cm^2	Batch No.	Temp. °F	Time, Days	Viscosity Change, % at 100°F	Viscosity Change, % at 210°F	Gas Evolved[a] cc/g	Remarks
C_{12}-C_{16}-Alkyl Diphenyl Ether	-	0	3868-61-1	600	20	-1.9	-1.5	0.7	
				650	20	-2.5	-11.6	0.6	
				700	20	-53.5	-39.8	30.6	
					20	-1.3	-3.0	0.8	
					20	-77.2	-58.0	8.0	
					6	-8.3	-1.9	0.8	
C_{12}-C_{16}-Alkyl Diphenyl Ether[b]		0	4658-5	600	20	-0.8	+0.7	-	
CALRESEARCH 216	-	0	4946-[illegible]	500[b]	20	-0.1	+0.6	-	
				500[b]	20	-2.9	-6.8	-	Red ppt. on cooling to 72°F
				600	20	-44.1	-34.6	1.0	"
				650	20	-65.4	-50.5	3.2	"
				700	20	-73.8	-59.7	5.8	"
					20	-90.1	-73.9	13.1	
					6	-78.5	-62.1	5.3	
CALRESEARCH 216	-	4.4	357-7	600	20	-44.4	-31.4	1.8	
				650	20	-75.3	-50.3	5.3	
				700	6	-72.8	-54.4	8.8	
					20	-93.0	-	22.5	
C_{12}-C_{16}-Alkyl Diphenyl Ether[c]	-	4.7	857-106	600	20	-53.0	-25.4	1.0	
				650	20	-51.5	-39.1	1.6	
				700	20	-91.3	-79.3	11.1	
				700	20	-58.6	-44.7	1.7	
		0.9	347-114	700	20	-2.7	+2.5	0.7	
C_{12}-C_{16}-Alkyl Diphenyl Ether[c]	0.001% DC	9.2	337-60	700	20	-9.6	-79.3	12.8	
C_{12}-C_{16}-Alkyl Diphenyl Ether[c]	0.001% DC	0.9	347-140	700	20	-37.7	-24.8	1.3	
n-Butyl Diphenyl Ether	-	0	4965-82	700	20	-29.9	-15.6	3.2	
Bis(1,1,3,3-tetramethylbutyl-phenyl) Ether	-	0	2.6770	600	20	-27.1	-6.2	-	
C_{12}-C_{16}-Alkyl Diphenyl Ether (dist.)		0	5018-61-1	700	20	-83.4	-66.2	15.6	
Dodecyl Diphenyl Ether	10% PB 126	0	4830-55-1	600	20	-2.4	-9.9	-	
Undecyl Diphenyl Ether	2% Paratone N	0	4830-55-2	600	20	-18.8	-25.8	-	
Dodecyl Diphenyl Ether	10% Piccolastic A-5	0	4830-55-3	600	20	-6.8	-4.0	-	
Dodecyl Diphenyl Ether	10% Dow Resin V-4	0	4830-55-4	600	20	-14.6	-8.1	-	
C_{12}-C_{16}-Alkyl Diphenyl Ether[c]	2% DBPC + 0.001% DC	0	4898-9-1	700	20	-9.1	-2.7	0.7	
C_{12}-C_{16}-Alkyl Diphenyl Ether[c]		0.9	347-146	700	20	-34.5	-21.0	1.0	
C_{12}-C_{16}-Alkyl Diphenyl Ether[c]		9.2	337-68	700	20	-83.5	-62.7	8.9	
C_{12}-C_{16}-Alkyl Diphenyl Ether[c]		4.7	347-100	700	20	-92.0	-79.4	13.8	
	2% C_{18}Se + 0.001% DC	0	4898-9-7	700	20	-34.4	-19.1	1.3	"
		0.9	347-148	700	20	-72.8	-54.8	5.4	
		9.2	337-60	700	20	-50.4	-39.8	0.3	"
		4.7	347-100	700	20	-90.2	-76.5	9.5	"
C_{12}-C_{16}-Alkyl Diphenyl Ether[c]	-	2.5	347-8-21	700	20	-51.6	-26.3	1.9	
C_{12}-C_{16}-Alkyl Diphenyl Ether[c]	2% C_{18}Se + 0.001% DC	4.4	347-8-23	700	20	-19.5	-12.6	2.2	
C_{12}-C_{16}-Alkyl Diphenyl Ether	14% PB 12A + 2% DBPC + 0.001% DC	0	4946-23-1	700	20	-98.0	-	16.6	
C_{12}-C_{16}-Alkyl Diphenyl Ether	14% PB 12A + 0.5% DNPD + 0.001% DC	0	4946-23-6	700	20	-25.2	-21.9	-	
C_{12}-C_{16}-Alkyl Diphenyl Ether	5% LM-MB + 2% C_{18}Se + 0.001% DC	0	4946-23-3	700	20	-47.1	-56.8	11.4	"
C_{12}-C_{16}-Alkyl Diphenyl Ether	1.5% S-50 + 2% C_{18}Se + 0.001% DC	0	4946-23-4	700	20	-86.6	-78.4	5.4	"
C_{12}-C_{16}-Alkyl Diphenyl Ether	2.6% S-60 + 2% C_{18}Se + 0.001% DC	0	4946-23-5	700	20	-69.6	-64.9	9.9	"
C_{12}-C_{16}-Alkyl Diphenyl Ether	14% PB 12A + 0.5% DNPD + 2% $BiMe_3$ + 0.001% DC	0	4946-23-7	700	20	-87.7	-75.7	10.6	"
C_{12}-C_{16}-Alkyl Diphenyl Ether	14% PB 12A + 0.5% Phenothiazine + 0.001% DC	0	4946-23-13	700	20	-94.4	-85.2	4.6	
C_{12}-C_{16}-Alkylbiphenyl[c]	-	0	D01269	700	20	-1.0	-1.0	0.5	
C_{12}-C_{16}-Alkylbiphenyl (dist.)	-	0	5018-41-1	600	20	-3.6	-2.6	0.7	
					20	-1.3	-0.7	-	
				650	20	-11.5	-7.3	0.7	
				700	6	-16.9	-11.1	0.7	
					20	-65.2	-39.0	8.3	
					20	-3.4	-1.7	1.1	
					20	-79.1	-54.2	8.9	
C_{12}-C_{16}-Alkylbiphenyl (dist.)	0.001% DC	0.9		700	20	-	-	10.7	
C_{12}-C_{16}-Alkylbiphenyl (dist.)	-	8.7	347-108	600	20	-27.8	-3.7	1.0	
				650	20	-38.6	-23.9	1.0	
				700	6	-86.6	-33.1	13.6	
					20	-74.5	-65.8	3.7	
					20	-18.3	-12.2	2.1	
Naphthenic White Oil	-	0	D01259	600	20	-3.0	-1.7	-	
				650	20	-19.1	-15.3	0.7	
				700	20	-67.2	-41.2	5.8	
					20	-63.0	-36.6	3.3	
		0.9	347-116	700	20	-94.0	-79.1	38.8	
Naphthenic White Oil	-	9.2	337-64	700	20	-78.1	-57.8	1.4	
Naphthenic White Oil	2% C_{18}Se	4	5018-80-1	700	20	-82.8	-59.8	15.9	
		0.9	347-110	700	20	-14.0	-8.6	1.2	
Naphthenic White Oil	2% DBPC	4	5018-10-2	700	20	-19.5	-8.2	0.5	
		0.9	347-110	700	20	-46.7	-26.4	1.8	
		4.4	337-60	700	20	-94.3	-78.1	9.5	
RP20 Fluid	-	0	3.4566	600	20	-47.6	-67.3	-	
					20	-67.6	-67.8		
				700	20	-80.7	-	74.1	
RP20 Fluid		2.7	337-5-1	600	20	-83.7	-	2.9	
				700	20	-32.9	-	51.0	
		0.9	347-158	700	20	-66.5	-61.9	1.8	
C_{12}-C_{16}-Alkylbiphenyl (dist.)	2% DBPC + 0.001% DC	0.9	347-1[illegible]C	700	20	-84.8	-67.6	17.5	
C_{12}-C_{16}-Alkylbiphenyl (dist.)	2% C_{18}Se + 0.001% DC	0.9	347-1[illegible]D	700	20	-88.1	-69.7	19.9	
Union DLR 1446	-	0	3.4582	600	20	-57.4	-	-	
Union DLR 1446	-	0.9	347-125	700	20	-	-	-	"
Union DLR 1446	2% C_{18}Se + 0.001% DC	0.9	347-1[illegible]A	700	20	-	-	-	"
Dibutyl Sebacate	-	0	3.8137	600	20	-38.5	-	-	Solid No. 06.2
Dibutyl Terephthalate	-	0	D01264	600	20	-	-	-	Solid ppt.[f]
9.15 Fluid	-	1.2	347-7-23	700	20	-50.3	+26.5	26.9	
08.45	-	1.3	347-7-24	700	20	-59.9	-47.0	10.2	
08.45-1		1.0	347-7-22	700	20	-27.5	-24.1	1.8	

[a] Bottoms product.
[b] Run in glass capsule.
[c] Blank cast in stainless steel capsule.
[d] Exposed in RPIT No. 2 static irradiation at Convair.
[e] Sufficient pressure generated to rupture capsule (estimated as 1000 psi minimum).
[f] Solid was identified as terephthalic acid.

The two base stocks of greatest interest, C_{14-16}-alkyl diphenyl ether and C_{16-18}-alkylbiphenyl, showed good stability in 20-hour tests at 600° F and 6-hour tests at 700° F. In 20-hour tests, decomposition was moderate at 650° F and usually heavy at 700° F. Irradiation reduced stability; significant decomposition occurred at 600°F on irradiated stocks.

Of the other base stocks tested, naphthenic white oil also was satisfactory at 600° F and moderately decomposed at 650° F. UCON DLB 144E, diisooctyl azelate, and diisooctyl terephthalate were unstable at 600° F. The polyglycol, in particular, developed very high pressures in the test at 700° F after irradiation, causing rupture of the steel capsules.

CALRESEARCH 216 was stable in 400°F thermal stability tests. At 500° F (20 hours in glass), a moderate viscosity decrease occurred, accompanied by a reddish precipitate on cooling to room temperature. This precipitate was probably metallic selenium from decomposition of the selenide inhibitor. At higher temperatures in 410 stainless steel capsules, larger viscosity decreases occurred, accompanied by the formation of a black coating on the inside of the vessel. The fluids remained clear, indicating that the selenium had reacted with the steel. In these thermal stability tests, the major effect of irradiating CALRESEARCH 216 appeared to be an increase in the gas evolution rate.

All blends containing V.I. improvers showed substantial decomposition, even in 600° F thermal stability tests. Polybutene 128 lost less of its thickening power in 600° F tests than any of the other hydrocarbon V.I. improvers being considered for use in the alkyl aromatics. The effect of inhibitors is not clearly defined by the available data. However, no blends satisfactory for 20 hours at 700° F were found. Irradiation of blends decreased stability as in the case of the base stocks.

4.6 Hydraulic Pump Tests

During 1957, four hydraulic pump tests were run using New York Air Brake 66WA300 pumps. Each pump was operated 150 hours at 160° F, followed by 100 hours at 275° F. As these were standard production pumps, operation at higher temperatures was not attempted.

Initially, tests were run to determine the operability and lubricity of a selenide-inhibited alkyl aromatic blend. Fluid O-1A[1] (developed earlier on AEC Contract AT(11-1)-174) was tested both before and after irradiation to 4.4×10^{10} ergs/g C. The composition of Fluid O-1A was as follows:

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

	Weight Per Cent
Mixed Alkylbenzenes (MW ~250)	74.45
Dow Resin V-9	15.00
Polybutene 128	5.50
Didodecyl Selenide	5.00
Quinizarin	0.05
	100.00

The fluid was not intended for high temperature use, as it had a viscosity at 210° F of 3.46 cs and a flash point of 260° F[1]

Results of pump tests on Fluid O-1A are given in Table LXIV and Figures 18 and 19. The pump operated satisfactorily on both the new and irradiated fluids. Wear of the bronze creep plate bearing was considerably higher with the irradiated oil. In the 275° F portion of the run, wear on the pistons, which had a bronze bearing surface, was also somewhat increased. Considerable darkening of nonload carrying surfaces of the bronze parts occurred during operation on the irradiated oil. Corrosion of silver and copper specimens immersed in the reservoir was also observed with irradiated O-1A at 275° F. None of the detectable changes affected the satisfactory operation of the pumps.

Results of tests on CALRESEARCH 216 are also shown in Table LXIV and in Figures 20 and 21. Again, the pumps operated satisfactorily on both original and irradiated fluids. However, in this case irradiation did not increase wear of bronze parts. After the 275° F run on the irradiated oil, pronounced blackening of the bronze surface was evident.

Viscosity changes of the fluids are shown in Figure 22. Both Fluid O-1A and CALRESEARCH 216 were V.I. improved with Polybutene 128. The pressure reduction in the pump test system occurred by loading on a fixed orifice followed by a Vickers pressure relief valve. This resulted in severe shearing conditions. The maximum viscosity change noted in any of the tests was well under 10%, indicating good shear stability for the fluids. The irradiated oils increased slightly in viscosity, during the pump tests, presumably due to loss of volatile radiolysis products.

These four tests establish the operability of alkylbenzene and alkyl diphenyl ether fluids containing selenide inhibitors in a currently available hydraulic pump. The successful results make further tests in high temperature pumps highly desirable.

[1] "Effects of Radiation on Aircraft Lubricants and Fuels," (California Research 1956 Summary Report on Contract AF 33(616)-3184) WADC Technical Report 56-646, p. 95.

TABLE LXIV

RESULTS OF NEW YORK AIR BRAKE HYDRAULIC PUMP TESTS
MODEL 66WA300
PRESSURE, 3000 PSI; FULL DELIVERY, 3450 RPM.
WEIGHT LOSS IN MILLIGRAMS

Fluid	O-1A[a]				CALMESEARCH 210[b]			
Dosage, ergs/g C x 10^{10}	0		4.4		0		4.4	
Run No.	NY-9		NY-10		NY-11		NY-12	
	150 Hours at 160°F	100 Additional Hours at 275°F	150 Hours at 160°F	100 Additional Hours at 275°F	150 Hours at 160°F	100 Additional Hours at 275°F	150 Hours at 160°F	100 Additional Hours at 275°F
Nutating Plate	6.0	16.2	12.9	19.6	2.8	10.9	6.9	8.8
Nutating Plate Pivot	0	0.7	1.5	5.4	0.5	0.2	1.3	4.9
Creep Plate	4.2	0.6	2.2	6.0	2.6	1.0	16.8	2.7
Bronze Creep Plate Bearing	182.5	97.8	923.0	550.5	533.3	267.6	50.4	194.7
Nine Pistons - Average	2.7	5.7	4.6	18.4	2.4	4.0	2.1	2.9
Maximum	5.1	16.4	6.6	25.1	4.2	8.1	3.0	3.6
Nine Piston Return Collars - Average	0.1	1.1	2.6	2.2	0.8	0.2	2.2	0.7
Maximum	0.6	1.6	4.1	5.1	1.5	0.5	3.0	1.4
Nine Piston Sleeves - Average	0.7	4.0	0.3	0.3	0.4	0.1	0.1	0.2
Maximum	1.6	9.5	0.8	0.9	0.7	0.4	0.4	0.5
Nine Check Valves - Average	0	0	0.8	2.7	0.6	0.9	0.3	1.3
Maximum	0	0	1.6	3.2	0.7	1.4	0.6	2.8
Corrosion Specimens[c] - Wt. Change, mg								
Copper	-	0	-0.7	-15.6	-0.1	0	0	-0.5
Beryllium-Copper	-	0	-0.5	-1.3	0	0	0	-0.5
Steel	-	0	0	0	0	0	0	0
Aluminum	-	0	-0.4	0	0	0	-0.2	-0.3
Silver	-	0	-0.7	+12.4	-0.6	0	0	-0.3

[a] Based on alkylbenzene (MW 250).

[b] Based on C_{16-18}-Alkyl diphenyl ether.

[c] One-inch square specimens located in reservoir.

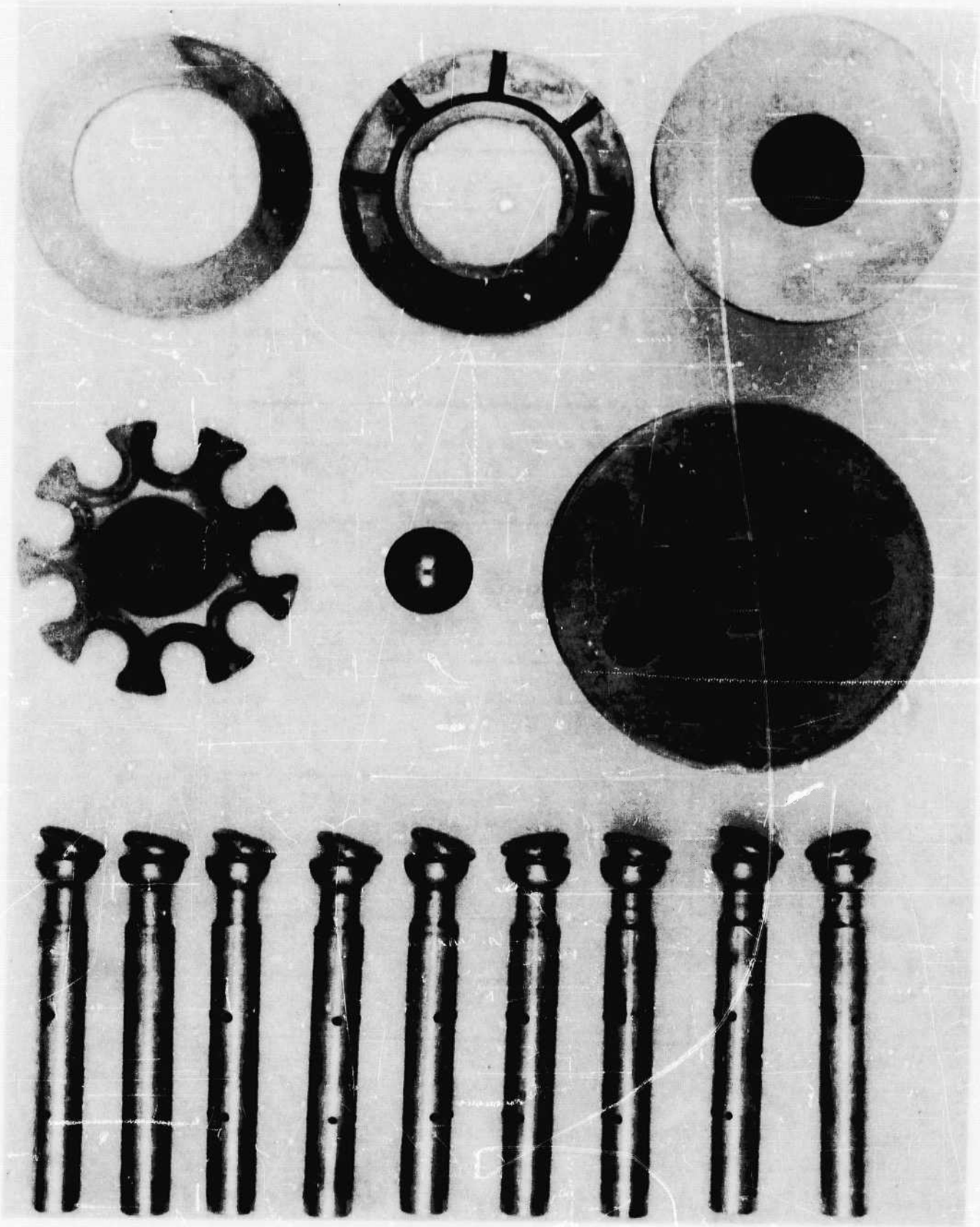


FIG. 18 - PUMP PARTS AFTER TEST NY-9

FLUID O-1A PRESSURE 3000 PSI SPEED 3450 RPM
150 HOURS AT 160°F AND 100 HOURS AT 275°F
NEW YORK AIR BRAKE MODEL 66WA300 PUMP

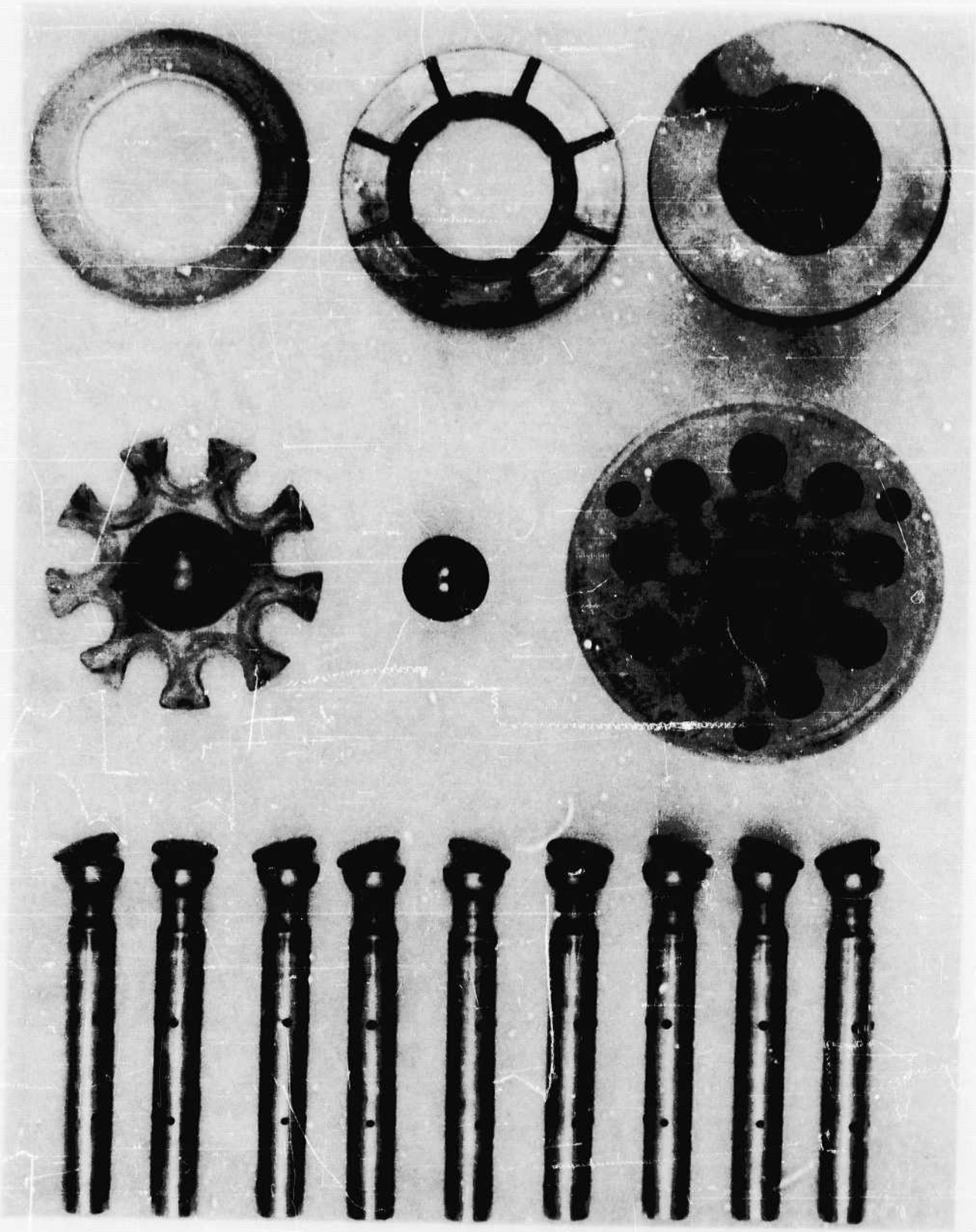


FIG. 19 - PUMP PARTS AFTER TEST NY-10

FLUID O-1A IRRADIATED TO 4.4×10^{10} ERGS/g. C
PRESSURE 3000 PSI SPEED 3450 RPM
150 HOURS AT 160°F AND 100 HOURS AT 275°F
NEW YORK AIR BRAKE MODEL 66WA300 PUMP

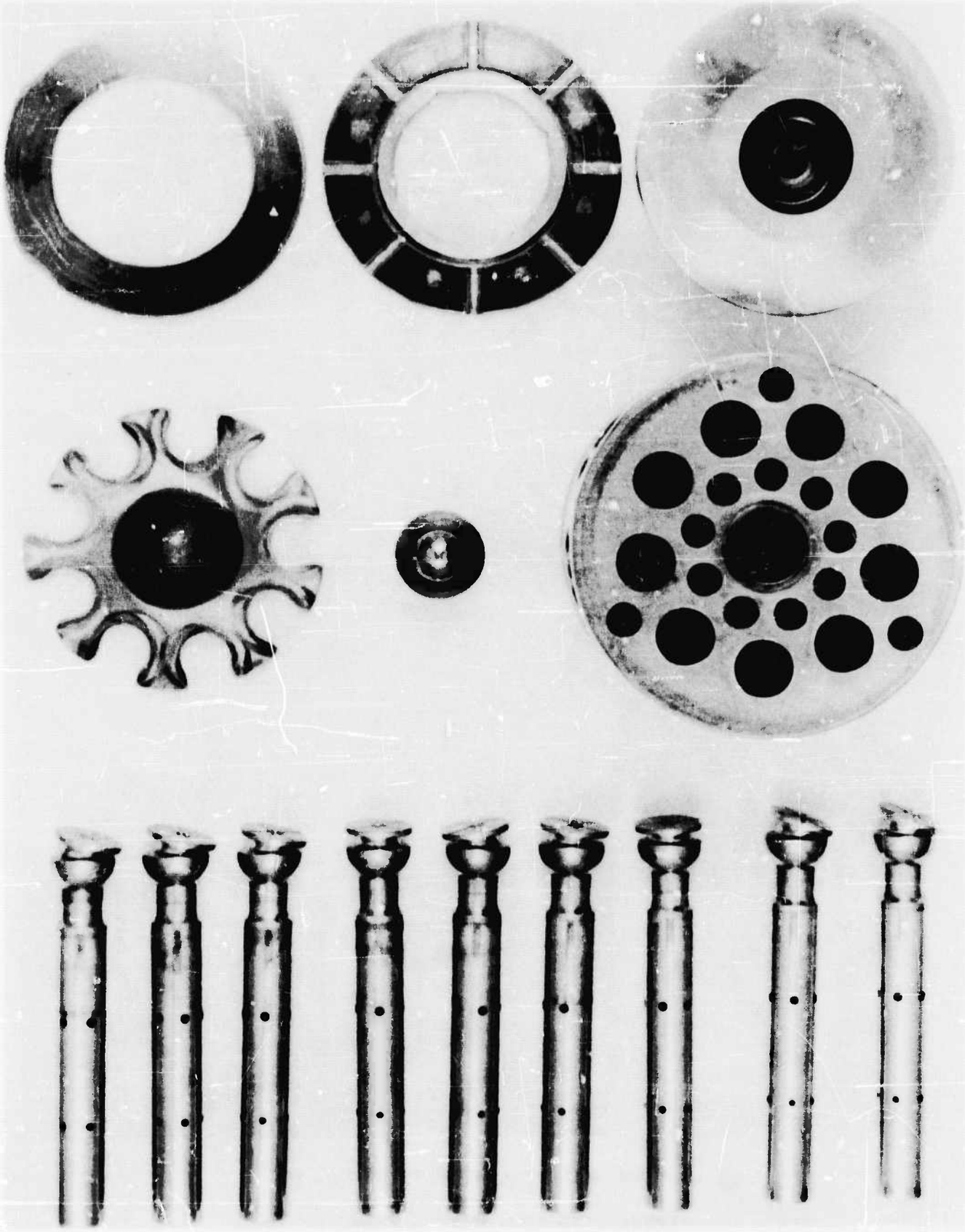


FIG. 20 - PUMP PARTS AFTER TEST NY-11

FLUID CALRESEARCH 216 PRESSURE 3000 PSI SPEED 3450 RPM
150 HOURS AT 160°F AND 100 HOURS AT 275°F
NEW YORK AIR BRAKE MODEL 66WA300 PUMP

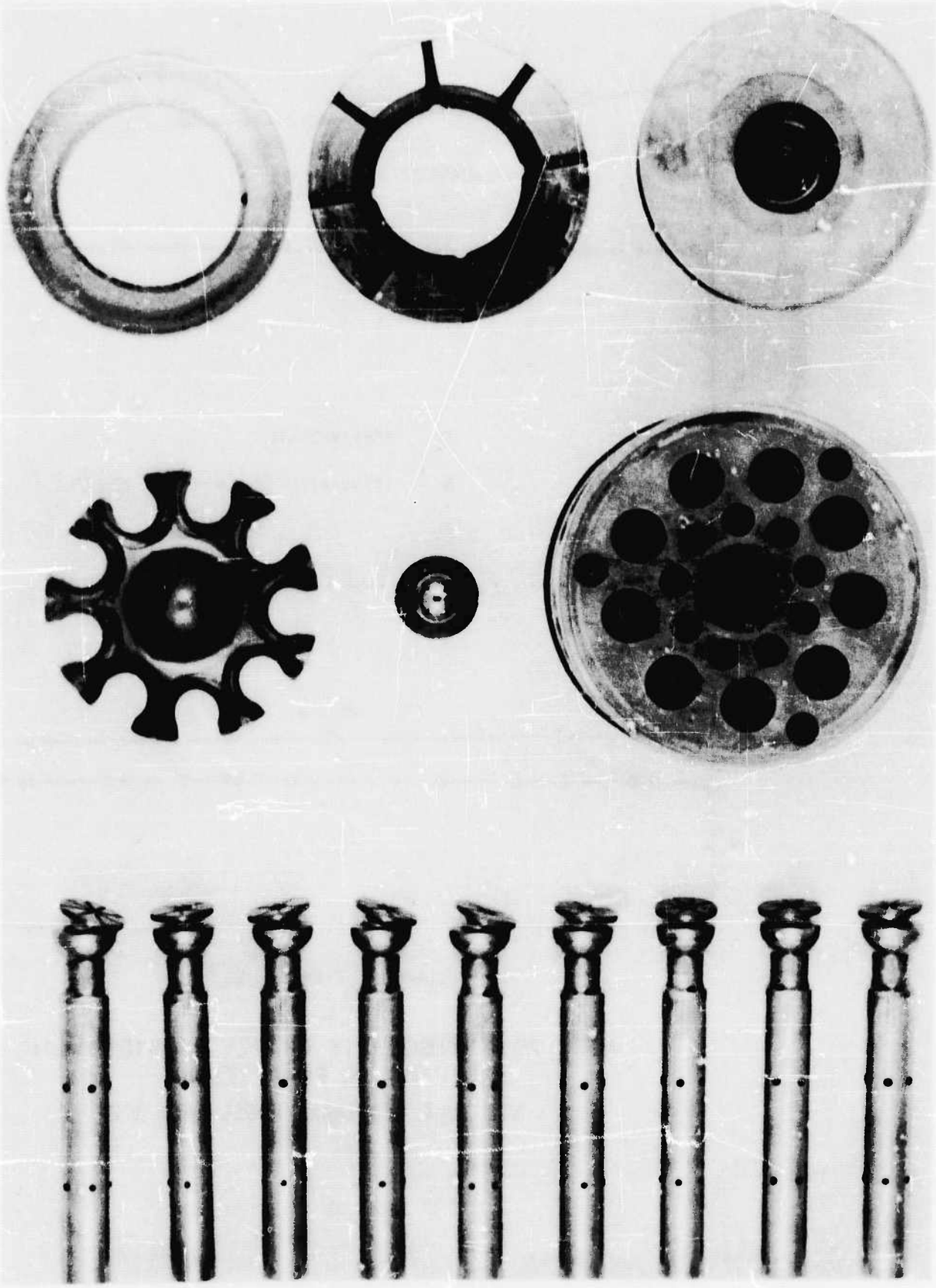


FIG. 21 - PUMP PARTS AFTER TEST NY-12

FLUID CALRESEARCH 216 IRRADIATED TO 4.4×10^{10} ERGS/g. C
PRESSURE 3000 PSI SPEED 3450 RPM
150 HOURS AT 160°F AND 100 HOURS AT 275°F
NEW YORK AIR BRAKE MODEL 66WA300 PUMP

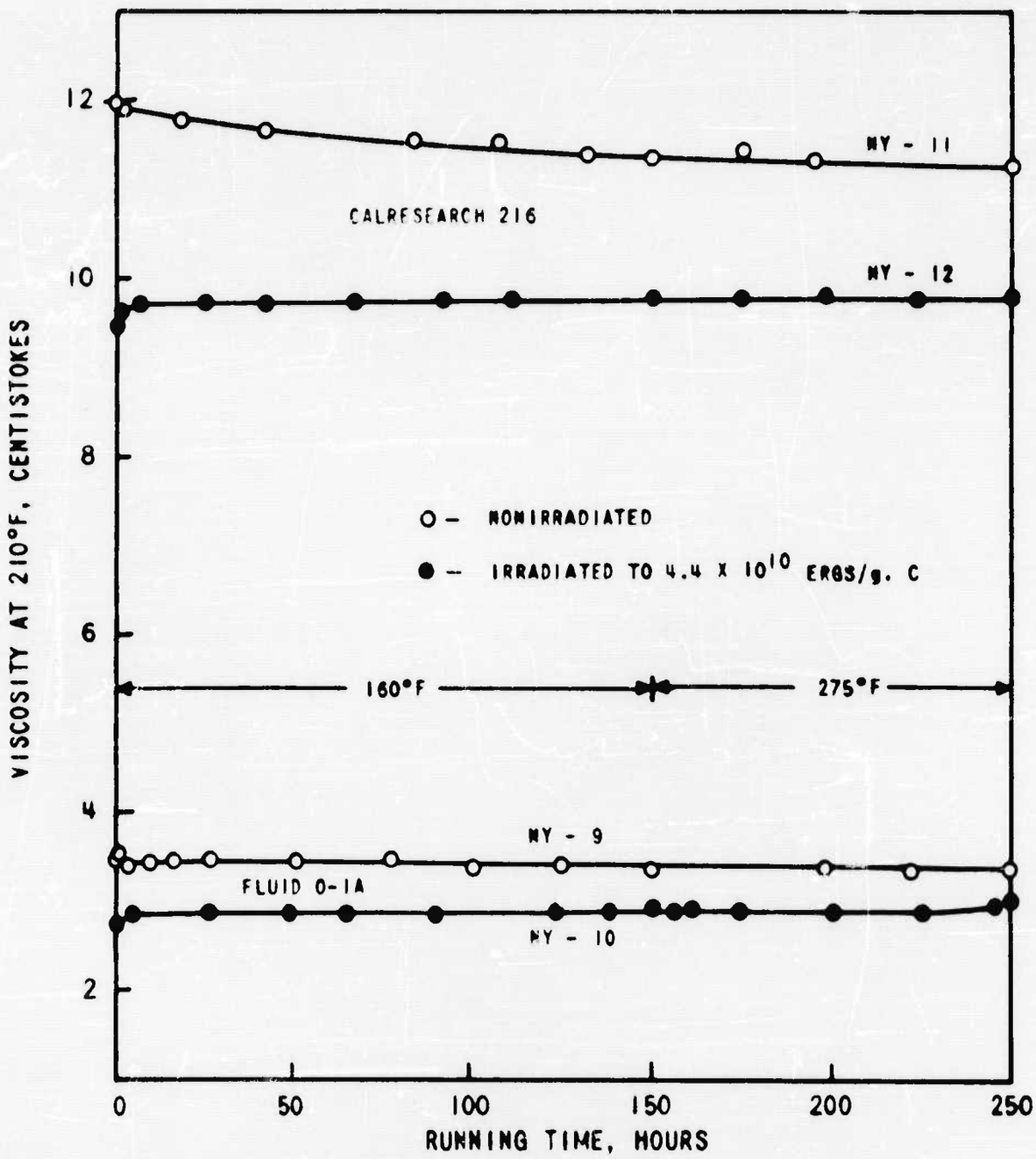


FIG. 22 - VISCOSITY CHANGE OF HYDRAULIC FLUIDS IN PUMP TESTS

NEW YORK AIR BRAKE MODEL 66WA 300

4.7 Bulk Modulus

4.7.1 Isothermal Bulk Modulus of Hydraulic Fluids in the Presence of Hydrogen

The presence of gas, either dissolved or as a second phase, can have an adverse effect on the performance of hydraulic systems. The natural frequency and the region of stable operation of the system are dependent on the bulk modulus of the hydraulic fluid. As gas evolution is one of the characteristic results of exposure to nuclear radiation and this gas is mostly hydrogen[1], P-V-T measurements were made on mixtures of hydrogen with hydraulic fluids. The three fluids used, MIL-0-5606 (now MIL-H-5606A) fluid, Oronite High Temperature Hydraulic Fluid 8200, and C_{14-16}-alkyl diphenyl ether, were representative of petroleum, silicate ester, and alkyl aromatic fluids, respectively.

As a result of this work, a paper[2] was prepared and presented at the Second WS-125A Radiation Effects Symposium. It is attached as Appendix X. Conclusions reached are summarized as follows:

a. A gaseous phase causes a very large reduction in bulk modulus even at pressures only slightly below the saturation pressure.

b. Dissolved gas decreases bulk modulus as the quantity of gas increases, but the effect is small compared to that caused by the presence of a gas phase.

c. The degassed fluids listed in decreasing order of their isothermal bulk moduli are C_{14-16}-alkyl diphenyl ether, MIL-0-5606 fluid, and 8200 fluid.

d. The order of decreasing solvency for hydrogen is 8200 fluid, MIL-0-5606 fluid, C_{14-16}-alkyl diphenyl ether.

e. Considering gas evolution rate and solubility for hydrogen, the order of decreasing allowable radiation dosage before reaching the two-phase region is C_{14-16}-alkyl diphenyl ether, 8200 fluid, MIL-0-5606 fluid.

f. The fluid in an operating hydraulic system should be kept in the single-phase region by an appropriate choice of hydraulic fluid species, radiation dosage, return pressure, temperature, and by venting evolved gases.

[1] "Effects of Radiation on Aircraft Lubricants and Fuels," (California Research 1956 Summary Report on Contract AF 33(616)-3184) WADC Technical Report 56-646, p. 106.

[2] R. L. Peeler and H. S. Yaplee, "Isothermal Bulk Modulus of Hydraulic Fluid-Hydrogen Mixtures," Proceedings, Semiannual 125A Radiation Effects, Vol II, Section 10, Battelle Memorial Institute, Columbus, Ohio, October 23, 1957.

Because of the importance of the two-phase region in limiting hydraulic system performance, a comparison of measured and calculated bulk modulus was desirable. Measured data were taken from Appendix X, calculations were made from the formula developed in Appendix XI. The comparisons are made in Figure 23. Except for the 24.4 gas:liquid ratio above 3000 psi, agreement appears satisfactory. Therefore, given the bulk modulus of a liquid, the solubility of hydrogen in it, and the hydrogen:liquid ratio, the bulk modulus of a two-phase mixture (at equilibrium) can be calculated as a function of pressure from the data in Appendixes X and XI, with an accuracy adequate for engineering purposes.

4.7.2 Adiabatic Bulk Modulus

The adiabatic bulk modulus of several types of hydraulic fluids was determined by the ultrasonic velocity method[1], both before and after irradiation of the fluids. Results are shown in Table LXV. The well known effect of aromaticity in increasing bulk modulus is evident[2]. Within experimental error, irradiation did not affect bulk modulus.

4.8 Results of Cooperative Tests

Oronite High Temperature Hydraulic Fluid 8200 was chosen by Vickers, Inc., as the fluid component of an operating hydraulic system for irradiation in the Nuclear Aircraft Research Facility (NARF), at Convair, Fort Worth. Results of tests on fluids removed periodically from the system during the Systems Panel Irradiation Test No. 2 (SPIT No. 2) are shown in Table LXVI.

Because the system was operated before inserting into the reactor, the viscosity of the fluid was reduced by shear breakdown prior to irradiation. At the relatively low radiation dose rate encountered, the point of marked viscosity increase due to radiation damage was not reached. The viscosity of the fluid appeared to be leveling off at around 8.5 cs at 210°F. No reduction in flash point was found, as measured by the relatively insensitive microapparatus.

Oxidation stability at 400°F was not markedly affected by the amount of irradiation received in this test. Hydrolytic stability, although a sensitive property of silicate base fluids, was affected only slightly through 300 hours of operation. Both the 400- and 500-hour samples, however, showed heavy deposition of insolubles.

[1] R. L. Peeler and J. Green, "Measurement of Bulk Modulus of Hydraulic Fluids," to be presented at ASTM Meeting, Houston, February 1958.

[2] L. Bergmann, "Ultrasonics," John Wiley and Sons, New York, 1938.

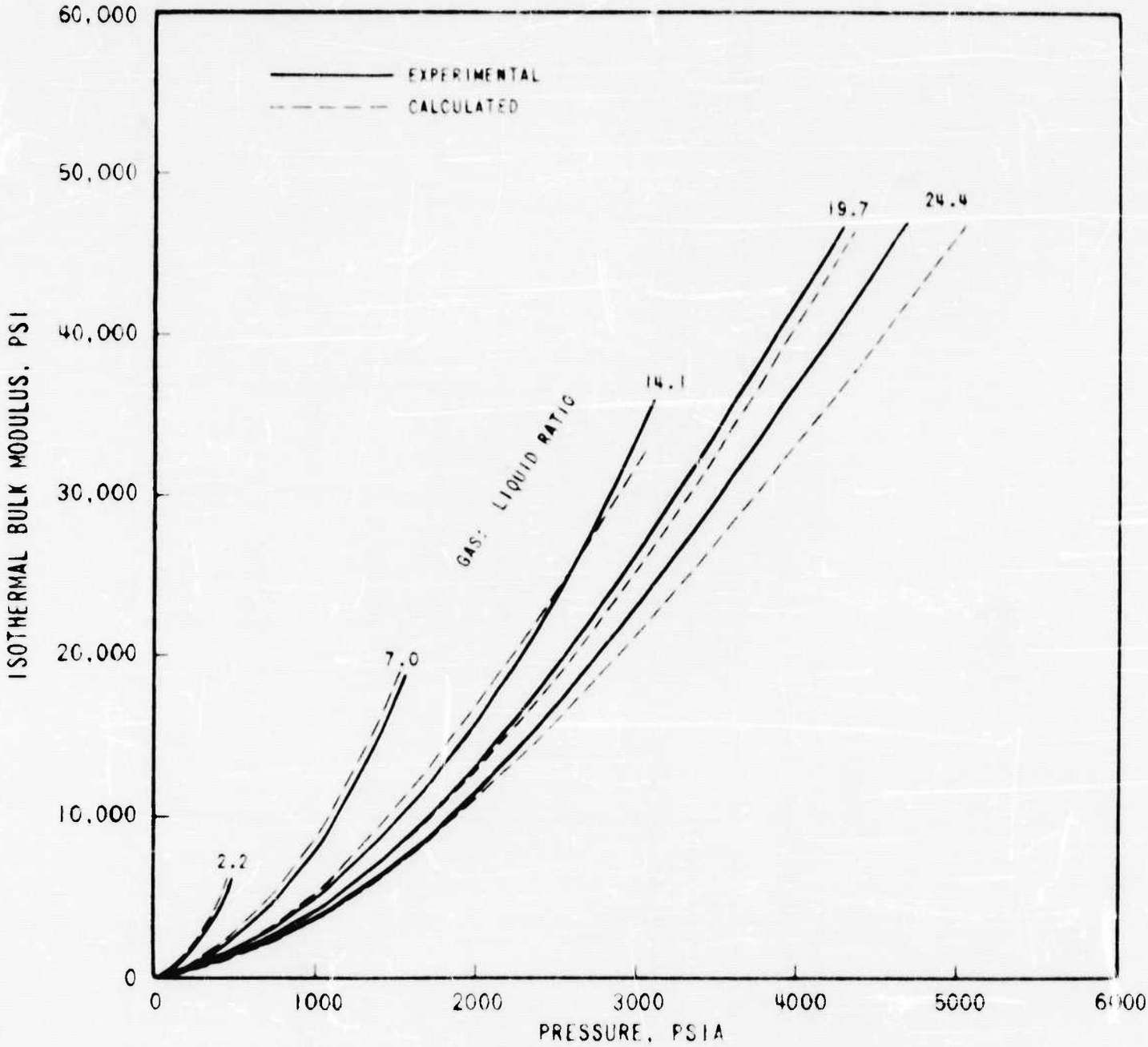


FIG. 23 - COMPARISON OF CALCULATED AND EXPERIMENTAL VALUES FOR TWO-PHASE BULK MODULUS OF HYDROGEN-8200 FLUID MIXTURES AT 200°F

TABLE LXV

EFFECT OF IRRADIATION ON ADIABATIC BULK MODULUS OF HYDRAULIC FLUIDS AT ATMOSPHERIC PRESSURE AND 76°F

Fluid	Additives	Sample No.	Bulk Modulus Before Irradiation, psi	Sample No.	Gamma Dosage, 10^{10} ergs/g C	Bulk Modulus After Irradiation, psi
CALRESEARCH 216	-	4946-16	290,000	G67-7	4.4	290,000
8200 Fluid	-	G14838	209,000	G-61	6.8	221,000
C_{16-18}-Alkylbiphenyl	-	DG 1269	280,000	G17-4A	8.7	291,000
Tetradecyl Diphenyl Ether		4658-3	269,000	G17-6D	6.5	288,000
Ucon DLB 144E	-	G14580	232,000	-	-	
Ucon DLB 144E	2% $C_{12}Se$ + 0.001% DC	-	-	G17-6A	6.5	249,000
Alkylbenzene (MW = 250)	-	SL 541	226,000	-	-	
Diisooctyl Terephthalate	-	DG 1264	270,000	-	-	

TABLE LXVI

PROPERTIES OF ORONITE P200 FLUID FOLLOWING IRRADIATION IN NARF SPIT NO. 2 TESTS

	Unused Fluid	Fluid Taken From Test Stand at Fort Worth						
Sample No.	014566	5014-5-1	5014-5-2	5014-5-3	5014-5-4	5014-5-5		5014-5-6
Time in Convair Source, hours	0	0	100	200	300	400		500
Radiation Dosage[a]								
Gamma, 10^{10} ergs/g C	0	0	0.021	0.051	0.081	0.097		0.13
Thermal, neutrons/cm² 10^{12}	0	0	13	32	51	62		85
Epicadmium, neutrons/cm² 10^{12}	0	0	16	39	62	75		103
Viscosity, cs, °F								
414	3.52	3.15						2.49
210	11.04	10.79	9.68	9.15	8.48	8.56		8.57
100	31.62	30.77	28.00	26.54	24.25	24.76		24.86
-65	2116	2088	2197	1924	2.083	1813		1784
Pour Point, °F	<-80	<-80	<-80	<-80	<-80	<-80		<-80
Flash Point, °F	400	400	410	400	420	405		400
Spontaneous Ignition Temp., °F	720	740	740	740	760	740		740
Density at 68°F, g/ml	0.931	0.9279	-	-	-	-		0.9277
Acid Number, mg KOH/g	0.07	0.38	0.40	0.42	0.40	0.42		0.41
Oxidation Corrosion								
Time, hours	72	48	48	48	48	48	48	48
Temperature, °F	400	400	400	400	400	400	400	400
Weight Change, mg/cm²								
Cu	+0.04	+0.19	+0.13	-0.16	-0.16	+0.03	0	-0.29
Cu-Be	-	+0.06	-0.42	-0.45	-0.19	0	+0.03	-0.35
Ag	-0.04	-0.06	0	-0.23	+0.26	-0.03	0	-0.19
Fe	-0.05	+0.13	+0.19	0	-0.03	-0.03	+0.06	-0.26
Al	-0.02	+0.06	+0.23	-0.19	-0.06	0	-0.10	-0.19
Insolubles, %	nil	nil	nil	nil	nil	nil	nil	nil
Viscosity Change, 100°F, %	-20.0	-15.4	-28.0	-18.7	-13.3	-19.4	-17.4	-17.3
Viscosity Change, 210°F, %	-28.0	-22.4	-41.1	-34.8	-23.0	-39.9	-25.6	-32.0
Neutralization Number Change	0.50	0.18	nil	2.4	0.28	nil	nil	0.41
Hydrolytic Stability 48 hours at 200°F in "Coke Bottle" test								
Viscosity Change, %								
At 100°F	+2.1	+2.3	+0.3	+2.5	+4.4	b		+49.2
At 210°F	+1.0	-0.9	+1.9	-3.0	-6.5	b		+20.4
Insolubles, %	0.05	0.05	0.03	0.18	0.24	b		5.61
Neutralization Number Change	nil	nil	nil	-	-	b		-
Copper Wt. Change, mg/cm²	-0.01	-0.02	-0.03	-0.03	+0.01	-0.01		-0.05

[a] Data from Fourth Information Brochure for Systems Panel Test No. 2, Convair.

[b] Gelatinous.

The hydraulic system was reported to have operated satisfactorily throughout the entire test[1]. Likewise, Dr. R. N. Miller[2] of Lockheed Aircraft Company reported satisfactory operation of a hydraulic system using 8200 fluid in a gamma radiation environment. These results, in conjunction with earlier[3] data, show that 8200 fluid can be used successfully in hydraulic systems exposed to moderate radiation dosages.

4.9 Conclusions

The conclusions reached in the hydraulic fluid work covered in this section are summarized as follows:

a. Alkyl aromatics and diphenyl ethers have many of the properties required for radiation resistant hydraulic fluids. The two materials of greatest promise from this work are C_{14-16}-alkyl diphenyl ether and the C_{16-18}-alkylbiphenyl (distilled). The presence of the long alkyl group imparts good liquid range and viscosity-temperature properties, while the aromatic portion gives good radiation resistance. The usable range of these materials is from temperatures below 0° F to the upper thermal stability limit, which lies between 600° F and 700° F.

b. The C_{14-16}-alkyl diphenyl ether is preferred to the C_{16-18}-alkylbiphenyl because of its better viscosity-temperature properties and good oxidation stability at 500° F. The pour point of the diphenyl ether, though higher than that of the distilled biphenyl, can be dropped by increasing the ratio of tetradecyl to hexadecyl groups.

c. Inhibitors, particularly organic selenides, improve the oxidation stability of both the alkyl aromatics and conventional base stocks before irradiation. After irradiation, inhibitors reduce damage as measured by viscosity change and oxidation stability at 400° F and 500° F. The effect decreases as the aromaticity of the base stock increases. However, inhibitors are still markedly beneficial in the alkyl aromatics selected for use in hydraulic systems.

d. A finished hydraulic fluid, CALRESEARCH 216, was prepared from the C_{14-16}-alkyl diphenyl ether, Polybutene 128, bis(tridecyl) selenide, and dimethyl silicone. It has excellent radiation stability, withstanding a dosage of 10×10^{10} ergs/g C with only a slight viscosity increase. Oxidation stability gradually decreases upon irradiation; but even at the highest dosages, the fluid remains liquid after the 500° F oxidation and corrosion tests.

[1] "Fourth Information Brochure for Systems Panels Test No. 2," p. 100, Convair, Fort Worth.

[2] R. N. Miller, "The Effect of Radiation Upon the Response Characteristics of a Flight Control System," Second WS-125A Symposium on Radiation Effects, Columbus, Ohio, October 22, 1957.

[3] N. W. Furby, "Operation of Hydraulic Pumps on Irradiated Fluids," First 125A Radiation Effects Symposium, 22-23 May 1957, ANP Document No. NARF-57-197, FZK-9-118, Vol 1.

The use of selenide inhibitor makes CALRESEARCH 216 corrosive to metals at high temperatures. Neither the inhibitor nor the V.I. improver is as thermally stable as the diphenyl ether base stock. Thus, the resulting blend has reduced stability. Raising the temperature of irradiation to 400° F causes a greater viscosity change in the blended fluid but not in the base stock.

e. The allowable radiation dosage for 8200 fluid is about 10^{10} ergs/g C. The addition of aromatic additives to 8200 fluid markedly increases radiation stability. The aromatics tested have an adverse effect on the physical properties of the blend[1].

f. Naphthenic white oil, even with inhibitors, is unattractive as a possible hydraulic fluid base stock from the standpoint of viscosity-temperature properties, 500° F oxidation stability, and radiation stability.

g. UCON DLB 144E has good radiation stability for an aliphatic material. In high temperature oxidation tests, solidification does not occur. However, thermal stability, particularly after irradiation, is unacceptable for a high temperature hydraulic fluid.

h. Bulk modulus of hydraulic fluid-hydrogen mixtures decreases radically when any gas phase is present. This emphasizes the necessity of maintaining a single-phase system in an operating hydraulic system.

4.10 Recommendations

In future work emphasis should be continued on alkyl aromatics and diphenyl ethers as offering the best hope of combining the physical properties and stability required of a high temperature radiation resistant hydraulic fluid. For extreme high temperature use, unthickened base stocks and inhibitors more stable than the dialkyl selenides should be considered. For lower temperature use, lower viscosity base stocks, e.g., alkylbenzenes, combined with V.I. improvers and inhibitors offer the optimum combination of properties.

Although the dialkyl selenides are effective oxidation and radiation damage inhibitors, their corrosivity and thermal instability at high temperatures make their replacement by more stable additives desirable. Study of suitable substitutes, including possible combinations of low temperature and high temperature inhibitors, should be carried out. Likewise, the thermal and radiation instability of Polybutene 128 is one of the major limitations of CALRESEARCH 216. More stable additives, e.g., APAMS (page 40), should be evaluated. The effect of high temperatures during irradiation in accelerating damage should be investigated further, both with base stocks and polymers. Likewise, the study of the effect of irradiation on thermal stability should be continued.

[1] Work now in progress on Contract No. AF 33(616)-3476 has developed several aromatic materials which may have a less severe effect on properties of the blend.

Several blends of aromatic materials with 8200 fluid should be evaluated further to determine the improvement in allowable radiation dosage that can be obtained. This appears to be the only approach likely to give a -65°F radiation resistant hydraulic fluid.

No further work on naphthenic white oil, UCON DLB 144E, or other aliphatic materials is desirable.

5 ENGINE OILS (M. A Pino)

5.1 Introduction

The objective of this research was to develop a high temperature lubricant for use in gas turbine engines in a nuclear environment. The pattern specification was MIL-L-9236 which represented the most advanced nonnuclear requirement for this use. During 1957 the development progressed along several lines. The evaluation of various base stocks with and without inhibitors both before and after irradiation comprised a substantial portion of the program. Formulation to achieve desired properties was carried out after a suitable base stock was selected. Some effort was devoted to screening additives for application in the formulation studies. The development and evaluation of appropriate test methods progressed hand in hand with this engine oil research.

5.2 Viscosity Changes of Various Irradiated Base Stocks and Effect of Inhibitors

Change in viscosity is a good over-all index of radiation damage, although changes in properties other than viscosity, in some cases, may be of greater functional importance. Figure 24 shows the effects of irradiation to 8.7×10^{10} ergs/g C on the viscosity at 100° F of various inhibited and uninhibited base stocks. To insure a valid comparison of viscosities, all data of Figure 24 were obtained on 600-ml samples which were irradiated in identical, square containers vented to the air at the MTR (see page 4). In a few cases where data at 8.7×10^{10} ergs/g C were not available, the viscosities were obtained by extrapolation of data at lower dosages.[1]

The inhibited samples of C_{16-18}-alkylbiphenyl (distilled) underwent the least change in viscosity. The selenide was superior to DBPC (di-tert-butyl para-cresol) as a radiation damage inhibitor at 2% concentration for this and most of the other base stocks. For inhibited C_{16-18}-alkylbiphenyl, the bottoms product showed a somewhat greater viscosity increase than did the distilled product. The increases in viscosity of these irradiated base stocks when uninhibited were from 20% to 100% greater than when inhibited.

Tetradecyl diphenyl ether had the least viscosity increase of the uninhibited materials. It appears doubtful that the radiation stability of this material can be improved further through the use of inhibitors because the stability of the related material, C_{14-16}-alkyl diphenyl ether, was not improved by either didodecyl selenide or DBPC.

The inhibited diesters, di(2-ethylhexyl) sebacate and diisooctyl terephthalate, suffered viscosity increases three to four times greater than those for inhibited C_{16-18}-alkylbiphenyl (distilled). Inhibited diisooctyl azelate was even worse with a 385% increase in viscosity.

[1] Log viscosity vs dosage plots were used. Such plots are very nearly straight lines to dosages beyond 8.7×10^{10} ergs/g C (J. G. Carroll, "Organic Selenides and Coking of Gas Turbine Oils," First Semiannual 125A Radiation Effects Symposium, Convair ANP Doc No. NARF-57-197, FZK-9-118, Vol 1).

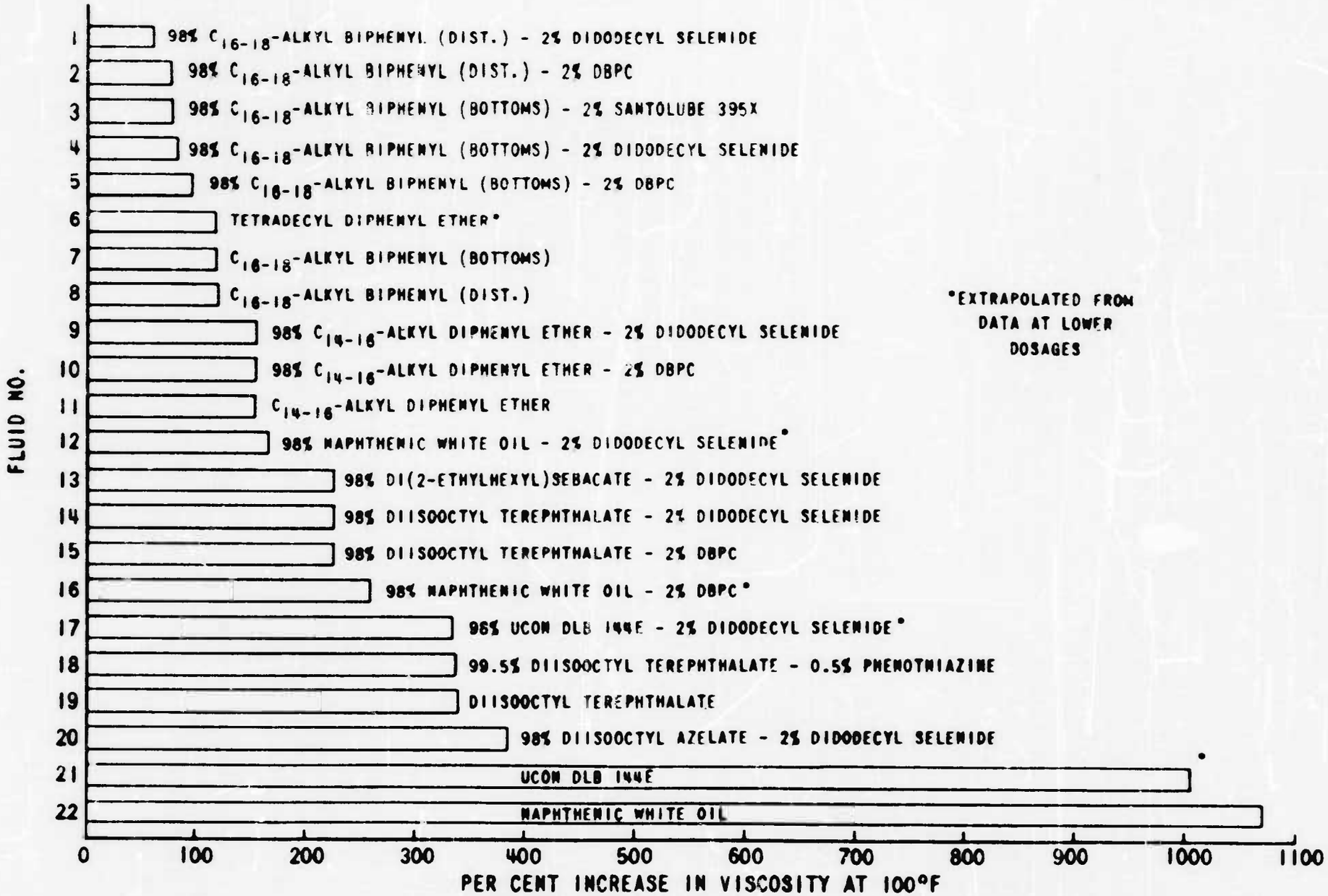


FIG. 24 - EFFECT OF IRRADIATION ON VISCOSITIES OF INHIBITED AND UNINHIBITED BASE STOCKS

GAMMA DOSAGE = 8.71×10^{10} ERGS/g. C

The beneficial effect of inhibitors was most marked in the cases of base stocks which in neat form had the poorest radiation stability. For example, the viscosity increase with uninhibited naphthenic white oil was seven times that with naphthenic white oil containing didodecyl selenide. Similar results were obtained on UCON DLB 144E.

These data show that inhibitors, particularly didodecyl selenide, can be effective in reducing radiation damage as indicated by viscosity change. This applies to static exposures in the presence of air (undegassed samples vented to air through about 20 feet of tubing).

5.3 Evaluation of Various Base Stocks

5.3.1 Alkyl Diphenyl Ethers

The properties of C_{14-16}-alkyl diphenyl ether with and without inhibitors and before and after irradiation are shown in Table LXVII. The outstanding property of this neat fluid before irradiation was its oxidation stability. It consistently survived the oxidation-corrosion test at 500° F with an increase in viscosity at 100° F of about 200%. Most of the other base stocks either solidified or showed much greater viscosity increases in this severe test. Although oxidation inhibitors were of questionable value for this material in the oxidation-corrosion tests, colloidal graphite appeared to be beneficial in reducing viscosity increase. It is possible that this was caused by a compensating decrease in viscosity as some of the graphite settled out. Of special interest was the apparent synergistic effect of dark oil-soluble dyes on the effectiveness of conventional inhibitors (see Section 5.4).

Viscosity index and pour point values for C_{14-16}-alkyl diphenyl ether were 116 and -25° F, respectively. A considerable lowering of the pour point is possible through the use of only the C_{14} component of the base stock. As shown in Table LXVIII, the pour point of tetradecyl diphenyl ether was about -70° F.

Two weaknesses of the alkyl diphenyl ethers for gas turbine fluid use are (a) high coking (about 500 mg at 700° F in Model C Panel Coker) and (b) relatively low lubricity (Mean Hertz Load value of about 13, see Appendix I). Both properties can be improved with appropriate additives (see Section 5.4).

The properties of 12 irradiated samples are included in Table LXVII. The most notable effects of irradiation on properties other than viscosity were the lower coke formation and the poorer foam characteristics. The former may be due to formation of high boiling substances which are good solvents for the coke formed in the test. These properties will be discussed later (see Section 5.4).

TABLE LXVII

LUBRICANTS BASED ON C_{14-18}-ALKYL DIPHENYL ETHER

Sample No. (of irradiated samples)							5040-49		5040-35		5116-15	5040-31		5040-21				
Additive	None														2% Didodecyl Selenide			
Radiation Dosage, 10^{10} ergs/g C	0.1						0.871[a,d]		0.871[d]		2.52[d]	8.71[d]		9.27[a,d]	0			
Viscosity, cs. °F																		
400	1.26[b]						1.18[e]		1.19[e]		1.31[e]	1.92[e]		2.62[b]				
210	4.83		4.85				5.11		5.20		6.08	10.0		9.40	4.76			
100	26.8		26.8				28.9		29.9		38.0	79.4		71.1	26.0			
0	1010		1060				1180		1180		1800	5070		5060	3060			
Pour Point, °F	-25						-25		-25		-20	-30		-30	-15			
Flash Point (COC), °F	425						450[f]		425[f]		440[f]	415[f]		485[f]	485			
Spontaneous Ignition Temperature, °F	800		810				820		820		500	820		810	1030			
Foaming																		
Sequence 1, foam height, ml	trace						90		30		305	505		550	trace			
collapse time, min	-						3.0		1.4		5	10.1		20.7	-			
Sequence 2, foam height, ml	trace						30		15		20	50		90	trace			
collapse time, min	1						0.7		0.2		0.5	0.7		1.4	5			
Sequence 3, foam height, ml	trace						40		70		100	755		675	trace			
collapse time, min	-						3.8		1.8		3	13.5		21.6	1.6			
Evaporation, 6-1/2 Hours, %																		
At 400°F	14.4						14.0		14.5		14.5	5.0		14.9	14.2			
SOD Lead Corrosion, mg/in.² (1 Hour at 325°F)	0.09														0.33			
Panel Coking, mg at																		
700°F, 8-Hour Test	112[i]		801		325		11[g]					2[g]		4[g]	24[g]			
Oxidation-Corrosion																		
Sample Size, ml	100	100	25	25	25	25	25	25	25	25	25	25	25	25	100	100	25	25
Time, Hours	72	48	48	48	48	48	48	48	48	48	48	48	48	48	72	48	48	48
Air Rate, liters/hour	5	5	1-1/4	1-1/4	1-1/4	1-1/4	1-1/4	1-1/4	1-1/4	1-1/4	1-1/4	1-1/4	1-1/4	1-1/4	5	5	1-1/4	1-1/4
Temperature, °F	400	400	500	400	400	500	500	500	500	400	500	500	400	500	400	400	400	500
Weight Change, mg/cm²																		
Be-Cu	+0.08	-0.24	+1.16	+0.10	+0.03	0.0	-0.14	+1.66	+0.06	-2.88	+1.13	+0.52	-0.45	+0.06	-0.47	-	-	-
Cu	-0.34	-0.21	-0.82	-0.35	-0.13	-0.36	-0.72	-1.19	-0.75	-4.06	-0.16	-6.55	-0.67	-0.20	-0.4	-	-	-
Ag	-0.03	-0.06	-0.14	+0.10	+0.26	-0.06	0.0	+0.09	-0.10	-0.06	0.0	0.0	-0.10	-0.04	-33.2	-	-	-
Fe	+0.06	-0.05	-0.07	+0.06	+0.06	0.0	-0.07	+0.09	-0.14	-0.03	0.0	0.0	-0.03	-0.13	-0.06	-0.01	+0.03	-0.03
Al	-0.03	-0.09	0.0	-0.10	-0.10	0.0	0.0	+0.06	-0.04	0.0	+0.06	0.0	0.0	-0.10	-0.06	0.0	+0.22	0.0
Viscosity Change, %																		
100°F	+97.0	+42.9	+229	+80.4	+59.4	+273	+64	+545	+124	+2000	+380	-	+568	+1300	+47.0	+11.5	+70.2	+164
210°F	+44.3	+23.7	+108	+39.2	+29.8	+117	+110	+198	+81.1	+268	+162	+801	+220	+331	+25.2	+22.7	+26.5	+77
Neutralization Number Change	11.1	5.9	5.6	11.4	-	11.1	6.1	7.5	9.2	5.7	9.2	8.0	10.8	6.4	5.6	1.7	3.2	5.8
Insolubles, % wt	0.1	Nil	1.3	Nil	Nil	3.3	1.3	1.3	0.5	Nil	[illegible]	4.5	Nil	2.8	0.06	0.04	Nil	0.9
Mean Hertz Load (Screening Test), kg	-15						~14		~17			~13		~14	~14			

[a] Contained 0.001% 60,000 Vis Silicone.
[b] At 413°F.
[c] 200-ml Sample in vented tin-plated container; MTR Canal Source.
[d] 600-ml Sample in vented aluminum container, MTR Canal Source.
[e] At 415°F.
[f] Micro Method.
[g] Four-hour test.
[h] Shell Four-Ball wear Test - Two hours at 167°F: 0.40 mm at [illegible] kg load, 0.56 mm at 10-kg load, 0.65 mm at 40-kg load.
[i] Ryder Gear Loading - 2240 and 1700 ppi in Micro Test.

TABLE LXVII (continued)

LUBRICANTS BASED ON [illegible]-ALKYL DIPHENYL ETHER

Sample No. (of irradiated samples)	5040-48		5116-20	5040-54					5040-47		5116-19	5040-55		
Additive	2% Dibenzyl Selenide						2% DHMC							
Radiation Dosage, 10^{10} ergs/g C	0.871[a,d]		3.70[a,d]	8.71[a,d]			0		0.87[a,d]		3.84[a,d]	8.71[a,d]		
Viscosity, cs, °F														
400	1.16[e]		1.49[e]	1.82[e]			1.19[b]		1.15[e]		1.30[e]	1.60[e]		
210	5.00		6.05	9.42			4.74		5.00		6.34	8.78		
100	28.0		47.1	71.7			28.5		28.7		41.8	67.7		
0	1270		2340	5000			1050		1120		2220	5110		
Pour Point, °F	-25		-30	-30			-25		-20		-20	-30		
Flash Point (COC), °F	440[f]		420[f]	410[f]			380		420[f]		440[f]	450[f]		
Spontaneous Ignition Temperature, °F	-		1040	1047			810		820		840	820		
Foaming														
Sequence 1, foam height, ml	45		555	650			trace		105		655	650		
collapse time, min	1.0		15	19.8			-		2.0		18	19.8		
Sequence 2, foam height, ml	30		60	80			trace		30		60	80		
collapse time, min	0.7		1.5	1.6			4		1.4		3	1.1		
Sequence 3, foam height, ml	55		430	665			trace		45		410	890		
collapse time, min	2.5		10	25.1			-		2.6		10	21.5		
Evaporation, 6-1/2 Hours, %														
At 400°F	14.4		15.1	15.4			15.4		16.1		15.3	15.1		
SCD Lead Corrosion, mg/in.[2] (3 Hour at 400°F)							0.51							
Panel Coking, mg at														
700°F, 8-Hour Test	32[d]			82[d]			304		108[d]			4[d]		
Oxidation-Corrosion														
Sample Size, ml	25	25	25	25	25	25	100	100	25	25	25	25	25	25
Time, Hours	48	48	48	48	48	48	72	48	48	48	48	48	48	48
Air Rate, liters/hour	1-1/4	1-1/4	1-1/4	1-1/4	1-1/4	1-1/4	5	5	1-1/4	1-1/4	1-1/4	1-1/4	1-1/4	1-1/4
Temperature, °F	400	500	500	500	500	400	400	400	500	400	500	500	500	400
Weight Change, mg/cm²														
Fe-Cu	-	-	-	-	-	-	-1.0	-0.42	+0.4	-0.9	-0.49	+1.10	+0.31	-0.20
Cu	-	-	-	-	-	-	-4.0	-1.60	-1.14	-1.80	-1.70	[illegible]	-0.55	-0.44
Ag	-	-	-	-	-	-	-0.80	-0.24	0.0	-0.14	0.0	+0.24	0.0	-0.22
Fe	-0.10	-1.8	-0.68	-1.06	-0.58	-0.10	0	+0.04	-0.04	+0.07	+0.04	-0.04	0.0	-0.20
Al	+0.14	+0.04	+0.03	0.0	-0.03	-0.10	+0.04	-0.05	0.0	-0.21	0.0	0.0	0.0	-0.22
Viscosity Change, %														
100°F	+45	+204	+252	-	+426	+156	425	+87.3	+102	+108	solid	+120	+204	+206
210°F	+22.8	+24.8	+17.6	+1600	+150	+65.7	177	+27.4	+51	+70.7	solid	+62	+115	+100.8
Neutralization Number Change	4.9	0.7	1.1	7.0	5.3	2.3	0.7	1.4	4.3	7.1	-	4.7	4.6	8.2
Insolubles, % wt	Nil	2.1	1.8	-	0.6	Nil	0.1	Nil	0.4	Nil	-	0.5	0.8	Nil
Wear Hertz Load (Screening Test), kg	-24			-16			-17			-15			-16	

[a] Contained 0.001% SC,000 Via Silicone.

[b] At 413°F.

[c] 200-ml Sample in vented tin-plated container, MTR Canal Source.

[d] 600-ml Sample in vented aluminum container, MTR Canal Source.

[e] At 41b°F.

[f] Micro Method.

[g] Four-hour test.

[h] Shell Four-Ball Wear Test - Two hours at 167°F, 0.45 mm at 8-kg load, 0.70 mm at 16-kg load, 0.65 mm at 40-kg load.

[i] Ryder Gear Loading - 32% and 1700 psi in Micro Test.

TABLE LXVII (continued)

LUBRICANTS BASED ON C_{14-18}-ALKYL DIPHENYL ETHER

Sample No. (of irradiated samples)				5116-14		
Additive	2% Diphenyl Selenide		2% Colloidal Graphite			
Radiation Dosage, 10^{10} ergs/g C	0		0	0.61[c]		
Viscosity, cs, °F						
400	-		-	-		
210	4.66		6.84	6.53		
100	25.1		38.9	38.2		
0	-		1420	1570		
Pour Point, °F				-25		
Flash Point (COC), °F				415[f]		
Spontaneous Ignition Temperature, °F						
Foaming						
Sequence 1, foam height, ml						
collapse time, min						
Sequence 2, foam height, ml						
collapse time, min						
Sequence 3, foam height, ml						
collapse time, min						
Evaporation, 6-1/2 Hours, %						
At 400°F						
SOD Lead Corrosion, mg/in.[e] (1 Hour at 325°F)						
Panel Coking, mg at						
700°F, 8-Hour Test						
Oxidation-Corrosion						
Sample Size, ml	100	100	25	25	25	25
Time, Hours	48	48	48	48	48	48
Air Rate, liters/hour	5	5	1-1/4	1-1/4	1-1/4	1-1/4
Temperature, °F	400	400	400	400	400	500
Weight Change, mg/cm²						
Be-Cu	-0.62	-	-0.10	-0.38	-0.06	-0.06
Cu	-6.42	-	-1.58	-1.09	-1.89	-0.36
Ag	+0.67	-	-0.13	-0.22	+0.13	0.0
Fe	+0.34	-0.10	-0.13	-0.03	+0.13	+0.09
Al	+0.46	-0.13	-0.10	-0.03	+0.06	+0.06
Viscosity Change, %						
100°F	+36.2	+63	+24.1	+162	+65.4	+95.5
210°F	+19.7	+32.6	+3.8	+83.7	+27.1	+41
Neutralization Number Change	5.5	5.1	8.5	8.4	10.3	7.0
Insolubles, % Wt	1.89	Nil	2.2	0.4	1.3	1.3
Mean Hertz Load (Screening Test), kg			-14			

[a] Contained 0.001% 60,000 Vis Silicone.

[b] At 413°F.

[c] 200-ml Sample in vented tin-plated container; MTR Canal Source.

[d] 600-ml Sample in vented aluminum container; MTR Canal Source.

[e] At 415°F.

[f] Micro Method.

[g] Four-hour test.

[h] Shell Four-Ball Wear Test - Two hours at 167°F; 0.40 mm at 4-kg load
0.56 mm at 10-kg load
0.65 mm at 40-kg load

[i] Ryder Gear Loading - 2240 and 1700 ppi in Micro Test.

TABLE LXVIII

LUBRICANTS BASED ON TETRADECYL DIPHENYL ETHER

Sample No. (of irradiated samples)	4976-17-16				
Additive	None		2% DBPC		2% Didodecyl Selenide
Radiation Dosage, 10^{10} ergs/g C	0	6.44[c]	0[b]		0
Viscosity, cs, °F					
400	1.12	1.31	-		
210	4.13	6.01	4.11		
100	22.3	39.3	22.2		
0	-	2160	-		
-40	13,700	50,500	-		
Pour Point, °F	-70	-50			
Flash Point (COC), °F	445	430[a]			
Spontaneous Ignition Temperature, °F	820	820			
Evaporation, 6-1/2 Hours, %					
At 400°F	25.2				24.2
Oxidation-Corrosion					
Sample Size, ml	25	25	100	100	
Time, Hours	48	48	72	72	
Air Rate, liters/hour	1-1/4	1-1/4	5	5	
Temperature, °F	400	400	347	347	
Weight Change, mg/cm²					
Be-Cu	-1.63	-0.84	-	-	
Cu	-2.72	-1.26	-0.21	-0.25	
Ag	0.0	-0.03	+0.15	+0.06	
Fe	0.0	-0.13	+0.05	+0.01	
Al	+0.06	-0.10	+0.04	+0.01	
Mg	-	-	+0.07	+0.29	
Viscosity Change, %					
100°F	+156[d]	+58.9	+4.1	+6.3	
210°F	+132[d]	+32.0	+3.0	+0.6	
Neutralization Number Change	9.2	4.9	0.44	0.36	
Insolubles, % Wt	trace	trace	0	0	
Mean Hertz Load (Screening Test), kg	~18	~12			

[a] Micro Method.

[b] Panel Coking - 368 mg in four-hour test at 700°F.

[c] 600-ml Sample in vented aluminum container; MTR Canal Source.

[d] Probably erroneous.

The superior oxidation resistance of the alkyl diphenyl ethers was apparently maintained even after irradiation. The inhibited samples had smaller viscosity increases in the oxidation-corrosion tests than the uninhibited samples, but the poor repeatability of these tests, especially at 500° F, makes difficult the evaluation of inhibitors. Most of the other properties (e.g., evaporation, flash and pour points, wear, etc.) of C_{14-16}-alkyl diphenyl ether were not affected appreciably by irradiation to dosages as high as 8.7×10^{10} ergs/g C.

The data on C_{14-16}-alkyl diphenyl ether containing 2% colloidal graphite should be noted. The radiation dosage on this blend was about 0.6×10^{10} ergs/g C. Viscosity at 100° F and 210° F decreased slightly due to irradiation. As with the oxidation-corrosion tests, this reversal of the usual increase in viscosity may be due to settling of some of the graphite. The results of the oxidation-corrosion tests on the irradiated graphite-containing sample are difficult to assess owing to the poor repeatability.

Oxidation-corrosion tests at 400° F on tetradecyl diphenyl ether (Table LXVIII) are also questionable, as the viscosity of the irradiated sample changed appreciably less than that of the unirradiated sample. A scarcity of this material precluded a recheck of these results. The high viscosity changes on the unirradiated sample are believed to be erroneous as this material should be very similar to the C_{14-16}-alkyl diphenyl ether with respect to oxidation stability.

5.3.2 C_{16-18}-Alkylbiphenyl

The properties of inhibited and uninhibited C_{16-18}-alkylbiphenyl (distilled) and C_{16-18}-alkylbiphenyl (bottoms) are given in Tables LXIX and LXX, respectively. Data on irradiated and unirradiated samples are included.

The unirradiated, distilled alkylbiphenyl had a pour point of -60° F, but its low temperature viscosities were appreciably higher than the corresponding ones for tetradecyl diphenyl ether. Stability was fair in oxidation-corrosion tests; the increase in viscosity at 100° F was about 50% for the 400° F test and about 200% for the 500° F test. The Panel Coke Test gave high values (ca 1000 mg), while Mean Hertz Load values were unusually low (less than 10).

A higher pour point and poorer oxidation stability were displayed by the unirradiated bottoms product, but these were offset by a higher Mean Hertz Load of about 15 and a lower coke formation of around 600 mg. Didodecyl selenide or DBPC in either the distilled or bottoms product reduced coke formation but did not have much effect on oxidation stability before irradiation.

TABLE LXIX

LUBRICANTS BASED ON [illegible]-ALKYLTRIPHENYL [illegible]

Sample No. (of irradiated samples)		[illegible]	[illegible]		[illegible]	[illegible]	[illegible]			[illegible]	[illegible]	[illegible]	[illegible]	
Additive	← None →			← 2% Dibutoxyl Selenide →					← 2% [illegible] →					2% Dibutoxyl Selenide
Radiation Dosage, 10^{10} ergs/g C	0[a]	0.371[b]	0.71[c]	0	0.371[b]	0.19[d]	0.94[e]	0.24[c]	0	0.371[b]	1.90[d]	4.01[e]	0.24[c]	0
Viscosity, cs. °F														
300	1.25	1.21[f]	1.48[f]		1.18[f]	1.20[f]	1.22[f]	1.4[f]	-	1.18[f]	1.21[f]	1.25[f]	1.4[f]	
210	5.27	5.68	8.64	5.07	5.81	[illegible]	6.18	6.97	5.19	6.4[f]	6.97	7.64	7.76	
100	45.5	48.7	77.8	46.4	47.3	41.1	49.5	54.8	45.4	49.2	48.8	51.8	56.5	
0	2500	2580	7000	-	4500	4610	4170	4450	-	2750	4500	4500	4450	
-40	61,700	-	-	-	-	-	117,000	-	-	-	111,000	-	-	
Pour Point, °F	-60	-50	-50	-10	-10	-25	-45	-50	-50	-50	-50	-45	-45	
Flash Point (COC), °F	450	465[f]	460[f]	450	465[f]	445[f]	440[f]	435[f]	440	455[f]	425[f]	450[f]	465[f]	
Spontaneous Ignition Temperature, °F	780	750	750	1010	1040	990	990	1000	800	770	770	770	770	
Foaming														
Sequence 1, foam height, ml		245		15	440	410	470		trace	450	185	204	710	
collapse time, min		0.5		5	4.8	10	15		1.5	7	10	15	28.7	
Sequence 2, foam height, ml		50		trace	25	10	50		trace	50	trace	40	50	
collapse time, min		2.7		0.25	0.5	1.75	5		0.5	0.8	0.75	2.5	1.8	
Sequence 3, foam height, ml		115		5	580	250	445		10	345	230	170	590	
collapse time, min		6.8		0	5.4	10	10		2.5	4.8	5	4	11.9	
Evaporation, 6-1/2 Hours, %														
At 400°F	11.2	10.0	9.8		11.8	11.7	11.9	12.1		12.8	12.5	13.7	12.1	
300 Steel Corrosion, mg/in.[2] (1 Hour at 325°F)				-4.9					-5.6					
Panel Coking, mg at														
700°F, 5-Hour Test	1000	125[g]		Rub	0[g]				Rub				50[g]	144
Oxidation-Corrosion														
Sample Size, ml	25	25	25	25	25	100	25	25	25	25	100	100	25	25	25	25	25	25	25
Time, Hours	48	48	48	48	48	48	48	48	48	48	72	48	48	48	48	48	48	48	48
Air Rate, liters/hour	1-1/4	1-1/4	1-1/4	1-1/4	1-1/4	5	1-1/4	1-1/4	1-1/4	1-1/4	5	5	1-1/4	1-1/4	1-1/4	1-1/4	1-1/4	1-1/4	1-1/4
Temperature, °F	400	500	500	400	400	400	400	500	400	400	347	400	500	500	400	400	400	400	500
Weight Change, mg/cm[2]																			
Fe-Cu	+0.01	-0.23	+0.52	+0.79	-0.58	-	-	-	-	-	-	-	+2.48	-0.99	-0.20	-0.16	-0.71	-1.59	
Cu	-0.32	-5.48	-0.28	-0.13	-0.43	-	-	-	-	-	-0.13	-1.55	+0.[illegible]	0.0	-0.9[illegible]	-1.[illegible]	-1.55	-0.07	
Mg	+0.45	0.0	0.0	0.0	0.0	-	-	-	-	-	0.0	+0.48	-0.[illegible]	0.0	-0.22	0.0	-0.50	-0.17	
Zn	+0.19	0.0	-0.37	-0.[illegible]	-0.[illegible]	-0.19	+0.16	-1.[illegible]	-0.32	-0.[illegible]	-0.02	-0.57	0.0	-0.56	-0.0[illegible]	-0.10	-0.1[illegible]	-0.[illegible]	
Al	+0.19	0.0	+0.17	0.0	0.0	-0.27	+0.15	-0.[illegible]	-0.22	-0.19	-	-0.54	0.0	+1.37	-0.16	-0.10	-0.[illegible]	-0.[illegible]	
Mg	-	-	-	-	-	-	-	-	-	-	+0.[illegible]	-	-	-	-	-	-	-	
Viscosity Change, %																			
100°F	+48.2	+208	solid	solid	+151	+54.3	+65.8	solid	+205	+62.[illegible]	+18	+50.0	+2.[illegible]	solid	+200	+[illegible]	-	+250	
210°F	+27.1	+68	solid	solid	+[illegible]	+25.6	+21.1	solid	+104	+34.[illegible]	+10.5	+29.6	+1.[illegible]	solid	+144	+[illegible]	+1.[illegible]	+114	
Neutralization Number Change	1.7	5.0	-	-	8.4	1.2	6.4	-	6.5	4.5	2.8	4.1	0.	-	7.1	7.6	7.6	4.0	
Insolubles, % at	1.6	2.6	-	4.8	41	0.8	41	-	1.8	trace	0	2.5	41	-	41	1.27	trace	0.5	
Wear Metals Load (Screening Test), mg	-8		-8	-14		-9			-14.5	-14	-14		-10		-10	-12			

[a] Neat.

[b] Sample contained 0.001% 50,000 Vis Silicone.

[c] 200-ml Sample in vented tin-plated container, MTR Canal Source.

[d] 500-ml Sample in vented aluminum container, MTR Canal Source.

[e] At 410°F.

[f] Micro Method.

[g] Four-hour test.

[h] Probably erroneous.

[i] Shell Four-Ball wear Test - Two hours at 167°F, [illegible] mm at 5-kg load
[illegible] mm at 10-kg load
[illegible] mm at 40-kg load

TABLE XXI

LUBRICANTS RAISED IN [illegible]-AXAY-DIPHENYL [illegible]

Sample No. (or irradiated sample)			1270-43				1270-45						
Additive	None				5% Didodecyl Selenide				5% Didodecyl Selenide				
Radiation Dosage, 10^{18} ergs/g [illegible]	0[1]		5.7[2]		0		5.7[2]		0	0.27[3]	0.73[3]	2.11[3]	4.66[3]
Viscosity, cs, °F													
100	-1.0[4]	-	1.90[4]		-	-	1.90[4]		-	-	-	-	-
210	7.96	7.14	11.7		6.91	6.06	10.1		5.97	5.36	5.49	5.96	5.35
100	55.0	55.3	115		52.14	52.5	84.0		51.6	50.0	51.0	51.7	49.6
%	[illegible]	-	14,000		-	-	10,000		-	-	-	-	-
Pour Point, °F	-25		-25		-20		-20						
Flash Point (COC), °F	500		450[5]				400[5]						
Spontaneous Ignition Temperature, °F	770		770				1000						
Foaming													
Sequence 1, foam height, ml	250	40[6]	205				150						
collapse time, min	7	10	7				7						
Sequence 2, foam height, ml	30	20	40				35						
collapse time, min	0.3	0.1	0.5				0.5						
Sequence 3, foam height, ml	0	trace	200				140						
collapse time, min	0.2	1	3				7						
Evaporation, 6-1/2 Hours, %													
at 400°F	0.2		0.5		0.6		0.6						
300 Lead Corrosion, mg/in.[2]	1.4				1.2								
~~72 Hour at 300°F~~													
Panel Coking, mg at													
700°F, 5-Hour Test	145		45[7]		177		65[7]		192, 21[8]				
Oxidation-Corrosion													
Sample Size, ml	25	25	25	100	100	25	25						
Time, Hours	48	48	48	72	72	48	48						
Air Rate, liters/hour	1-1/4	1-1/4	1-1/4	5	5	1-1/4	1-1/4						
Temperature, °F	500	500	500	347	347	500	500						
Weight Change, mg/cm[2]													
Mg	-0.32	-0.10	-0.35	-	-	-	-						
Cu	-0.04	-0.10	0.3	-13.0	-	-	-						
Ag	-0.10	-0.10	-0.4	-23.0	-	-	-						
Fe	-0.43	-0.16	0.3	0	-0.08	-0.01	-1.02						
Al	1.0	-0.04	1.0	-0.01	-0.04	0.04	0.0						
Mg	-	-	-	0	-0.02	-	-						
Viscosity Change, %													
100°F	-29.0	gelled	-40.3	+19.4	+17.0	+14,400	+144						
210°F	+52.8	+400	+17.7	+27.4	+7.4	+2,500	+66						
Neutralization Number Change	1.7	5.0	7.4	2.1	1.1	5.0	4.0						
Insolubles, %	1.0	1.4	0.5	-	-	1.4	1.4						
Four-Ball Lead (Screening Test), kg	~15		~14				~20						

[1] 100-ml Sample in sealed aluminum container, WTR Canal Source.
[2] 10-ml Sample in capsule of 410 stainless steel sealed under helium, WTR Canal Source.
[3] Milpk Method.
[4] Contains 0.005% DB 200.
[5] At 410°F.
[6] Four-hour test.
[7] Test void - excessive bumping.
[8] Two-hour test.
[9] Shell Four-Ball Wear Test - Two hours at 167°F, 0.04 mm at 5-kg load
0.07 mm at 10-kg load
0.77 mm at 40-kg load

TABLE LXX (continued)

LUBRICANTS BASED ON [illegible]-ALKYLRIPHENYL (BOTTOMS)

Sample No. (of irradiated samples)						4976-47					4976-48
Additive	2% Dibenzyl Selenide		5% Dibenzyl Selenide	← 2% DBPC →			0.5% Selenium Metal	0.5% Phenothiazine	2% Phenyl-α-naphthylamine	2% Santolube 395X	
Radiation Dosage, 10^{10} ergs/g C	0		0	0		8.71[a]	0	0	0	0	8.71[a]
Viscosity, cs, °F											
400	-	-		-	-	1.82[e]			-	-	1.69[e]
210	[illegible]	8.87		6.89	6.89	10.9			7.02	[illegible]	10.5
100	51.8	76.8		53.9	53.6	107			54.8	56.3	100
0	-	-		-	-	13,200			-	-	10,900
Pour Point, °F						-25				-25	-30
Flash Point (COC), °F						460[f]					460[f]
Spontaneous Ignition Temperature, °F						770					760
Foaming											
Sequence 1, foam height, ml						160					630
collapse time, min						5					30
Sequence 2, foam height, ml						35					50
collapse time, min						0.3					0.2
Sequence 3, foam height, ml						475					775
collapse time, min						5					14
Evaporation, 6-1/2 Hours, %											
at 400°F						9.5					9.5
300 Lead Corrosion, mg/cm²[g] (1 Hour at [illegible])		0.4		0.9				0.5	0.3		
Panel Coking, mg at											
700°F, 5-Hour Test	410	240[f]	56[h]	[illegible]	104	52[f]	> 382	382	453		46[f]
Oxidation-Corrosion											
Sample Size, ml	100	100		100	25	25		100	100	25	25[g]
Time, Hours	72	72		72	48	48		72	72	48	48
Air Rate, liters/hour	5	5		5	1-1/4	1-1/4		5	5	1-1/4	1-1/4
Temperature, °F	347	347		347	500	500		347	347	500	500
Weight Change, mg/cm²											
Be-Cu	-	-		-	0.0	+1.3[g]		-	-	-3.62	-
Cu	-35.3	-		-0.17	-0.16	0.0		-0.02	-0.06	-7.84	-
Ag	-49.5	-		-0.02	-0.13	-0.07		-0.10	-0.07	+0.10	-
Fe	+0.05	+0.01		-0.04	-0.18	-0.04		-0.24	-0.03	+1.67	-
Al	+0.05	+0.12		-0.02	0.0	0.0		-0.10	-0.07	+0.60	-
Mg	+0.05	-0.04		0	-	-		-0.05	0.0	-	-
Viscosity Change, %											
100°F	+50	+34		+26	+9750	+2530		+22	+31	+2480	-
210°F	+30	+19		+15	-2050	+502		+12	+16	+1330	-
Neutralization Number Change	5.6	7.1		2.2	8.9	6.4		4.7	3.6	6.2	-
Insolubles, % wt	-	-		-	1.4	1.3		-	-	5.4	-
Mean Hertz Load (Screening Test), kg						-23					

[a] 600-ml Sample in vented aluminum container, MTR Canal Source.

[b] 10-ml Sample in capsule of 410 stainless steel sealed under helium, MTR Canal Source.

[c] Micro Method.

[d] Contains 0.0018% NO 200.

[e] at 410°F.

[f] Four-hour test.

[g] Test void - excessive dumping.

[h] Two-hour test.

[i] Shell Four-Ball Wear Test - Two hours at 107°F, 0.24 mm at 4-kg load
0.27 mm at 10-kg load
0.71 mm at 40-kg load

Although these base stocks showed unusually small viscosity changes upon irradiation, especially when inhibited, other properties did change appreciably. Coking was greatly reduced, and a small improvement in lubricity occurred in both materials. The distilled C_{16-18}-alkylbiphenyl became less stable toward oxidation; several samples, both inhibited and uninhibited, solidified in the oxidation-corrosion test at 500° F. By contrast, the oxidation stability of the bottoms product seemed to benefit through irradiation. The viscosity changes of the irradiated samples were appreciably less than those of the unirradiated samples in the oxidation-corrosion test at 500° F. Didodecyl selenide appeared to benefit the irradiated C_{16-18}-alkylbiphenyl (bottoms) in this test. The poor repeatability of the oxidation-corrosion tests makes doubtful the value of inhibitors to the irradiated distilled product.

5.3.3 Diisooctyl Terephthalate

Table LXXI shows the properties of diisooctyl terephthalate with and without inhibitors. The neat ester had good low temperature properties, its pour point being about -65° F. Lubricity, as indicated by either the Four-Ball Wear Test or the Mean Hertz Load, was somewhat poorer than desired. Less than 1 mm wear (see footnote page 77) or a value of at least 20 (see Appendix I) are the goals in these two tests, respectively. Panel coking at 700° F was about 500 mg; and oxidation stability, especially in the oxidation-corrosion test at 500° F, was quite poor. The use of didodecyl selenide improved stability in the oxidation-corrosion test at 400° F, but not at 500° F. The selenide reduced coking very markedly. Other inhibitors did not appear to be beneficial with respect to oxidation stability, and some, such as DBPC, were deleterious with respect to coking.

The effects of irradiation on the viscosity of diisooctyl terephthalate with and without inhibitors were noted in Section 5.2 (page 147). The effect of irradiation on oxidation stability is difficult to assess, as all but two of the oxidation-corrosion tests at 500° F resulted in solidification of the ester. In the two exceptions, a malfunction of the apparatus is suspected.

Of interest was the substantial reduction in coking brought about by irradiation of both inhibited and uninhibited diisooctyl terephthalate. As little as 0.87×10^{10} ergs/g C sufficed to effect this reduction. As with other base stocks, foaming increased greatly after irradiation, whether or not silicone antifoam was present originally.

5.3.4 Naphthenic White Oil

A naphthenic petroleum white oil was tested fairly extensively as a reference material. Its high degree of refinement assured maximum response for a petroleum fraction to oxidation inhibitors. Results appear in Table LXXII. In comparison with some of the synthetic base stocks, naphthenic white oil was not promising as a base stock for engine oils.

TABLE LXXI

LUBRICANTS BASED ON DIISOOCTYL TEREPHTHALATE

Sample No. (of irradiated samples)			5040-39	4976-49					5040-41	4976-17-1[illegible]	4976-17-1[illegible]	4976-50	
Additive	None								2% Didodecyl Selenide				
Radiation Dosage, 10^{10} ergs/g C	0[a]		0.871[d]	9.32[d]	0				0.871[d]	5.9[d]	7.4[d]	9.33[d]	
Viscosity, cs, °F													
400	1.50		1.31[e]	2.16[e]					1.18[e]	1.72[e]	2.59[d]	1.8[e]	
210	5.09		5.83	13.6	5.11				5.87	6.84	8.54	11.1	
100	31.7		40.0	153	30.5				35.2	51.[illegible]	71.5	107	
0	20,40[illegible]		2000	24,800	-				-	-	7690	24,500	
-40	49,600		89,700	-	-				-	-	-	-	
Pour Point, °F	-65		-5[illegible]	-25	-5				-20	-40	-35	-35	
Flash Point (COC), °F	480		[illegible][f]	280[f]					[illegible][f]	435[f]	430[f]	[illegible][f]	
Spontaneous Ignition Temperature, °F	860		840	820	1020				1040	1020	1040	1020	
Foaming													
Sequence 1. foam height, ml	20		215	420	10				30	645	525	580	
collapse time, min	0.3		15	30	0.5				15	30+	30+	20	
Sequence 2. foam height, ml	0		50	140	trace				20	10	35	125	
collapse time, min	0		4.4	1.5	0.2				4	1.5	2.75	2.5	
Sequence 3. foam height, ml	140		570	350	trace				440	225	640	665	
collapse time, min	15		15	23	0.3				15	20	30+	20	
Evaporation, 6-1/2 Hours, %													
at 400°F	19.6		19.7	19.1	15.8				16.3	17.1	18.1	18.7	
300 Lead Corrosion, mg/in.[g] 72 Hour at [illegible]	18.5				18.60								
Panel Coking, mg at													
700°F, 8-Hour Test	50[i]		[illegible][j]	[illegible][j]	49				9[j]			2[j]	
Oxidation-Corrosion													
Sample Size, ml	25	25	25	25	100	100	25	25[h]	25	25	25	25	25
Time, Hours	48	48	48	48	72	48	48	48	48	48	48	48	48
Air Rate, liters/hour	1-1/4	1-1/4	1-1/4	1-1/4	5	5	1-1/4	1-1/4	1-1/4	1-1/4	1-1/4	1-1/4	1-1/4
Temperature, °F	400	500	500	500	347	100	500	500	500	400	400	500	500
Weight Change, mg/cm²													
Mg-Cu	-1.34	+0.75	-0.50	-0.10	-	-							
Cu	-3.33	-1.00	-0.71	-0.62	-10.0[illegible]	-							
Ag	-0.25	-0.14	-0.17	-0.10	-4.[illegible]	-							
Fe	-0.[illegible]	-0.07	+0.04	-0.31	+0.03	-0.00	-0.75	-2.1[illegible]	+1.7[illegible]	-0.35	-0.[illegible]	+0.56	+0.19
Al	+0.0[illegible]	-0.14	-0.10	-0.07	-	-0.07	+0.10	0.0	-0.07	-0.07	0.0	0.0	+0.13
Viscosity Change, %													
100°F	+1.8	solid	solid	solid	+14	+[illegible]	+0.0[illegible]	solid	solid	+[illegible].5	+27.1	solid	+23.1
210°F	+7	solid	solid	solid	+7.4	+11.4	-0.0[illegible]	solid	solid	+8.5	+11.6	solid	+10.4
Neutralization Number Change	22.6	-	-	-	0.4	12.2	16.2	-	-	19.1	2[illegible].5	-	27.2
Insolubles, % at	trace	-	-	-	-	0.15	0.4	-	-	trace	1.7	-	Nil
Mean Hertz Load (Screening Test), kg	~18		~18	~20			~14		~15	~22	~18	~20	

[a] Boils at 414°F.

[b] 10-ml Sample in capsule of 410 stainless steel sealed under helium; MTR Canal Source.

[c] Sample contained 0.531% 60,000 Vis Silicone.

[d] 600-ml Sample in vented aluminum container; MTR Canal Source.

[e] At 415°F.

[f] Micro Method.

[g] 200-ml Sample in vented tin-plated container; MTR Canal Source.

[h] Bis tridecyl selenide substituted for didodecyl selenide.

[i] Four-hour test.

[j] Probably erroneous.

[k] Shell Four-Ball Wear Test - Two hours at 167°F, 0.21 mm at 4-kg load, 0.75 mm at 10-kg load; 1.08 mm at 40-kg load.

TABLE [illegible] (Continued)

Page [illegible] of [illegible]

HYDROLAYED BASE OF DIDODECYL [illegible] PROPERTIES

Sample No. (of irradiated samples)							
Additive	4% Didodecyl Selenide			2% Didodecyl Selenide	5% Didodecyl Selenide	2% Sarkosine [illegible]	[illegible]
Radiation Dosage, 10^{10} ergs/g C	0	0.4^{b}	1.0^{b}	0	0	0	0.4^{b}
Viscosity, cs, °F							
400	-	-	-	-	-	[illegible]	[illegible]
210	[illegible]	5.10	8.27	[illegible]	-	[illegible]	[illegible]
100	[illegible]	[illegible]	[illegible]	[illegible]	-	[illegible]	[illegible]
0	-	-	-	-	-	[illegible]	[illegible]
-40	-	-	-	-	-	[illegible]	-
Pour Point, °F						[illegible]	[illegible]
Clear Point (Cut), °F						[illegible]	[illegible]
Continuous Ignition Temperature, °F						[illegible]	[illegible]
Foaming							
Sequence 1. Foam height, ml						[illegible]	[illegible]
collapse time, min						[illegible]	[illegible]
Sequence 2. Foam height, ml						[illegible]	[illegible]
collapse time, min						[illegible]	[illegible]
Sequence 3. Foam height, ml						[illegible]	[illegible]
collapse time, min						[illegible]	[illegible]
Evaporation, 6-1/2 Hours, %							
At 400°F							[illegible]
SAE Lead Corrosion, mg/in.[a] (3 Hour at 325°F)							
Rust Coating, MIL 41							
700°F, 6-Hour Test				[illegible]		[illegible]	[illegible]
Oxidation-Corrosion							
Sample Size, ml				[illegible]	[illegible]	[illegible]	[illegible]
Time, Hours				[illegible]	[illegible]	[illegible]	[illegible]
Air Rate, liters/hour				[illegible]	[illegible]	[illegible]	[illegible]
Temperature, °F				[illegible]	[illegible]	[illegible]	[illegible]
Weight Change, mg/cm²							
Mg-Cu				-	-	[illegible]	[illegible]
Cu				-	[illegible]	[illegible]	[illegible]
Ag				-	[illegible]	[illegible]	[illegible]
Fe				[illegible]	[illegible]	[illegible]	[illegible]
Al				[illegible]	-	[illegible]	[illegible]
Viscosity Change, %							
100°F				[illegible]	[illegible]	[illegible]	[illegible]
210°F				[illegible]	[illegible]	[illegible]	[illegible]
Neutralization Number Change				[illegible]	[illegible]	-	-
Insolubles, % at				[illegible]	-	-	-
Mean Hertz Load (Screening Test), kg						[illegible]	[illegible]

[a] Notls at 414°F.
[b] 10-ml Sample in capsule of 410 stainless steel sealed under helium, MTR Canal Source.
[c] Sample contained 0.001% 60,000 Vis Silicone.
[d] 500-ml Sample in vented aluminum container, MTR Canal Source.
[e] At 410°F.
[f] Wilson Method.
[g] 200-ml Sample in vented tin-plated container, MTR Canal Source.
[h] Dialkylthenyl selenide substituted for didodecyl selenide.
[i] Four-hour test.
[j] Probably erroneous.
[k] Shell Four-Ball Wear Test - Ten hours at 167°F, 0.71 mm at 8-kg load, 0.75 mm at 15-kg load, 1.08 mm at 40-kg load.

TABLE LXXI (continued)

LUBRICANTS BASED ON DIISOOCTYL TEREPHTHALATE

Sample No. (of irradiated samples)				5040-40	4976-17-10	4976-17-9	5040-2			5116-4	5040-25
Additive	← 2% DBPC →								← 0.5% Phenothiazine →		
Radiation Dosage, 10^{10} ergs/g C	0			0.871[c,d]	2.35[g]	4.53[g]	9.32[d]		0	0.871[c,d]	8.80[d]
Viscosity, cs, °F											
400	-			1.23[e]	3.27[e]	2.26[e]	2.90[e]		-	1.24[e]	(a)
210	5.10			5.51	7.49	9.50	10.8		5.09	5.50	13.8
100	31.8			37.0	51.4	89.8	109		32.1	37.3	144
0	-			2860	6750	12,100	16,700		-	2820	25,500
-40	-			88,700	-	-	-		-	79,400	-
Pour Point, °F	-55			-50	-45	-	-35		-60	-45	-30
Flash Point (COC), °F				360[f]	420[f]	[illegible]	280[f]			435[f]	485[f]
Spontaneous Ignition Temperature, °F	830			840	830	840	820				830
Foaming											
Sequence 1, foam height, ml	trace[c]			500	515	720	565			640	500
collapse time, min	0.75			15	20	30+	30			15	30
Sequence 2, foam height, ml	trace			30	15	20	105			45	540
collapse time, min	0.5			2.2	0.3	0.5	1.5			0.9	4
Sequence 3, foam height, ml	trace			465	35	35	590			520	680
collapse time, min	1.25			10	15	5	25			6.5	30
Evaporation, 6-1/2 Hours, %											
At 400°F				19.0	19.0	19.2	19.6			16.2	18.9
SOD Lead Corrosion, mg/in.[a] (1 Hour at 325°F)	-34.2[a]										
Panel Coking, mg at											
700°F, 8-Hour Test	1120			11.6			13		785	162	31
Oxidation-Corrosion											
Sample Size, ml	100	100	25	25	25	25	25	25	25	25	25
Time, Hours	72	48	48	48	48	48	48	48	48	48	48
Air Rate, liters/hour	5	5	1-1/4	1-1/4	1-1/4	1-1/4	1-1/4	1-1/4	1-1/4	1-1/4	1-1/4
Temperature, °F	387	400	500	500	400	400	500	400	500	500	500
Weight Change, mg/cm²											
Be-Cu	-	-	-0.14	-0.10	-0.22	-0.61	-1.64	-1.15	-1.62	-1.20	-1.30
Cu	-9.3	-7.79	-1.58	-1.13	-0.82	-1.58	0.0	-1.63	-1.29	+0.10	-1.00
Ag	-0.06	-0.14	-1.37	-0.17	+0.02	-0.10	+0.62	-0.06	0.0	-0.07	-0.17
Fe	+0.02	+0.02	-18.1	-0.07	+0.01	-0.90	-5.35	-0.51	+0.19	-0.31	-0.68
Al	-	+0.02	0.0	+0.20	+0.03	-0.19	0.0	-0.06	+0.10	0.0	-0.10
Viscosity Change, %											
100°F	+45	-	solid	solid	+143	+269	solid	+433	-	solid	solid
210°F	+26	+47	solid	solid	+80	+135	solid	+202	-	solid	solid
Neutralization Number Change	7.7	18.7	0.70	-	19.7	26	-	27.2	45.4	-	-
Insolubles, % wt	-	0.51	-	-	Nil	1.08	-	-	9.83	-	-
Mean Hertz Load (Screening Test), kg		~15		~18	~21	~16	~20			~16	

[a] Boils at 414°F.

[b] 10-ml Sample in capsule of 410 stainless steel sealed under helium; MTR Canal Source.

[c] Sample contained 0.001% 50,000 Vis Silicone.

[d] 600-ml Sample in vented aluminum container; MTR Canal Source.

[e] At 415°F.

[f] Micro Method.

[g] 200-ml Sample in vented tin-plated container; MTR Canal Source.

[h] Bis(tridecyl) selenide substituted for didodecyl selenide.

[i] Four-hour test.

[j] Probably erroneous.

[k] Shell Four-Ball Wear Test - Two hours at 167°F; 0.71 mm at 4-kg load; 0.75 mm at 10-kg load; 1.08 mm at 40-kg load.

TABLE LXXII

LUBRICANTS BASED ON NAPHTHENIC WHITE OIL

Sample No. (of irradiated samples)			5040-W		5040-1[b]					5040-3[b]		4370-17-1	4370-17-1[b]
Additive	← None					→ 2% Didodecyl Selenide							
Radiation Dosage, 10^{10} ergs/g C	0		0.871[a]		9.24[a]	0				0.871[a,b]		4.35[a]	5.47[a]
Viscosity, cs, °F													
400	1.51	-	1.44[d]		1.72[d]	-				1.43[d]		2.10[d]	1.84[d]
210	7.44	7.50	6.59		41.2	7.41				7.80		14.1	12.1
100	70.4	74.5	88.8		1010	72.0				74.8		221	150
0	-	14,500	17,000		-	-				20,600		79,000	4000
Pour Point, °F		-30	-30		-5	0				-20		-15	-20
Flash Point (COC), °F		435	430[f]		390[f]	395				395[f]		400[f]	390[f]
Spontaneous Ignition Temperature, °F		735	720		740	840				840		840	850
Foaming													
Sequence 1, foam height, ml			680		470	500		trace[g]		335		475	
collapse time, min			9.3		40+	18		1		9.2		30+	
Sequence 2, foam height, ml			40		480	50		5		50		80	
collapse time, min			0.5		8.5	0.6		1.4		2.8		4	
Sequence 3, foam height, ml			710		450	550		trace		310		480	
collapse time, min			10		12+	14		-		5.5		30+	
Evaporation, 5-1/2 Hours, %													
At 400°F	25.8		25.0		28.2	19				25.6		24.0	24.6
300 Lead Corrosion, mg/in.[2] (1 Hour at 325°F)	15.1					0.11							
Ryder Gear Loading, ppi						1100[f]		1250[f]					
Panel Coking, mg at													
700°F, 8-Hour Test	445					567		1157		24[h]			
Oxidation-Corrosion													
Sample Size, ml	25	25	25	25	25	100	100	100	25	25	25	25	25
Time, Hours	48	48	48	48	48	72	48	48	48	48	48	48	48
Air Rate, liters/hour	1-1/4	1-1/4	1-1/4	1-1/4	1-1/4	5	5	5	1-1/4	1-1/4	1-1/4	1-1/4	1-1/4
Temperature, °F	400	500	400	500	500	347	400	400	500	500	400	400	400
Weight Change, mg/cm[2]													
Pb-Cu	-0.10	-0.10	+0.10	0.0	-0.10	-	-	-	-	-	-	-	-
Cu	-1.22	-1.61	-1.37	-0.11	-0.14	+0.42	-	-	-	-	-	-	-
Ag	-0.20	-0.10	-1.40	0.0	-0.10	-34	-	-	-	-	-	-	-
Fe	-0.03	0.0	+0.06	0.0	0.0	+0.04	+0.10	+0.03	-0.06	-0.55	+0.10	-0.06	+0.10
Al	-0.03	-0.06	-0.03	0.0	-0.14	-	+0.11	+0.02	+3.4	0.0	+0.26	+0.03	-0.14
Mg	-	-	-	-	-	-	-	-	-	-	-	-	-
Viscosity Change, %													
100°F	tar	solid	+500	solid	solid	+0.1	-	+2.7	solid	solid	+105	+240	+210
210°F	tar	solid	+171	solid	solid	+5.5	+14	+2.8	solid	solid	+87	+100	+48.8
Neutralization Number Change	-	-	10.4	-	-	1.0	0.54	0.0	-	-	4.6	4.0	3.2
Insolubles, %	-	-	0.2	-	0.5	0	0.23	0.09	16.7	-	Nil	trace	trace
Mean Hertz Load (Screening Test), kg	~14		~12			~18				~14		~23	~14

[a] 600-ml Sample in vented aluminum container, MTR Canal Source.

[b] 10-ml Sample in capsule of 410 stainless steel sealed under helium, MTR Canal Source.

[c] Contained 0.001% 50,000 Vis Silicone.

[d] At 414°F.

[e] 200-ml Sample in vented tin-plated container; MTR Canal Source.

[f] Micro Method.

[g] Four-hour test.

TABLE LXXII (continued)

LUBRICANTS BASED ON NAPHTHENIC WHITE OIL

Sample No. (of irradiated samples)							5040-37		4976-17-2	4976-17-15			
Additive	5% Didodecyl Selenide			2% Dibenzyl Selenide	← 2% DBPC →						2% Didodecyl Selenide 5% Tricresyl Phosphate		2% Phenyl-α-naphthyl-amine, 5% Tricresyl Phosphate
Radiation Dosage, 10^{10} ergs/g C	0	0.288[b]	2.88[b]	0	0		0.871[a,c]		2.09[e]	6.48[a]	0		0
Viscosity, cs, °F													
400	-	-	-		-		2.61[d]		1.76[d]	1.82[d]			
210	8.76	7.51	11.6		7.41		8.46		11.3	12.4	6.87		
100	79.3	67.3	132		72.2		89.3		116	165	62.7		
0	-	-	-		14,600		22,100		49,620	-	-		
Pour Point, °F					-25		-15		-15	-15	+5		
Flash Point (COC), °F					380		410[f]		395[f]	380[f]	400		
Spontaneous Ignition Temperature, °F					700		710		710	740			
Foaming													
Sequence 1, foam height, ml					trace[c]		665		445	200			
collapse time, min					-		15.4		30+	37			
Sequence 2, foam height, ml					10		70		50	80			
collapse time, min					2.8		1.5		1.5	1.1			
Sequence 3, foam height, ml					trace		640		610	595			
collapse time, min					-		25.4		20	16.5			
Evaporation, 6-1/2 Hours, %													
At 400°F							25.4		25.1	24.4			
SOD Lead Corrosion, mg/in² (1 Hour at 325°F)					1.15[c]								
Ryder Gear Loading, ppi											1700[f]	2070[f]	
Panel Coking, mg at													
700°F, 8-Hour Test				823	402					20[g]	1210		-
600°F, 5-Hour Test				-	-					-	-		185
Oxidation-Corrosion													
Sample Size, ml					100	25	25	25	25	25	100	25	100
Time, Hours					48	48	48	48	48	48	72	48	72
Air Rate, liters/hour					5	1-1/4	1-1/4	1-1/4	1-1/4	1-1/4	5	1-1/4	5
Temperature, °F					400	500	400	500	400	400	347	500	347
Weight Change, mg/cm²													
Be-Cu					-	0.0	-0.22	0.0	+0.03	+0.13	-	-	-
Cu					+0.03	-3.23	-1.02	0.0	-0.87	-0.68	-0.59	-	+0.13
Ag					-0.01	0.0	-0.35	0.0	0.0	0.0	-39.5	-	+0.04
Fe					-0.01	0.0	-0.16	0.0	+0.10	+0.03	+0.08	+2.09	+0.08
Al					-	-0.06	+0.03	0.0	+0.03	0.0	-	0.0	-
Mg					-0.02	-	-	-	-	-	-	-	-
Viscosity Change, %													
100°F					-	solid	+2500	solid	+241	+258	+41	solid	+6.7
210°F					+4.6	solid	+1300	solid	+83.3	+108	-	solid	-
Neutralization Number Change					0.03	-	15.8	-	6.2	6.6	3.6	-	0.29
Insolubles, % wt					0	-	Nil	-	trace	trace	0	22.4	-
Mean Hertz Load (Screening Test), kg							~14		~22	~23	~27		

[a] 500-ml Sample in vented aluminum container; MTR Canal Source.

[b] 10-ml Sample in capsule of 410 stainless steel sealed under helium; MTR Canal Source.

[c] Contained 0.001% 50,000 Vis Siltrone.

[d] At 410°F.

[e] 200-ml Sample in vented tin-plated container; MTR Canal Source.

[f] Micro Method.

[g] Four-hour test.

It possessed mediocre viscosity-temperature and low temperature properties. Evaporation at 400° F, SOD lead corrosion, and panel coking at 700° F were high. Oxidation stability of the uninhibited oil was poor as indicated by formation of tar in the oxidation-corrosion test at 400° F. At 500° F, all white oil samples solidified in this test.

Inhibitors were quite effective at 400° F but had virtually no effect at 500° F in the oxidation-corrosion tests. Coking was not reduced through the use of inhibitors. Aside from the viscosity changes already discussed, irradiation appeared to be beneficial with respect to oxidation stability at 400° F and coking at 700° F.

5.3.5 UCON DLB 144E

This polyglycol also served as a reference material. The properties of inhibited and uninhibited base stock appear in Table LXXIII. The very high evaporation of the uninhibited and unirradiated UCON DLB 144E at 400° F is typical of a polyglycol. It is attributable for the most part to oxidative breakdown to lower molecular weight materials. Probably related to this effect were the negative changes in viscosity in the oxidation-corrosion tests.

A good Mean Hertz Load value of about 24 was obtained for the neat base stock. The low temperature properties (pour point = -65° F) were also good. Didodecyl selenide had the effect of reducing evaporation at 400° F markedly and of reducing the viscosity change in the oxidation-corrosion tests.

Although the viscosity changes in UCON DLB 144E due to irradiation were quite large (see Figure 24), this base stock when inhibited with didodecyl selenide retained most of its oxidation stability after irradiation. This seemed to apply even in the severe oxidation-corrosion test at 500° F, although data were limited.

5.3.6 Aliphatic Diesters

Test results on di(2-ethylhexyl) azelate, diisooctyl azelate, and di(2-ethylhexyl) sebacate are given in Tables LXXIV, LXXV, and LXXVI. All these diesters had original pour points below -60° F.

Surprising differences were found in the coking levels and oxidation stabilities of diisooctyl azelate and di(2-ethylhexyl) azelate. The latter was far superior in these two respects. Didodecyl selenide effected a marked improvement in the oxidation stability and a large reduction in coking for diisooctyl azelate. On the other hand, the coking value was higher for the di(2-ethylhexyl) sebacate with 5% didodecyl selenide than it was for the neat ester. Also, the viscosity increase in the oxidation-corrosion test at 500° F was higher for the sebacate with 2% selenide than for the ester without inhibitor.

Although these ester based fluids suffered relatively large viscosity increases during irradiation, coking remained unchanged or was reduced.

TABLE LXXIII

LUBRICANTS BASED ON UCON DLB 1882

Sample No. (of irradiated samples)	5040-42				5040-43	5040-17-8	5040-17-11	5040-17-1									
Additive	None			5% Didodecyl Selenide					5% Didodecyl Selenide			5% Dibenzyl Selenide		5% Phenyl-α-naphthyl amine	5% Phenyl-β-naphthylamine		
Radiation Dosage, 10^{19} ergs/g C	0[a]		0.871[a]	0		0.871[a]	4.28[a]	5.46[a]	7.15[b]	0	0.279[c]	2.11[c]	0		0	0.00[c]	7.24[c]
Viscosity, cs, °F																	
400	2.12		2.11[e]	-		1.93[e]	1.48[e]	[f]	[f]	-	-	-	-		-	-	-
210	7.10		8.34	7.00		7.37	8.62	14.7	11.2	6.88	6.78	7.15	7.00		7.42	8.04	-
100	70.0		79.2	29.9		35.0	42.9	90.6	72.2	30.1	29.6	32.2	30.0		38.2	41.5	-
0	760		1210	-		-	1840	4750	2900	-	-	-	-		-	-	-
-40	16,500		25,000	-		-	-	145,000	72,100	-	-	-	-		-	-	-
Pour Point, °F	-65		+60	+50		-35	-50	-40	-50								
Flash Point (COC), °F	495		520[e]	475		380[e]	370[e]	310[e]	375[e]								
Spontaneous Ignition Temperature, °F	770		730	930		900	900	920	900								
Foaming																	
Sequence 1, foam height, ml			445	10[d]		530	100		350								
collapse time, min			3.7	0.75		5.5	15		30								
Sequence 2, foam height, ml			40	15		65	80		90								
collapse time, min			0.5	0.3		1.1	3.5		3.25								
Sequence 3, foam height, ml			940	5		365	540		570								
collapse time, min			3.1	0.7		3.9	20		20								
Evaporation, 6-1/2 Hours, %																	
At 400°F	95.0		98.2			12.0	52.2	21.7	20.0								
SAE Lead Corrosion, mg/in.[e] 1 Hour at 300°F				-4.4	-7.2[d]												
Ryder Gear Loading, ppm				1900[e]	2140[e]												
Panel Coking, mg at																	
700°F, 6-Hour Test	242			314	585								210				
Oxidation-Corrosion																	
Sample Size, ml	25	25	25	100	25	25	25	25	25				100	100	100		
Time, Hours	48	48	48	48	48	48	48	48	48				72	72	72		
Air Rate, liters/hour	1-1/4	1-1/4	1-1/4	5	1-1/4	1-1/4	1-1/4	1-1/4	1-1/4				5	5	5		
Temperature, °F	400	500	500	400	500	500	400	400	400				347	347	347		
Weight Change, mg/cm²																	
Mg-Cu	0.0	+0.10	0.0										-0.5	-	+0.08		
Cu	-0.03	+0.08	0.0										-0.7	-	+0.12		
Mg	-0.10	-0.03	0.0										+0.02	+0.08	+0.11		
Fe	-0.15	-15.4	0.0	+0.32	-0.20	-2.57	-0.22	+0.26	0.0				+0.06	+0.03	-		
Al	-0.19	0.0	0.7	0	0.0	0.0	-0.13	0.0	-0.03				+0.06	+0.07	-		
Viscosity Change, %																	
100°F	-19.4	-18.0	solid	-0.9	+33.1	-39.8	-28.8	-49.9	-39.4				-24	-7.0	-12		
210°F	-34.8	-24.8	solid	-5.7	-0.5	-33.6	-33.4	-60.2	+4.5				-38	-16.4	-14		
Neutralization Number Change	15.4	3.2	-	1.7	8.5	0.4	5.9	6.2	6.4				17.7	8.6	5.9		
Insolubles, % wt	trace	0.4	-	0.12	0.9	1.6	trace	trace	trace				0	ppt	-		
Mean Hertz Load (Screening Test), kg	-24		-23	+27		+32	-30	-31	+30								

[a] 500-ml Sample in vented aluminum container, MTR Canal Source.
[b] 200-ml Sample in vented tin-plated container, MTR Canal Source.
[c] 10-ml Sample in capsule of 410 stainless steel sealed under helium, MTR Canal Source.
[d] Sample contained 0.001% 60,000 Vis Silicone.
[e] Micro Method.
[f] Solid at 414°F.
[g] At +15°F.
[h] Shell Four-Ball Wear Test - Ten hours at 167°F, 0.20 mm at 4-kg load; 0.34 mm at 10-kg load; 0.52 mm at 40-kg load.

TABLE LXXIV

LUBRICANTS BASED ON DI(2-ETHYLHEXYL) AZELATE

Sample No. (of irradiated samples)		5040-50	5040-22
Additive	← None →		
Radiation Dosage, 10^{10} ergs/g C	0	0.87[a]	8.80[a]
Viscosity, cs, °F			
400	0.933	(b)	(b)
210	3.00	3.47	18.3
100	11.2	13.9	135
0	160	235	7450
-40	1170	1920	-
Pour Point, °F	< -60	< -60	< -60
Flash Point (COC), °F	425	405[c]	275[c]
Spontaneous Ignition Temperature, °F	760	740	760
Foaming			
Sequence 1, foam height, ml		30	670
collapse time, min		4	30
Sequence 2, foam height, ml		25	600
collapse time, min		0.6	5
Sequence 3, foam height, ml		30	770
collapse time, min		2.3	20
Evaporation, 6-1/2 Hours, %			
At 400°F		32.6	30.1
Panel Coking, mg at			
700°F, 8-Hour Test	20[d]	8[d]	21[d]
Oxidation-Corrosion			
Sample Size, ml	25	25	25
Time, Hours	48	48	48
Air Rate, liters/hour	1-1/4	1-1/4	1-1/4
Temperature, °F	500	500	500
Weight Change, mg/cm²			
Be-Cu	-0.23	+0.17	0.0
Cu	-1.22	-0.58	-0.07
Ag	-0.16	+0.10	-0.04
Fe	-0.06	-1.61	-6.4
Al	0.0	-1.16	-0.04
Viscosity Change, %			
100°F	+213	solid	+3440
210°F	+123	solid	+1047
Neutralization Number Change	24.6	-	-
Insolubles, % Wt	4.41	21.6	0.4
Mean Hertz Load (Screening Test), kg	~19	~16	~21

[a] 600-ml Sample in vented aluminum container; MTR Canal Source.

[b] Boils at 414°F.

[c] Micro Method.

[d] Four-hour test.

TABLE LXXV

LUBRICANTS BASED ON DIISOOCTYL AZELATE

Sample No. (of irradiated samples)			5116-2	5040-2[a]												
Additive	None	2% Didodecyl Selenide			5% Didodecyl Selenide			5% Dibenzyl Selenide	2% Dibenzyl Selenide		2% Phenothiazine			5% Dibenzothiophene		
Radiation Dosage, 10^{10} ergs/g C	0[f]	0	0.871[b,c]	8.60[b,c]	0	4.88	9.67	0	4.88	12.4	0	4.79	12.2	0	4.79	12.2
Viscosity, cs, °F																
400	-	-	1.86[d]	1.61[d]	-	-	-	-	-	-	-	-	-	-	-	-
210	3.39	3.36	3.97	8.07	3.30	5.07	7.59	3.26	3.88	4.96	3.42	5.86	15.0	3.30	7.45	23.7
100	12.4	12.3	17.0	59.8	12.2	22.9	43.2	11.8	15.4	21.8	12.9	27.7	98.2	12.3	37.6	180
0	-	-	396	4430	-	-	-	-	-	-	-	-	-	-	-	-
-45	6990	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Pour Point, °F	<-80	+5	-60	-40		-45	-60		<-80	<-80	<-80	<-80	-65	<-80	<-80	-70
Flash Point (COC), °F			435[e]	440[e]												
Spontaneous Ignition Temperature, °F	770		1000	800												
Foaming																
Sequence 1, foam height, ml		trace[b]	510	765												
collapse time, min		0.75	4.1	30												
Sequence 2, foam height, ml		trace	70	70												
collapse time, min		0.75	0.8	4												
Sequence 3, foam height, ml		trace	540	870												
collapse time, min		1.25	4.1	20												
Evaporation, 6-1/2 Hours, %																
at 400°F			21.5	15.3												
SAE Lead Corrosion, mg/in.[2] (1 Hour at 325°F)		0.29[b]														
Panel Coking, mg at																
500°F, 8-Hour Test	1766	104	112[a]	80[a]	54[a]	27[a]	747[a]	620[a]	110[a]	248[a]	1534[a]	5720[a]	4750[a]	266[a]	2720[a]	6510[a]
600°F, 8-Hour Test	-	-	-	-	-	-	-	[illegible][a]	304[a]	-	-	-	-	-	-	-
Oxidation-Corrosion																
Sample Size, ml	25	25	25	25												
Time, Hours	48	48	48	48												
Air Rate, liters/hour	1-1/4	1-1/4	1-1/4	1-1/4												
Temperature, °F	500	500	500	500												
Weight Change, mg/cm²																
Ag-Cu	-0.61	-	-	-												
Cu	-1.40	-	-	-												
Ag	-0.16	-	-	-												
Fe	-0.13	-0.81	-1.88	-0.14												
Al	+0.06	+0.10	0.0	-0.07												
Viscosity Change, %																
100°F	+13,800	+670	+255	+93												
210°F	+4,000	+348	+144	+41												
Neutralization Number Change	48.8	42.1	21.6	-												
Insolubles, % wt	Nil	2.2	1.3	0.4												
Mean Hertz Load (Screening Test), kg	-25		-20	+13												

[a] Four-hour test.

[b] Contained 0.001% 60,000 Vis Silicone.

[c] 600-ml Sample in vented aluminum container, [illegible] Canal Source.

[d] At 415°F.

[e] Micro Method.

[f] Shell Four-Ball Wear Test - Two hours at 167°F. 0.72 mm at 5-kg load
0.86 mm at 10-kg load
1.10 mm at 40-kg load

TABLE XXXVI

LUBRICANTS BASED ON DI(2-ETHYLHEXYL) SEBACATE

Sample No. (of irradiated samples)				5116-5	5040-24												
Additive	None		2% Didodecyl Selenide			5% Didodecyl Selenide			5% Dibenzyl Selenide			2% Phenothiazine			5% Dibenzothiophene		
Radiation Dosage, 10^{10} ergs/g C	0		0	0.871[a,c]	8.80[a,c]	0	4.88	9.67	0	4.88	9.67	0	4.88	12.4	0	4.70	12.2
Viscosity, cs, °F																	
400	1.00[d]	-	-	1.04[d]	(c)	0.86[d]	-	-	-	-	-	-	-	-	-	-	-
210	3.34	3.29	3.28	3.56	7.96	3.31	5.44	9.24	3.2[e]	4.07	5.98	3.30	6.90	11.7	3.28	8.78	23.8
100	12.7	12.5	12.4	14.2	42.4	12.5	25.0	52.3	12.2	16.7	27.6	13.2	35.0	83.1	12.7	40.5	175
0	181	-	-	-	1500	-	-	-	-	-	-	-	-	-	-	-	-
-40	-	-	-	-	16,300	-	-	-	-	-	-	-	-	-	-	-	-
-65	8220	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Pour Point, °F	<-80		-5	+10	<-60	-30	-50	-60	<-80	<-80	<-80		<-60	<-65		<-80	-70
Flash Point (COC), °F	450			450[e]	500[e]	440											
Spontaneous Ignition Temperature, °F	770				1000												
Foaming																	
Sequence 1, foam height, ml	trace[d]			50	800	0[a]											
collapse time, min	8			5	30	0											
Sequence 2, foam height, ml	trace			40	140	0											
collapse time, min	0.8			1	5	0											
Sequence 3, foam height, ml	trace			40	465	0											
collapse time, min	5			3.7	10	0											
Evaporation, 6-1/2 Hours, %																	
At 400°F	25.0			19.5	29.3	11.7 14.7			16.5		31.6						
300 Lead Corrosion, mg/in.^{2} (1 Hour at 300°F)	44.3					0.0											
Panel Coking, mg at																	
700°F, 8-Hour Test	149			33[b]	6[b]	431[b]	218[b]	1207[b]	700[b]	178[b]	500[b]		5720[b]				
500°F, 8-Hour Test	-			-	-	-	-	-	0[b]	17[b]	-		-				
Oxidation-Corrosion																	
Sample Size, ml	100	25	25	25	25	100											
Time, Hours	48	48	48	48	48	48											
Air Rate, liters/hour	5	1-1/4	1-1/4	1-1/4	1-1/4	5											
Temperature, °F	400	500	500	500	500	400											
Weight Change, mg/cm^2																	
Fe-Cu	-	-0.84	-	-	-	-											
Cu	-5.77	-0.84	-	-	-	-											
Ag	0.00	-0.10	-	-	-	-											
Fe	0.00	-0.42	0.0	-18.0	-6.7	+0.16											
Al	-0.04	+0.04	+0.15	0.0	0.0	+0.15											
Mg	-5.23	-	-	-	-	-											
Viscosity Change, %																	
100°F	+42.2	+1180	+12,700	-10.5[f]	+17,500	+11.3											
210°F	+29.4	+1450	+3610	-6.28	+5800	+0.9											
Neutralization Number Change	10.5	33.3	84.5	5.2	-	4.0											
Insolubles, % wt	trace	Nil	0.9	0.8	-	0.41											
Mean Hertz Load (Screening Test), kg	[illegible]			[illegible]	[illegible]	[illegible]											

[a] Sample contained 0.001% 60,000 Vis Silicone.
[b] Four-hour test.
[c] Boils at 416°F.
[d] At 410°F.
[e] Micro Method.
[f] 600-ml Sample in vented aluminum container, MTR Canal Source.
[g] Probably erroneous.

5.4 Formulations

Two promising base stocks applicable to the engine oil development were the C_{14-16}-alkyl diphenyl ether and the C_{16-18}-alkylbiphenyl. The former possessed higher stability toward oxidation even after irradiation, while the latter had the better resistance to viscosity changes due to irradiation. The diphenyl ether was judged to have a superior combination of properties and was, therefore, selected as the principal base stock for formulation studies.

The effects of compounding on the properties of C_{14-16}-alkyl diphenyl ether are shown in Table LXXVII. None of the samples in the table was irradiated. A comparison of Sample 1 with Sample 2 shows that 2% didodecyl selenide reduced coking more than 50% and reduced somewhat the viscosity change in the 500° F oxidation-corrosion test.

A much greater reduction in coking was achieved through the use of certain high boiling materials as blending agents. Table LXXVIII shows the effects on coking of a number of such blending agents. The California (solvent refined) bright stock gave consistently low values. The results of tests with various amounts of bright stock are shown in Table LXXVIII and plotted in Figure 25.

The combination of 2% didodecyl selenide and 15% bright stock in Sample 4 (Table LXXVII) produced an even lower coke value than the 25% bright stock in Sample 3. In Sample 5, a 5% concentration of tricresyl phosphate was tried in order to improve lubricity. This raised the Mean Hertz Load value to over 20, but it also increased coking at 700° F and the viscosity change in the oxidation-corrosion test at 400° F. In Sample 6, a 3% concentration of tricresyl phosphate improved lubricity to the equivalent of that of Sample 5, and the deleterious effects were proportionately less.

The inhibiting effects of colloidal graphite are shown in the oxidation-corrosion tests on Samples 7 and 8. The viscosity changes in these samples were appreciably less than the corresponding ones in Samples 1 and 2. Comparison of Samples 9 and 11 indicates that even a 0.2% concentration of graphite had some inhibiting effect in the 500° F oxidation-corrosion test. Unfortunately, the antioxidant effects of colloidal graphite were more than offset by the large increase in coking which it promotes (Samples 7 and 10).

Dark oil-soluble dyes, e.g., Petrol Black A, showed a substantial synergistic effect on the oxidation-inhibiting properties of dialkyl selenides. This can be seen in the low viscosity changes in the 400° F oxidation-corrosion tests for Samples 14 and 15 in Table LXXVII. The effect of Petrol Black A was very small in complex blends such as Samples 12 and 13. It is possible that the tricresyl phosphate, the most reactive ingredient in these blends, had a deactivating effect on the dye and that substitution of another extreme pressure agent for tricresyl phosphate would restore this desirable synergism. Results of Dornte oxidation tests on formulations containing tricresyl phosphate are shown in Table LXXIX. The samples containing the dye had only a small advantage over the sample without the dye.

TABLE LXXVII

EFFECTS OF ADDITIVES ON PROPERTIES OF C_{14-18}-ALKYL DIPHENYL ETHER

Reference	4976-3	4976-3	4976-44	5040-5	5116-22	5116-23	5116-24	5116-39	5116-40	5116-45	5116-47	5105-20	5105-20	5105-34	5116-39	5116-39	
Sample Number	1	2	3	4	5	6	7	8	9	10	11	12	13	13	14	15	16
Composition, Wt %																	
C_{14-18} Alkyl Diphenyl Ether	100	98	75	81	77.9	79.9	78.4	79.4	81.9	81.4	81.7	96.7	81.7	81.7	97.8	97.8	99.8
Didodecyl Selenide		2		2								2	2	2	2	2	
Bis(tridecyl) Selenide					2	2	2	2	2	2	2						
RPM 210 Bright Stock			25	15	15	15	14.5	15	15	15	15		15	15			
Tricresyl Phosphate					5	3	5	3	1	1	1	1	1	1			
Silicone	0.001	0.001			0.1	0.1	0.2	0.1	0.1	0.1	0.1	0.1	0.1	0.001			
Colloidal Graphite							2	0.5		0.5	0.2						
Petrol Black A												0.2	0.2	0.2	0.2		0.2
Oil Jet Black 1699																0.2	
Viscosity at 415°F, cs	1.26		1.57		1.51	1.57			1.41		1.55			1.41			
Viscosity at 210°F, cs	4.85	4.76	7.80	6.27	6.19	6.22	11.7	6.55	6.51		6.19	4.73	6.25	6.25	4.80	4.80	4.84
Viscosity at 100°F, cs	26.8	26.0	56.5	39.6	39.5	40.1	71.0	41.5	40.1		38.0	26.0	40.0	39.6	26.2	26.2	26.2
Viscosity at 0°F, cs	1060	3960	3553	1875	2080	2000	3210		1990		856						
Viscosity Index	116	115	112	116	114	112	141	119	115		120	113	114	115	117	117	
Pour Point, °F	-25	-15	-20	-20	-20	-20	-20		-20		-20			-15			
Flash Point, °F	430	445			470	460	555		460		435			485			
SIT, °F	810	1030			1040	1020	1020		1010					980			
Coking at 700°F, 4 hr, mg	801[a]	248[a]	62.7 44.4	24.8	61.3	39.1	2730			1134	89						
Oxidation-Corrosion																	
48 Hours at 400°F																	
Vis Change at 100°F, %	+59.4	+70.5		+50.2	+62.3	+52.7	-7.05	+32.3						+58.1	+11.8	+15.3	+37.8
Vis Change at 210°F, %	+29.8	+25.6		+30.6	+36.0	+33.1	-5.13	+17.7						+35.6	+6.3	+8.3	+16.1
48 Hours at 500°F																	
Vis Change at 100°F, %	+229	+164							+190		+143		+157	+184			
Vis Change at 210°F, %	+108	+77							+94.2		+73.0		+80.9	+94.5			
Mean Hertz Load (Screening Test), kg	15	16		16	23	23	23							~26			

[a] Eight-hour test.

TABLE LXXVIII

COKE TESTS AT 700°F ON C_{14-16}-ALKYL DIPHENYL ETHER BLENDS

Blending Agent	Weight, Per Cent	Coke, mg[a]
Tridodecyl Diphenyl Ether	25	250
Distillation Bottoms from C_{16-18}-Alkylbiphenyl	25	45;98
Heavy Distillation Cut from C_{16-18}-Alkylbiphenyl	25	153
Piccolastic A-5 (Polystyrene)	25	179
Dow Resin V-9 (Poly-α-methylstyrene)	25	218
Polybutene 128	25	78;277
Kenflex L (Naphthalene-Formaldehyde)	25	473
Polystyrene Glycol, Dow 174-500	17 (Saturated)	432
Polyglycol G5	25	99
Bright Stock[b]	25	99
Bright Stock	100	13
Bright Stock	50	26
Bright Stock	10	94

[a] Four-hour test in Model C Panel Coker.
[b] California Solvent Refined 210 Bright Stock.

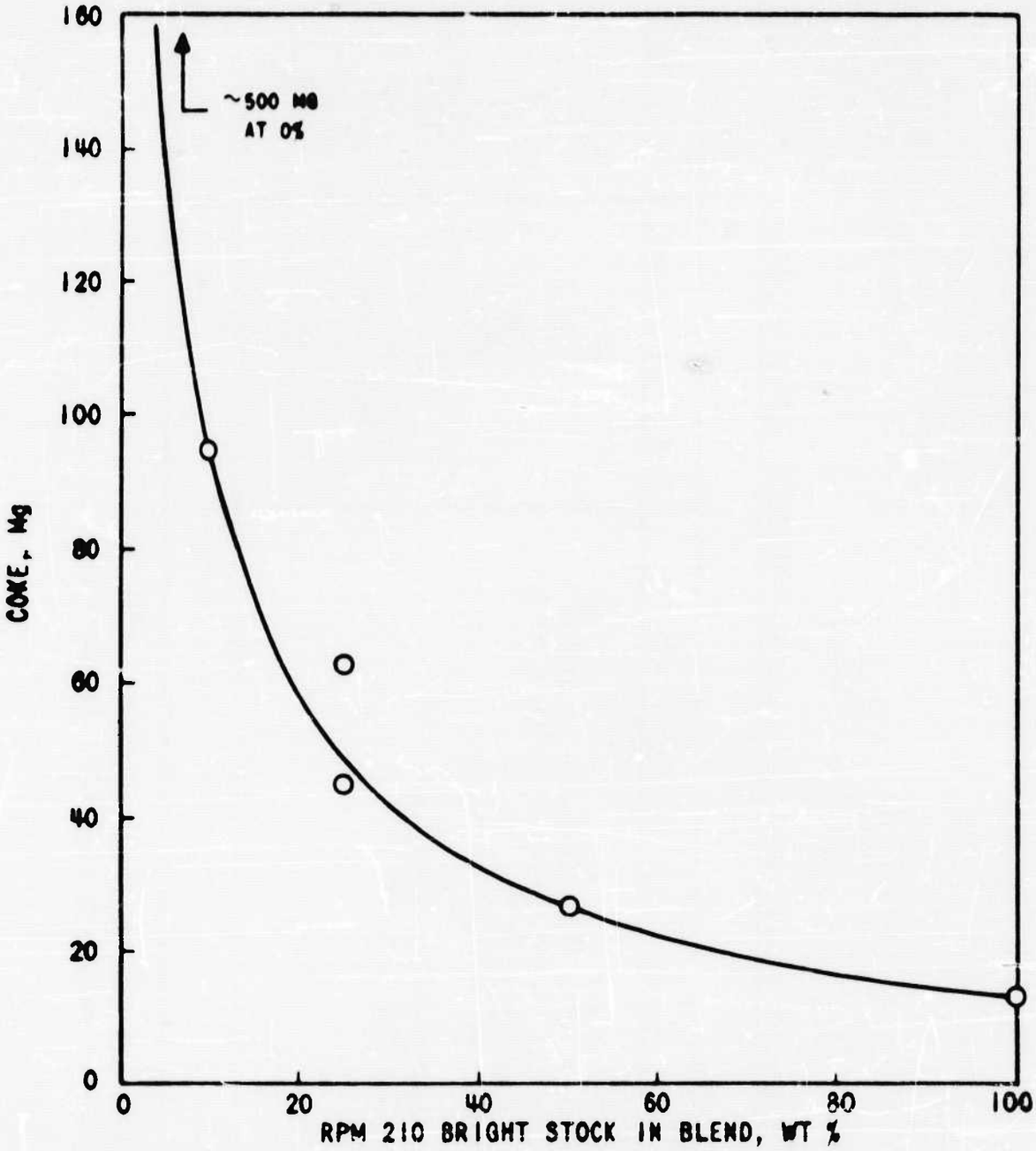


FIG. 25 - COKE FORMATION OF VARIOUS BLENDS
C_{16-18}-ALKYL DIPHENYL ETHER AND RPM 210 BRIGHT STOCK
WITHOUT RADIATION
(4 HOUR TEST AT 700°F TEST IN MODEL C PANEL COKER)

Table LXXIX

Inhibiting Effect of Petrol Black A in Formulations Containing Tricresyl Phosphate

Blend No.	1	2	3
Composition			
C_{14-16}-Alkyl Diphenyl Ether	81.9	81.7	81.7
210 Bright Stock	15	15	15
Didodecyl Selenide	2	2	
DBPC			2
Tricresyl Phosphate	1	1	1
60,000 Vis Silicone (1% in kerosene)	0.1	0.1	0.1
Petrol Black A		0.2	0.2
Dornte Oxidation Test			
Sample Size, g	25	25	25
Catalyst	None	None	None
Temperature, °F	400	400	400
Time to Absorb 1000 ml O_2, hours	4.9	5.5	5.7

The properties of some formulations, based on C_{14-16}-alkyl diphenyl ether, before and after irradiation are shown in Table LXXX. Blends 1 and 2 were the same except for the concentration of tricresyl phosphate. Of interest is the large increase in coking caused by a relatively low radiation dosage of 1.77×10^{10} ergs/g C. The increase was greater in Blend 1 which contained the larger concentration of tricresyl phosphate. As the dosage became greater, coking decreased from the initial maximum. A corresponding rise and fall was found in the Mean Hertz Load values. This may indicate a change in the tricresyl phosphate due to irradiation and suggests that: (a) omission of the phosphate from a formulation would yield a more radiation-stable fluid; (b) the phosphate contributes to coking of irradiated fluids.

The percentage changes in viscosity due to irradiation in Blends 1 and 2 were of the same order of magnitude as for the neat C_{14-16}-alkyl diphenyl ether base stock. Viscosity changes in the oxidation-corrosion test at 400° F appeared to go through a maximum at about 1.77×10^{10} ergs/g C and through a minimum at about 5.45×10^{10} ergs/g C.

TABLE LXXX

EFFECTS OF IRRADIATION ON PROPERTIES OF GAS TURBINE OIL FORMULATIONS

Reference	5116-22	5165-21	5165-25	5165-29	5116-23	5165-22	5165-26	5165-30	5116-24	5165-23	5165-27	5165-31	5116-25	5165-24	5165-28	5165-32	5165-34	5165-47	5165-38	5116-48	5165-41	5165-45
Blend Number	1				2				3				4				5			6		
Dosage, 10^{10} ergs/g C	0	1.77	5.45	8.96	0	1.77	5.45	8.96	0	1.77	5.45	8.96	0	1.77	5.45	8.96	0	0.09	0.98	0	4.44	8.89
Composition, Wt %																						
C_{14-16}-Alkyl Diphenyl Ether	78				80				76.5				80				81.7					
210 Bright Stock	15				15				14.5								15			15		
Tricresyl Phosphate	5				3				5				3				1			1		
Bis(tridecyl) Selenide	2				2				2				2				2			2		
60,000 Vis Silicone	0.1				0.1				0.1				0.1				0.001			0.1		
Colloidal Graphite									2													
Kendex 0834													15									
Petrol Black A																	0.2					
C_{14-16}-Alkylbiphenyl																				82		
Viscosity at 210°F, cs	6.19	6.94	8.47	11.0	6.22	6.97	8.50	11.3	11.7	18.6	16.2	14.7	8.66	8.47	12.6	16.8	6.25	6.32	6.63	7.13	8.67	11.1
Viscosity at 100°F, cs	39.5	46.9	63.1	93.4	40.1	47.2	63.9	97.9	71.0	105	127	134	62.0	63.1	106	164	39.6	40.7	43.8	56.6	76.1	110
Pour Point, °F	-20	-20	-25	-35	-20	-20	-25	-30	-20	-30	-25	-35	-30	-25	-20	-25	-15		-15	-30		
Flash Point, °F	470				460				555				435				485		455	445		
Spontaneous Ignition Temperature, °F	1040	1020	1020	1000	1020	1020	980	980	1020	1010	[illegible]	990	960	1020	1000	1010	980		930	980		
Foaming (Good or Bad)	G	B	B			B				B				B			G		B	B		
Evaporation, 6-1/2 hr at 400°F, %	13.4				13.5				13.0				13.4				12.8		13.2	10.4		
Mean Hertz Load (Screening Test), kg	23	55		30	23	40		27	23	32		27	23				26		26			
Oxidation-Corrosion[b], 48 hr at 400°F																						
Iron, mg/cm²	+0.19	+1.70	+2.75	+1.82	+0.16	+1.12	+0.45	+1.82	-0.06	+1.25	+1.70	+0.32	-0.10	+1.80	+1.50	+2.24	+0.26		+0.38			
Aluminum, mg/cm²	+0.10	+1.41	+2.50	+0.61	+0.13	+0.39	+1.19	+0.61	0.0	-0.22	+1.82	+0.45	+0.10	+2.05	+1.25	+0.99	+0.16		+0.48			
Vis at 100°F, cs (% change)	+62.3	Tar	+145	+475	+52.7	Tar	+437	+660	-7.05	Tar	Tar	+900	+87.1	Tar	Tar	Tar	+58.1		Tar			
Vis at 210°F, cs (% change)	+36.0	Tar	+90.5	+221	+33.1	Tar	+213		-5.13	Tar	Tar	+586	+54.3	Tar	Tar	Tar	+35.6		+200c			
Neutralization No.	5.0	Tar	5.4		4.3	Tar	7.1		4.8	Tar	Tar		2.0	Tar	Tar	Tar	5.0		3.3			
Insolubles, %	Nil	Tar	Nil	Nil	Nil	Tar	Nil	Nil	1.1	Tar	Tar	Nil	Nil	Tar	Tar	Tar	Nil		Nil			
Evaporation Loss, %	1.3	8.0	5.0	7.2	2.2	4.3	5.1	7.2	1.3	5.6	10.2	14.9	0.4	12.8	5.5	15.7	1.5		10.7			
Panel Coking, 4 hr at 700°F, mg	61	1370	1360	880	39	800	573	445	2730				178	158	510	518	60		-			
WADC Deposition Test, 5040°F																	0.67		1.03			

a. CRC-REFERENCE 250. b. 75-ml Sample, 1-1/4 liters air/hour. c. Didodecyl selenide

The use of the relatively large concentration (0.1%) of silicone antifoam agent failed to achieve the desired foam suppression after irradiation. Several solid globules, believed to be crosslinked silicone polymer, were found in the irradiated samples.

A comparison of the radiation-induced viscosity changes in Blends 1 and 3 shows the beneficial effect of colloidal graphite in reducing radiation damage. Percentagewise, the changes in Blend 3, which contained 2% graphite, were about half as great as those in Blend 1. However, the results in the 400°F oxidation-corrosion test were poorer.

In Blend 4 of Table LXXX, Kendex 0834, a propane-precipitated resin from Pennsylvania residuum, was substituted for bright stock as an anticoke agent. Initially, the Kendex 0834 was less effective than the bright stock in suppressing coke formation in the panel coke test at 700°F. After irradiation, however, it appeared to be equal to or better than the bright stock in this respect. The percentage changes in viscosity upon irradiation and the stability to oxidation were worse for the Kendex 0834 blend than for the corresponding Blend 2 containing bright stock.

Blend 5 in Table LXXX was the most promising engine oil formulation to emerge from the work. It was designated CALRESEARCH 230 and was recommended to WADC for testing in a J-57 engine. (Available data on CALRESEARCH 230 are in Table III, page viii.) The results of bench tests on this formulation without irradiation were satisfactory for the most part. Particularly good was the low value of 0.67 obtained in the WADC Model F Deposition Tests. Postirradiation properties should be somewhat better than those for Blend 2 inasmuch as a lower concentration of tricresyl phosphate was used in Blend 5.

A relatively small amount of formulation work was done with base stocks other than C_{14-16}-alkyl diphenyl ether. Table LXXXI presents properties of various unirradiated base stocks blended with California (solvent refined) 210 Bright Stock and bis(tridecyl) selenide. Available data on the base stocks inhibited with didodecyl selenide are included for comparison. The beneficial effects of the bright stock in reducing coking appeared to be applicable to all these base materials, but the effect on the biphenyl bottoms was less than that on the distilled product. The bright stock caused much greater viscosity changes in the oxidation-corrosion tests at 400°F than were obtained with the base stock-selenide blends.

Blend 6 in Table LXXX is a formulation based on C_{16-18}-alkylbiphenyl. Comparison of the viscosity changes after irradiation for this blend with those for Blend 2 in the same table shows that the higher radiation stability of the alkylbiphenyl carries over into its blends.

TABLE LXXXI

EFFECTS OF BRIGHT STOCK ON PROPERTIES OF BASE STOCKS

Blend Number	1	2	3	4	5	6	7	8	9	10
Composition, Wt %										
C_{18}-$_{18}$-Alkylbiphenyl (distilled)	85	98								
C_{18}-$_{18}$-Alkylbiphenyl (bottoms)			85	98						
Diisooctyl Terephthalate					85	98				
Naphthenic White Oil							85	98		
UCON DLB 1442									85	98
210 Bright Stock	15		15		15		15		15	
Bis(tridecyl) Selenide	2		2		2		2		2	
Didodecyl Selenide		2		2		2		2		2
Viscosity at 210°F, cs	6.69	5.17	8.87	6.86	6.67	5.11	9.56	7.41	8.44	7.00
Viscosity at 100°F, cs	51.6	35.3	77.0	52.3	48.5	30.5	101	72.0	41.6	29.9
Viscosity Index	88	76	96	93	100	105	74	60	154	168
Panel Coking, 4 hr at 700°F, mg	-	804 [a]	70	173 [a]	5	49 [a]	29	800 [a]	5	450 [a]
Oxidation-Corrosion										
Sample Size, ml	25	100	25		25	100	25	100	25	100
Time, hours	48	48	48		48	48	48	48	48	48
Air Rate, liters/hour	1-1/4	5	1-1/4		1-1/4	5	1-1/4	5	1-1/4	5
Temperature, °F	400	400	400		400	400	400	400	400	400
Weight Change, mg/cm²										
Iron	+0.26	+0.19	+0.15		+0.32	-0.02	+0.15	+0.03	+0.10	+0.02
Aluminum	+0.19	+0.27	+0.10		+0.06	-0.07	+0.10	+0.02	0.0	0.0
Viscosity Change at 100°F, %	+2000	+54.5	Tar		+161	+26.0	Tar	+2.7	+51.4	-0.9
Viscosity Change at 210°F, %	+363	+25.6	Tar		-24.8	+11.4	Tar	+2.0	+15.9	-5.7
Neutralization Number Change	7.5	3.2	-		16	10.2	-	0.03	12.4	1.7
Insolubles, Wt %	Nil	0.9	-		Nil	0.2	-	0.1	Nil	0.1

[a] Eight-hour test

5.5 Results of Cooperative Tests

Sixteen samples of various base stocks, inhibited and uninhibited, were tested in oxidation-corrosion tests at 500° F both at the Materials Laboratory, WADC, and at California Research Corporation. The results appear in Table LXXXII. Except in one or two cases, the agreement was very poor both with respect to fluid properties after the test and with respect to weight changes in the metal specimens. The comparison of results emphasizes the need for caution in reaching conclusions on the basis of oxidation-corrosion tests at 500° F.

Five samples (GTO-582 through 586) were sent to Southwest Research Institute for Micro Ryder Gear Tests. The results are given in Table LXXXIII together with available Mean Hertz Load (screening test) data.

Table LXXXIII

Micro Ryder Gear Loading Tests on Exploratory Blends

GTO No.	582	583	584	585	586
Composition					
Naphthenic White Oil, wt %	98	93			
C_{14-16}-Alkyl Diphenyl Ether, wt %			100	88	
UCON DLB 144E, wt %					98
Tricresyl Phosphate, wt %		5			
Didodecyl Selenide, wt %	2	2		2	2
Polybutene 128, wt %				10	
60,000 Vis Silicone (1% in kerosene), wt %	0.1	0.1	0.1	0.1	0.1
Micro Ryder Gear Loading, ppi	1100, 1280	1700, 2070	2240, 1700	2080, 1630	1890, 2140
Mean Hertz Load (Screening Test), kg	18	27	15	-	27

Surprisingly high Ryder Gear Loading values were obtained for the samples based on C_{14-16}-alkyl diphenyl ether. These are in disagreement with the Mean Hertz Load (screening test) results which are fairly low (about 15). High values were obtained in both tests on the UCON DLB 144E blend. The over-all correlation between the two tests appears to be poor.

TABLE LXXXII

COMPARISON OF OXIDATION-CORROSION TEST RESULTS AT 500°F RUN AT CALIFORNIA RESEARCH CORPORATION AND AT WADC

CALRESEARCH No.	185		186		187		188		189		190		191		192	
Composition, Wt %																
Naphthenic White Oil	100		98		98		93									
C_{18-18}-Alkylbiphenyl (distilled)									100		98		98			
C_{18-18}-Alkyl Diphenyl Ether															100	
UCON DLB 144E																
Diisooctyl Terephthalate																
DPPC			2								2					
Didodecyl Selenide					2		2						2			
Tricresyl Phosphate							5									
Polybutene 128																
60,000 Vis Silicone (1% in kerosene)	0.1		0.1		0.1		0.1		0.1		0.1		0.1		0.1	
Test Results	a	b	a	b	a	b	a	b	a	b	a	b	a	b	a	b
Viscosity Before Test, cs,																
At 100°F	70.1	71.4	67.9	71.1	65.0	65.4	61.1	60.9	37.6	36.6	36.7	36.0	35.3	35.0	26.8	26.6
At 210°F	7.42	7.56	7.23	7.21	7.20	7.23	6.91	6.90	5.36	5.35	5.30	5.21	5.17	5.22	4.81	4.84
Viscosity After Test, cs																
At 100°F	solid	solid	solid	106	solid	148	solid	60.4	116	solid	37.4	solid	-	44.7	87.9	26.3
At 210°F	solid	solid	solid	9.01	solid	12.7	solid	6.72	9.02	solid	5.35	solid	-	5.90	10.0	4.72
Viscosity Change, %																
At 100°F	-	-	-	+49	-	+126	-	-0.9	+208	-	+2.0	-	-	+27.6	+229	-1.1
At 210°F	-	-	-	+25	-	+76	-	-2.6	+68	-	+1.0	-	-	+13.0	+108	-2.5
Neutralization No. Change	-	-	-	2.1	-	3.3	-	1.3	5.9	-	0.3	-	-	0.47	5.6	1.0
Insolubles, %	-	-	-	2.2	16.7	4.6	22.4	6.5	2.6	-	0	-	-	0.33	1.3	0.65
Evaporation Loss, %	-	55.6	-	22.0	0	6.2	0	0.2	-	27.0	-	22.2	-	4.5	2.5	17.5
Weight Change, mg/cm²																
Al	-0.06	-13.3	-0.06	+0.46	+5.72	+0.97	0.0	+0.37	0.0	+2.01	0.0	+3.06	-	0.0	0.0	+0.25
Ag	-0.10	+0.30	0.0	-0.16	-	-	-	-	0.0	+2.42	-0.06	+4.02	-	-	-0.23	+0.38
Cu	-1.61	-0.42	-3.23	-0.92	-	-	-	-	-5.48	-2.81	+0.06	-2.28	-	-	-1.37	-0.46
Cu-Be	-0.10	+0.09	0.0	-0.28	-	-	-	-	-3.28	-1.46	+2.58	-0.16	-	-	+1.94	+0.88
Fe	0.0	+0.39	0.0	-0.56	-1.09	+0.21	+3.49	+1.11	0.0	+0.64	0.0	+3.61	-	+0.54	-0.11	+0.23

a. California Research Corporation 48-hour test on 25-ml sample with 1-1/4 liters air/hour.
b. WADC results shown are average of duplicate runs, 48-hour test on 20-ml sample with 1 liter air/hour.

TABLE LXXXII (continued)

COMPARISON OF OXIDATION-CORROSION TEST RESULTS AT 500°F
RUN AT CALIFORNIA RESEARCH CORPORATION AND AT WADC

CALRESEARCH No.	193		194		195		196		197		198		199		200	
Composition, wt %																
Naphthenic White Oil																
C_{16-18}-Alkylbiphenyl (distilled)																
C_{16-18}-Alkyl Diphenyl Ether	98		98		88											
UCON DLB 144E							100		98							
Diisooctyl Terephthalate											100		98		98	
DPPC	2												2			
Didodecyl Selenide			2		2				2						2	
Tricresyl Phosphate																
Polybutene 128					10											
60,000 Vis Silicone (1% in kerosene)	0.1		0.1		0.1		0.1		0.1		0.1		0.1		0.1	
Test Results	a	b	a	b	a	b	a	b	a	b	a	b	a	b	a	b
Viscosity Before Test, cs.																
At 100°F	26.4	26.9	26.0	26.4	59.0	59.3	30.5	30.3	29.6	29.5	31.6	31.2	31.7	31.4	30.3	30.1
At 210°F	4.77	4.83	4.78	4.88	9.17	9.17	7.12	6.96	7.00	6.94	5.04	5.05	5.00	5.00	4.98	5.00
Viscosity After Test, cs.																
At 100°F	53.3	41.5	68.6	39.0	-	74.6	25.0	23.8	39.4	25.2	solid	-	solid	-	32.1	-
At 210°F	7.27	6.26	8.36	5.92	24.8	9.50	5.39	4.66	7.18	5.10	solid	-	solid	-	4.95	-
Viscosity Change, %																
At 100°F	+102	+54.4	+164	+47.7	-	+25.8	-18	-21.4	+33.1	-14.6	-	-	-	-	+6.0	-
At 210°F	+53	+29.6	+77	+21.4	+172	+3.6	-24.8	-33.0	+2.5	-26.6	-	-	-	-	-0.6	-
Neutralization No. Change	5.3	0.5	5.8	2.0	5.7	4.5	3.2	10.2	8.6	6.0	-	5.8	-	5.5	16.2	5.0
Insolubles, %	0.4	0.03	0.9	0.05	1.9	0.06	0.4	0.11	0.9	0.07	-	8.73	-	11.2	0.4	6.3
Evaporation Loss, %	-	0.5	-	2.0	3.7	4.5	-	10.2	13.0	6.0	11.3	5.8	7.1	5.5	-	5.0
Weight Change, mg/cm²																
Al	0.0	-0.03	0.0	+0.86	0.0	+2.58	0.0	-0.05	0.0	+0.02	-0.23	-0.06	0.0	-0.07	+0.17	-0.08
Ag	0.0	-0.21	-	-	-	-	-0.03	-0.20	-	-	-0.23	-0.15	-2.28	-0.28	-	-
Cu	-0.10	-0.62	-	-	-	-	+0.06	+0.02	-	-	-1.66	-3.55	-2.63	-5.28	-	-
Cu-Fe	+2.24	+0.12	-	-	-	-	+0.10	+0.04	-	-	+1.26	-1.90	-0.23	-3.66	-	-
Fe	-0.06	-0.04	-0.03	-0.18	-0.97	-0.64	-15.4	+0.21	-0.34	+0.06	-0.11	+0.14	-23.5	-0.09	-1.25	-0.66

a. California Research Corporation 48-hour test on 25-ml sample with 1-1/4 liters air/hour.
b. WADC results shown are average of duplicate runs, 48-hour test on 20-ml sample with 1 liter air/hour.

5.6 Miscellaneous

Metal specimens were placed in various fluid samples for irradiation. This was to determine the corrosive tendencies of the products. After exposure, the specimens were cleaned and reweighed. Data are in Table LXXXIV. Weight changes were minor except in a few instances where DBPC was a constituent of the sample. Here changes amounted to about 0.1%.

5.7 Status, Conclusions, and Recommendations

Substantial progress was made in the development of a radiation resistant high temperature gas turbine engine oil. The formulation, CALRESEARCH 230[1], was sufficiently advanced to warrant testing in an engine, even though radiation stability was less than that desired. The oxidative stability after irradiation for this product and similar formulations was poor, although that of the base stock was relatively good. Two ingredients are suspected of causing the loss in stability: the tricresyl phosphate and the 210 Bright Stock. It is believed that substitutes with greater stability can be found for both materials. Elimination of tricresyl phosphate should not only improve the oxidation stability of the blend but reduce postirradiation coking. There is also a possibility that the tricresyl phosphate interferes with the synergistic effect of oil-soluble dyes on the inhibitive properties of selenides. A specially synthesized high boiling substance, essentially aromatic in structure, would resist oxidation and radiation damage better than 210 Bright Stock while possibly performing the same function in reducing coke formation.

Improvement of low temperature properties of CALRESEARCH 230 can probably be achieved by using a base stock which is predominantly C_{14}-alkyl diphenyl ether instead of the C_{14-16}-mixture. With respect to base stocks other than the alkyl diphenyl ethers, test results indicate that naphthenic white oil and the aliphatic esters lack the thermal and radiation stability to warrant further consideration. Diisooctyl terephthalate also falls short of the requisite stability, but variations of this compound may hold promise. Alkylbiphenyls possess a high radiation stability which makes these hydrocarbons attractive for further study. UCON DLB 144E, which showed a reversal in the usual viscosity change in oxidation-corrosion tests, may be a useful blending agent for other base stocks to counteract excessive viscosity increases due to oxidation.

[1] C_{14-16}-Alkyl diphenyl ether containing petroleum 210 Bright Stock, didodecyl selenide, tricresyl phosphate, Petrol Black A, and silicone (see Table LXXX, page 174).

TABLE LXXXIV

CORROSION DURING IRRADIATION

	Gamma Dosage, 10^{10} ergs/g C	Corrosion					
		Steel	Silver	Magnesium	Copper	Titanium	Aluminum
C_{18-18}-Alkylbiphenyl (bottoms)	8.7	H	M	H	L	L	H
98% C_{18-18}-Alkylbiphenyl (bottoms) - 2% Didodecyl Selenide	8.7	L	M	H	L	L	L
98% C_{18-18}-Alkylbiphenyl (bottoms) - 2% Parabar 441	8.7	L	L	H	L	M	M
98% C_{18-18}-Alkylbiphenyl (bottoms) - 2% Santolube 395X	8.7	L	L	M	M	L	L
Diisooctyl Terephthalate	9.3	L	L	L	L	L	L
98% Diisooctyl Terephthalate - 2% Didodecyl Selenide	9.3	L	L	L	L	L	L
98% Diisooctyl Terephthalate - 2% Parabar 441	9.3	L	L	L	L	L	M
98% Diisooctyl Terephthalate - 2% Santolube 395X	9.3	L	L	L	M	L	L
98% UCON DLB 144E - 2% Didodecyl Selenide	6.5	L	L	L	H	H	M
98% Naphthenic White Oil - 2% Didodecyl Selenide	6.5	L	M	M	L	H	M
98% Naphthenic White Oil - 2% Parabar 441	6.5	H	M	M	L	H	H
Tetradecyl Diphenyl Ether	6.5	L	L	H	H	H	M
98% Naphthenic White Oil - 2% Didodecyl Selenide	4.4	L	L	H	L	M	M
98% Naphthenic White Oil - 2% Parabar 441	2.1	H	L	H	L	H	H
98% UCON DLB 144E - 2% Didodecyl Selenide	7.1	L	L	M	L	L	M
98% UCON DLB 144E - 2% Didodecyl Selenide	5.0	L	L	H	M	M	M
98% Diisooctyl Terephthalate - 2% Parabar 441	4.0	L	L	L	L	L	L
98% Diisooctyl Terephthalate - 2% Parabar 441	1.9	L	L	L	L	L	L
98% Diisooctyl Terephthalate - 2% Didodecyl Selenide	7.9	L	L	H	L	L	L
98% Diisooctyl Terephthalate - 2% Didodecyl Selenide	6.2	L	L	L	L	H	H
98% C_{18-18}-Alkylbiphenyl - 2% Parabar 441	4.5	H	L	M	H	H	H
98% C_{18-18}-Alkylbiphenyl - 2% Parabar 441	2.3	L	L	M	L	L	M
98% C_{18-18}-Alkylbiphenyl - 2% Didodecyl Selenide	7.4	M	L	M	H	M	M
98% C_{18-18}-Alkylbiphenyl - 2% Didodecyl Selenide	5.6	L	L	M	M	L	L

H - High

M - Medium

L - Low

6 GEAR LUBRICANTS (S. R. Calish)

6.1 Introduction

The objective of this phase of the work was to develop a high temperature gear lubricant suitable for use in radiation atmospheres. The pattern nonnuclear specification was MIL-L-7499. This included a wide useful temperature range and film strength values high enough to require additives in any base oil under consideration. It was apparent from the beginning of the research that the gear oil and engine oil phases would be closely allied. Any potential engine oil would be considered a base oil candidate for further gear oil development. A very small effort went into the latter in 1957.

Work in 1956[1] on gear oils consisted of screening 16 extreme pressure agents in four principal base oils, a mineral oil, a polyglycol, a terephthalate ester, and an alkylbiphenyl. It was determined in earlier research[2] that chlorine-containing extreme pressure agents tended to become corrosive during exposure to radiation. Thus, the additives used in 1956 were compounds of phosphorus and sulfur. From these results, samples were selected late in 1956 for full-scale Mean Hertz Load determinations. Tests were made by Inland Testing Laboratories (Division of Cook Electric Company), and results became available in 1957.

6.2 Test Results

Mean Hertz Load Tests were performed on 11 compounded fluids before and after irradiation to 6.8×10^{10} ergs/g C. In addition, C_{14-16}-alkyl diphenyl ether was tested before irradiation. Results are in Table LXXXV. These data show considerable difference in film strength among base oils; but, more important, there was even greater difference in response to extreme pressure additives. In every case, the addition of sulfurized olefins produced a finished blend which met the 40-kg Mean Hertz Load requirement of MIL-L-7449.

The results of Mean Hertz Load Tests after irradiation indicated even more clearly that the base oil-additive combination must be carefully selected if desired high film strength is to be maintained in use. Of the sulfur-containing additives, only the diparaffin sulfide remained effective after irradiation in the ester base oil. In the more radiation resistant base oil, C_{16-18}-alkylbiphenyl, film strength was not appreciably affected by irradiation regardless of additive.

[1] "Effects of Radiation on Aircraft Lubricants and Fuels," (California Research 1956 Summary Report on Contract AF 33(616)-3184) WADC Technical Report 56-646, p. 126.

[2] J. G. Carroll and S. R. Calish, "Some Effects of Gamma Radiation on Commercial Lubricants," Lubrication Engineering 13, No. 7, 338 (1957).

TABLE LXXXV

VISCOSITY AND FILM STRENGTH OF GEAR OILS

Base Stock	Additives	Sample No.	Original Viscosity, cs 100°F	Original Viscosity, cs 210°F	Mean Hertz Load, kg Before Irradiation	Mean Hertz Load, kg After Irradiation to 6.8 x 10^{19} ergs/g C
C_{14-18}-Alkyl Diphenyl Ether	2% Dibenzyl selenide	4535-29-2	51.78	6.81	9.45, 9.51	-
UCON DLB 144E	5% Diparaffin sulfide, 2% Dibenzyl selenide	4535-31-1	32.01	7.27	37.3, 41.5	34.7, 39.2
	5% Zinc dialkyldithiophosphate, 2% Dibenzyl selenide	4535-31-2	30.31	6.89	55.8, 58.3	40.4, 46.2
	5% Sulfurized olefin, 2% Dibenzyl selenide	4535-31-3	29.12	6.76	65.5, 71.7	46.3, 48.6
	0.1% Alkylamine salt of alkylphosphoric acid, 2% Dibenzyl selenide	4535-31-5	30.09	7.01	35.5, 31.9	34.3, 30.7
	5% Santolube 395X, 2% Dibenzyl selenide	4535-31-6	33.71	6.72	44.2, 44.5	37.1, 36.4
C_{14-18}-Alkylbiphenyl	2% Dibenzyl selenide	DG 1269	51.78	6.81	12.1, 14.0	20.6, 18.2
	5% Sulfurized olefin, 2% Dibenzyl selenide	4535-31-7	49.45	6.59	44.3, 45.0	41.3, 46.3
	0.1% Alkylamine salt of alkylphosphoric acid, 2% Dibenzyl selenide	4535-31-8	51.78	6.83	15.1, 18.4	18.9, 16.2
	5% Santolube 395X, 2% Dibenzyl selenide	4535-31-12	58.09	7.57	31.5, 28.2	26.0, 26.2
Diisooctyl Terephthalate	5% Sulfurized olefin, 2% Dibenzyl selenide	4535-31-10	29.43	4.85	54.1, 55.1	33.8, 35.5
	0.1% Alkylamine salt of alkylphosphoric acid, 2% Dibenzyl selenide	4535-31-11	29.96	4.98	22.3, 22.1	21.5, 23.1

[a] MTR Canal Source.

6.3 Status, Conclusions, and Recommendations

This portion of the project was largely dormant during 1957 because of planned emphasis on engine oil base stocks, which will provide the basis for a radiation resistant gear oil. The results reported are final tests on oils blended during 1956.

It is recommended that the gear lubricating ability of engine oils continue to be an important aspect of their evaluation. The alkyl aromatics, preferred base stock for engine oils, appear to have poor lubricity, based on Mean Hertz Load Tests. The addition of extreme pressure agents, such as diparaffin sulfide, may improve this property. However, the effect of these compounds on corrosion and radiation resistance under dynamic conditions is not known and should be evaluated.

7 JET FUELS (J. T. Guerin)

7.1 Introduction

The study of effects of radiation on jet fuel properties was continued and expanded from previous work on this contract[1]. It was found in 1956 that jet fuel properties (with the exception of thermal stability) pertinent to aircraft operation were affected only slightly as a result of exposure to 0.87 to 4.35 x 10^{10} ergs/g C of gamma radiation. The JP-5 grade fuels had less radiation tolerance than JP-4 fuels. This was not greater radiation instability for JP-5's, but resulted from less margin between initial JP-5 properties and limiting properties (MIL-F-5624C) for satisfactory engine operation. Until the effects of radiation on thermal stability were investigated, it appeared that viscosity increase was the critical item. The work in 1957 emphasized the effect of radiation on thermal stability. This property may be a problem at radiation dosages too low to affect other fuel properties materially.

7.2 Test Fuels

Nine fuels were used in the 1957 work. Table LXXXVI identifies these. Eight were production fuels chosen to represent different geographical crude petroleum sources so that results obtained would have as broad an application as possible. The ninth was a highly refined naphthenic kerosene, a type of fuel which has been proposed for use in supersonic aircraft.

Table LXXXVI

Identity of Jet Fuels

California Research No.	Description
J-813	JP-4, West Texas Crude
J-852	JP-4, Salt Lake (Rangely) Crude
J-782	JP-4, Middle East Crude (RAF 105-55)
J-872	JP-4, Mid-Continent Crude (RAF 106-55)
J-770	JP-4, San Joaquin Crude (RAF 107-55)
J-728	Special JP-5, A Highly Refined, Aromatic-Free Kerosene From Eastern U.S. Crude (Pratt and Whitney F-112)
J-771	JP-5, Los Angeles Basin Crude (RAF 104-55)
J-746	Special JP-5, Eastern U.S. Crude (RAF 99-55)
J-1118	RP-1, Highly Refined California Kerosene

[1] "Effects of Radiation on Aircraft Lubricant and Fuels," (California Research 1956 Summary Report on Contract AF 33(616)-3184) WADC Technical Report 56-646, p. 134.

The production fuels were irradiated during 1956, and the observed changes in physical properties were reported on four JP-4's and two JP-5's[1]. Similar data are reported herein (Section 7.4.1) for the remaining two fuels.

7.3 Test Procedures

Irradiations of all fuels (except J-1118) were conducted in the MTR Canal Source for nominal dosages of 0.87×10^{10}, 4.3×10^{10}, and 8.7×10^{10} ergs/g C (1×10^8, 5×10^8, and 10×10^8 r). Aluminum containers[2] filled with 12,000 ml of fuel were used for these irradiations. J-1118 received various treatments: (a) 55 gallons was irradiated in a standard steel, Type 17-E drum, in NARF at Convair, Fort Worth, during SPIT-2; (b) three 12,000-ml samples were irradiated at the MTR for gamma dosages of 8.7×10^7, 8.7×10^8, and 8.7×10^9 ergs/g C; (c) nine irradiations were conducted in the Cal Research cobalt-60 source in a circulating loop for dosages between 8.7×10^5 and 8.7×10^7 ergs/g C. During one exposure dry, clean air was continuously bubbled into the fuel in the reservoir; during two exposures helium was used instead of air. The remaining exposures were conducted with the sump vented to the atmosphere.

Thermal stability was determined in a Model 03FC automatic CFR Fuel Coker (see Appendix I). Tests conformed to present procedures[4] with one exception: because of the small volume of irradiated fuel available, test duration was shortened to 2-1/2 to 3 hours as required.

7.4 Test Results

7.4.1 Laboratory Inspections of J-746 and J-770

Table LXXXVII presents the results of inspections on these two fuels, a JP-4 and a special JP-5. Data were obtained on the whole fuels only. Fractional distillations were not made because the results obtained on the whole fuels did not show any significant departure from the trends shown previously for the other JP-4 and JP-5 fuels. The ASTM D 86 distillations gave increasing distillation temperatures past the 30% points for both fuels. Also, the increasing "front-end" volatility of the JP-5 with increasing irradiation showed the formation of low molecular weight material in this stock. This was also true of the two other JP-5 fuels[3]. The increased front-end volatility indicated a lower flash point, although this property was not actually measured on any of the irradiated JP-5 samples.

[1] "Effects of Radiation on Aircraft Lubricants and Fuels," (California Research 1956 Summary Report on Contract AF 33(616)-3184) WADC Technical Report 56-646, p. 134.

[2] Ibid, p. 5.

[3] Ibid, p. 138, 140.

[4] "Instructions for Operation and Maintenance of CFR Fuel Coker," Coordinating Research Council Manual No. 3, March 1957.

TABLE LXXXVII

LABORATORY INSPECTIONS ON FUELS J-746 AND J-770

Fuel	J-746 (JP-5 Special)				J-770 San Joaquin JP-4			
Radiation Dosage, 10^{10} ergs/g C	0	0.87	4.36	8.71	0	0.87	4.35	8.10
Inspection or Test								
1. Color, Saybolt	+26	+18	B-16	B-16	-13	-12	B-16	B-16
2. Gravity, °API	48.0	47.4	46.9	41.4	47.3	46.4	44.9	40.8
3. Specific Gravity, 60°F/60°F	0.7885	0.7909	0.7932	0.8184	0.7914	0.7954	0.8002	0.8212
4. Aniline Point	175	177	186	206	118	117	121	132
5. Distillation, D 86								
Per Cent Recovered at °F								
Start	357	373	319	197	150	137	133	140
5	410	405	390	366	194	194	196	203
10	415	410	401	399	229	222	230	232
20	420	420	418	420	272	267	268	279
30	428	426	430	434	299	295	297	299
40	435	432	441	450	316	310	315	331
50	438	438	451	476	329	325	333	347
60	443	445	464	516	341	338	346	362
70	452	452	487	568	350	350	363	397
80	460	462	540	600	361	364	390	507
90	472	486	89% at 567	-	383	398	497	89% at 590
95	483	516	-	-	416	474	94% at 590	
End Point	496	520	-	-	459	504	-	-
Recovered	97	95.5	-	-	98	98	-	-
Residue	1	1.0	-	-	1	1	-	-
Loss	2	3.5	-	-	1	1	-	-
6. Hydrocarbon Analysis FIA Method								
Aromatics, Vol. %	0	0	1	1	10	16	50	Would not separate
Olefins, Vol. %	1	6	13	17	2	3	0	
Saturates, Vol. %	99	94	86	82	88	81	50	
7. Kinematic Viscosity, cs								
at -40°F	10.6 at -20°F*	12.0 at -20°F*	24.6 at -20°F*	217.1**	3.49	3.70	5.54	11.8
at 0°F	6.60	7.35	13.7	50.6	2.09	2.17	2.87	5.26
at 100°F	1.62	1.74	2.74	6.82	0.953	0.978	1.15	1.64
8. Refractive Index	1.4366	1.4380	1.4447	1.4542	1.4401	1.4392	1.4471	1.4560
9. Filter Residue, mg/500 ml	3.2	2.4	Not determined. Water and sediment in sample	5.3	1.2	2.6	6.3	1.5
10. Adherent Gum, mg	-	6.5		10.0	-	7.1	7.2	6.8
11. Aniline-Gravity Constant	8400	8390	8723	8528	5581	5449	5433	5386
12. Net Heating Value, Btu/pound (calc)	18,820	18,820	18,850	18,830	18,540	18,530	18,525	18,520

* Frozen at -40°F
** 93.5 at -20°F

Figure 26 shows graphically the effect of irradiation on the API gravity, the initial boiling point, and the 80% distilled point of the two fuels. The formation of high molecular weight material reduced the API gravity of both the JP-4 and the JP-5. The initial boiling point of the latter was markedly reduced, while that of the JP-4 (about 250° F below that of the JP-5 originally) was not affected in this regard. This may be explained by a loss of volatile products from the lower boiling fuel during exposure in the MTR Canal Source. Figure 26 also shows that the 80% distilled points of both fuels were affected in about the same way by irradiation. Viscosity increases resulting from irradiation are shown in Figure 27. At the highest dosage, the JP-4 viscosity was marginal at -40° F; however, the viscosity at 0° F for JP-5 was marginal at half this dosage.

As before with the other six fuels[1], suspended gum and adherent gum as determined by the Filter Residue Test (see Appendix I) did not appear to be influenced by irradiation.

7.4.2 Fuel Loss from Irradiation

Because loss in API gravity with the irradiated fuels was accompanied by increasing aniline point, gravimetric heating values remained approximately constant throughout the dosage range investigated (see Table LXXXVII). Some fuel was lost during exposure through gas evolution. Weight losses observed after exposure of J-746 and J-770 are shown in Table LXXXVIII:

Table LXXXVIII

Weight Loss of Fuel on Irradiation

Fuel No.	Gamma Dosage, ergs/g C	Weight Loss, grams	Weight Loss, Per Cent
J-746, JP-5	0.87	175	1.87
	4.3	Not determined[a]	-
		Water in sample	
	8.7	895	9.52
J-770, JP-4	0.87	45	0.48
	4.3	720	7.60
	8.1	855	9.04

[a] 750 grams of water found in sample on return from MTR.

These losses were considerably higher than estimates made previously from irradiations of the other six JP-4 and JP-5 fuels[1] (1.5 and 0.5 volume per cent, respectively, at about 8.7×10^{10} ergs/g C).

[1] "Effects of Radiation on Aircraft Lubricants and Fuels, (California Research 1956 Summary Report on Contract AF 33(616)-3184) WADC Technical Report 56-646, p. 155.

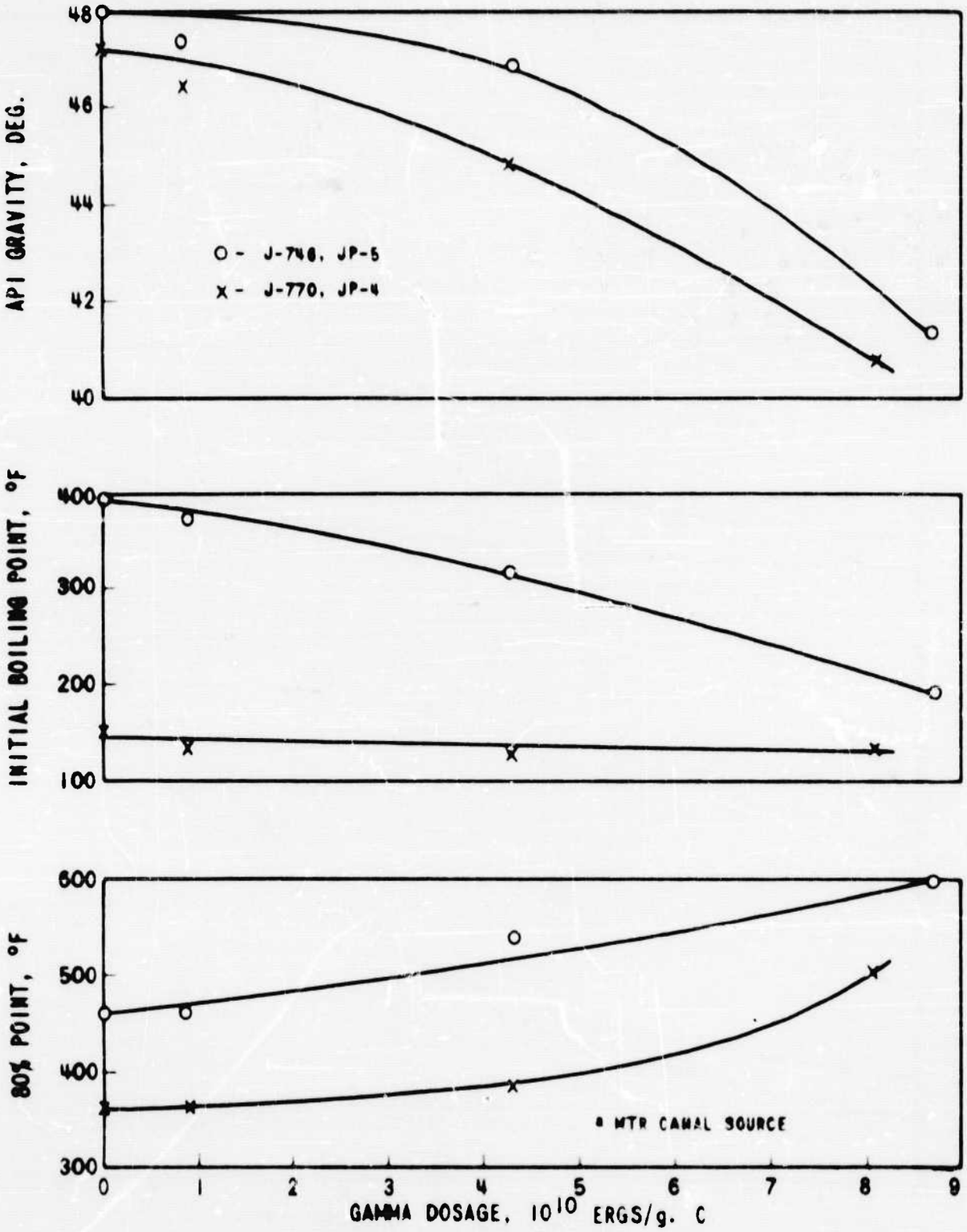


FIG. 28 - TYPICAL EFFECTS OF GAMMA IRRADIATION[a] ON API GRAVITY, INITIAL BOILING POINT AND 80% DISTILLED POINT OF JET FUELS

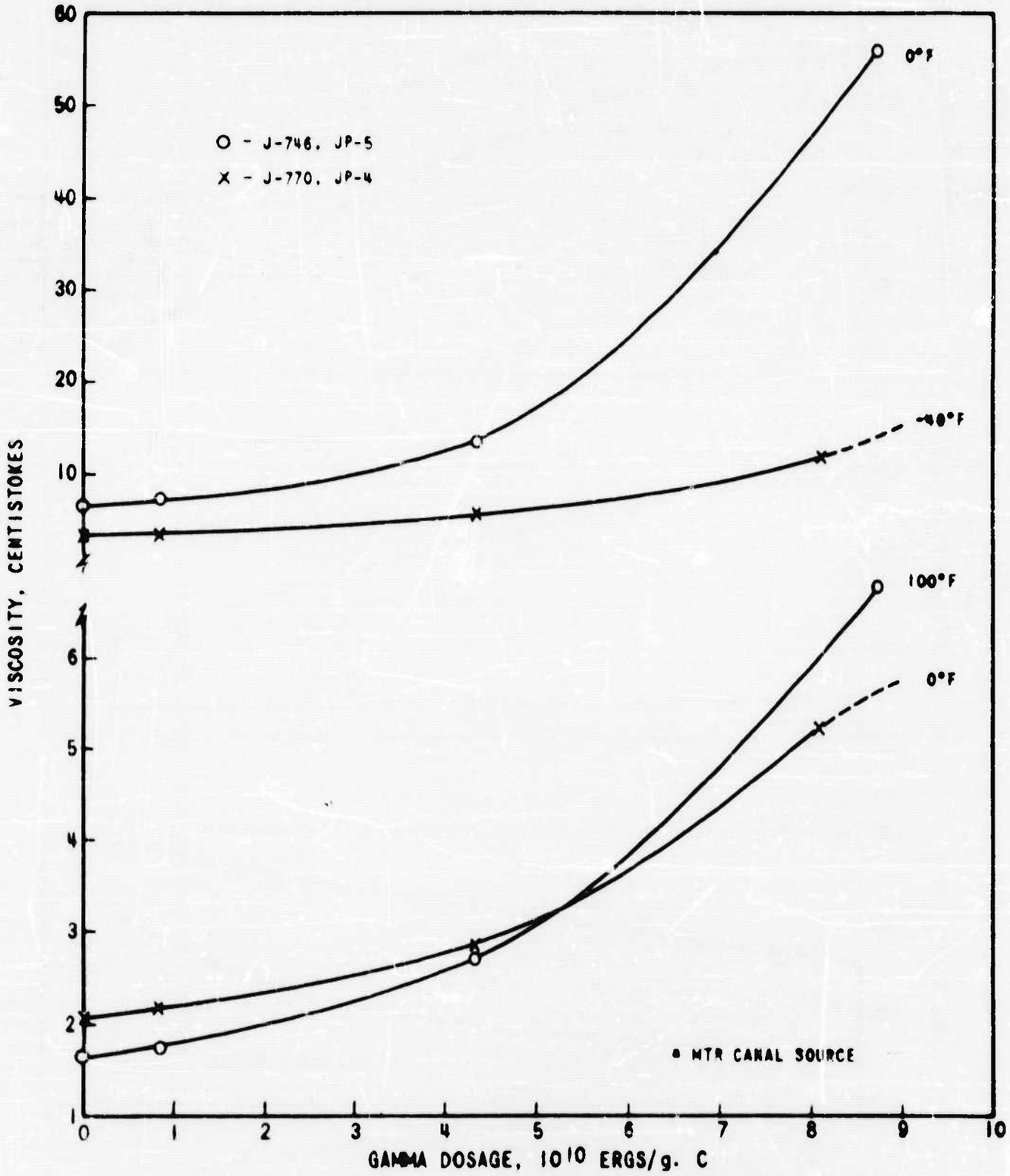


FIG. 27 - TYPICAL EFFECTS OF GAMMA IRRADIATION[a] ON VISCOSITY OF JET FUELS

7.4.3 Prediction of Viscosity Changes Resulting from Irradiation

With the viscosity measurements obtained on the eight fuels irradiated during 1956[1], the following equation between radiation dosages, initial viscosity, and final viscosity was developed. The relationship was based on exposures measured in roentgens; however, conversion to ergs/g C can easily be made where desired, by the factor, 87.1 ergs/g C per roentgen (see page 3).

$$my = \log \frac{(\eta_y - C)}{(\eta_0 - C)}$$

where η_y = viscosity in centistokes after exposure to y in 10^8 r.

y = gamma dosage divided by 10^8 r.

η_0 = viscosity in centistokes before exposure.

m = index of susceptibility of the fuel to viscosity change caused by irradiation

C = a constant for a particular fuel at the particular temperature at which the viscosity is determined

To test the fit of the equation to the actual measurements, viscosities were calculated for the eight irradiated JP-4 and JP-5 fuels. Empirical relationships were used to determine "C." Good agreement is shown in Figure 28 between measured and calculated viscosities. Further illustrations and observations are contained in Appendix XII.

7.4.4 Thermal Stability Tests on Eight Jet Fuels

The results of CFR Fuel Coker Tests are summarized in Table LXXXIX. A total of 56 tests was made, of which 19 were on J-1118 (highly refined kerosene). Tests on unexposed fuels were made first in order to establish preheater and filter temperatures which would permit the detection of either increases or decreases in stability. Plots of the filter pressure drop versus test time for the five JP-4's (J-813, J-852, J-782, J-872, and J-770) and the three JP-5's (J-728, J-771, and J-746) are given in Figures 29, 30, 31, 32, 33, 34, 35, and 36, respectively. The curves show test results for the unirradiated base fuels and for each of the three radiation dosages employed. The use of actual pressure drops rather than the customary pressure drop increases spreads the curves to permit easier comparisons. It also shows the initial effect of differences in viscosity of original and irradiated fuels.

[1] "Effects of Radiation on Aircraft Lubricants and Fuels," (California Research 1956 Summary Report on Contract AF 33(616)-3184) WADC Technical Report 56-646, p. 152.

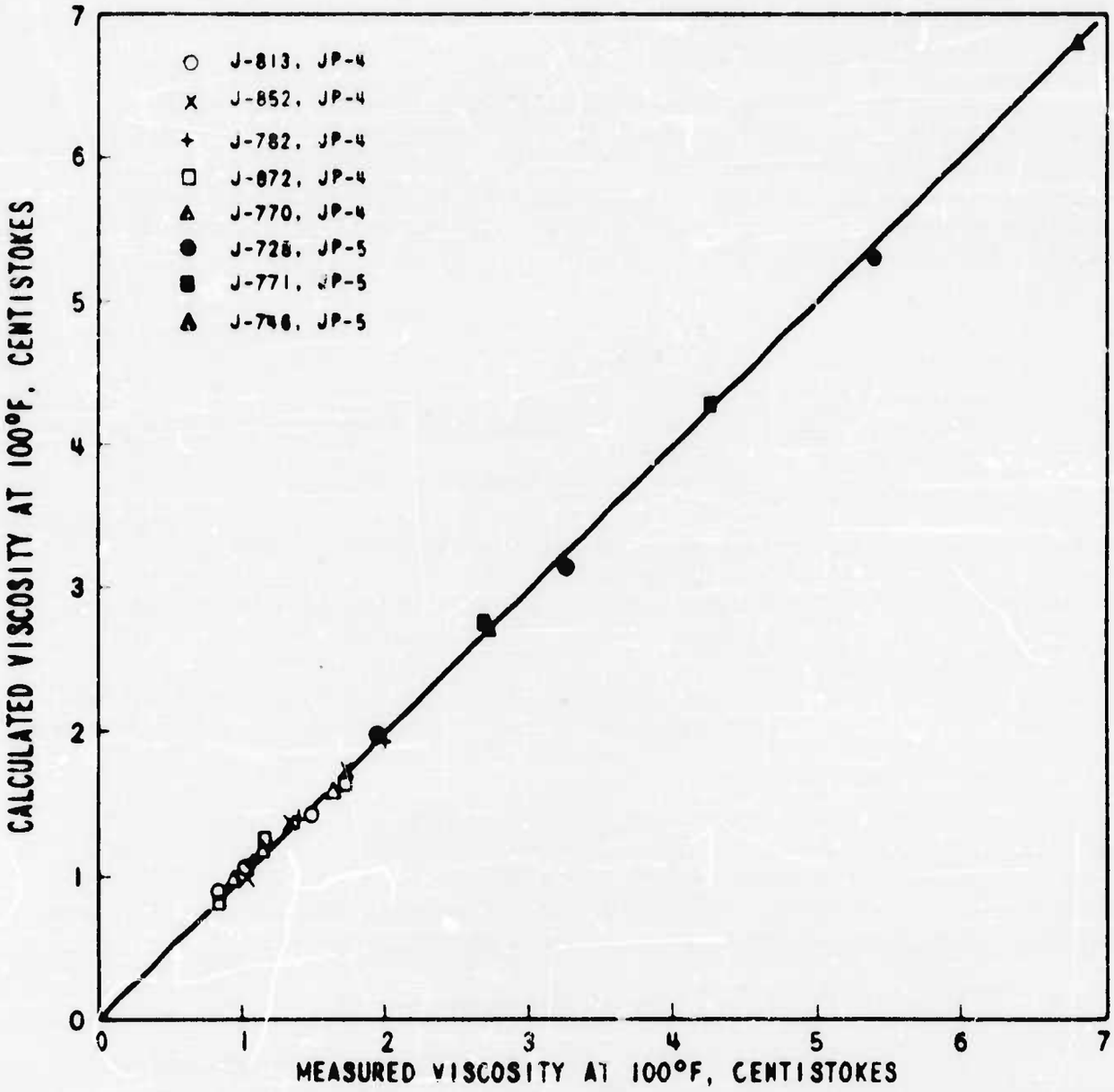


FIG. 28 - CORRELATION OF MEASURED AND CALCULATED VISCOSITIES AT 100°F, JP-4 AND JP-5 FUELS

SUMMARY OF CFR FUEL COKER TESTS
ON IRRADIATED FUELS

Fuel Number	Fuel Description	Radiation Dosage, ergs/g	Radiation Source	Coker Test Conditions	Test Duration, minutes	Filter ΔP Increase, in. Hg	Goodness Rating	Filter Merit Rating	Preheater Deposit Description	Preheater Deposit Code, mgs	Preheater Rating (Log of Deposit, Function[1])
J-R17	Heat Transfer JP-4	0	-	500/400/R	500	0.55	757	74	None	0	0
		0	-	175/400/R	500	0.24	845	79	None	0	0
		0	-	400/400/R	500	4.65	570	60	None	0	0
		0.87 x 10^{10}	γ-n	400/400/R	95	25.00	180	35	50% Tan	1	2.12
		4.35 x 10^{10}	Canal	400/400/R	95	25.00	157	31	5% Very Lt. Tan	1	0.82
		7.40 x 10^{10}	Gamma	400/400/R	145	0.15	765[b]	74[b]	10% Slt. Stain	2	0
J-R02	Mongoly JP-4	0	-	350/400/R	500	0.00	900	92	50% Haze	1	0
		0	-	175/400/R	500	0.27	810	78	4% Very Lt. Tan	1	1.45
		0	-	400/400/R	500	14.10	480	51	10% Brown	4	2.64
		0.87 x 10^{10}	γ-n	400/400/R	145	1.00	410[b]	40[b]	25% Tan	1	1.82
		4.35 x 10^{10}	Canal	400/400/R	150	0.12	800[b]	72[b]	5% Tan	1	2.00
		7.71 x 10^{10}	Gamma	400/400/R	145	0.00	900[b]	90[b]	1% Tan	1	1.47
J-R0	RAF 100-99, JP-4	0	-	350/400/R	250	25.00	480	41	20% Very Lt. Tan	1	1.34
		0.42 x 10^{10}	γ-n	350/400/R	50	25.00	91	25	50% Very Lt. Tan	1	2.1
		4.34 x 10^{10}	Canal	350/400/R	145	0.03	870[b]	97[b]	50% Very Lt. Tan	1	1.46
		8.29 x 10^{10}	Gamma	350/400/R	150	0.05	850[b]	84[b]	15% Very Lt. Tan	1	1.52
J-R72	RAF 100-99, JP-4	0	-	350/400/R	168	25.00	290	41	1% Lt. Grey Haze	1	0
		0.84 x 10^{10}	γ-n	350/400/R	150	0.05	860[b]	84[b]	25% Very Lt. Tan	1	1.55
		4.04 x 10^{10}	Canal	350/400/R	145	7.35	120[b]	44[b]	None	0	0
		7.50 x 10^{10}	Gamma	350/400/R	150	0.05	850[b]	84[b]	5% Very Lt. Tan	1	0.90
J-R79	RAF 101-55, JP-4	0	-	500/400/R	500	1.30	481	61	10% Slt. Stain	2	0
		0	-	175/400/R	168	25.00	110	27	None	0	0
		0.87 x 10^{10}	γ-n	175/400/R	150	2.85	770[b]	78[b]	15% Brown	4	1.50
		4.35 x 10^{10}	Canal	175/400/R	150	7.25	900[b]	91[b]	4% Very Lt. Tan	1	1.82
		7.15 x 10^{10}	Gamma	175/400/R	150	0.00	900[b]	90[b]	None	0	0
J-R8	F and W F-112, JP-5	0	-	450/500/R	500	0.80	770	74	None	0	0
		0.78 x 10^{10}	γ-n	450/500/R	150	5.50	560[b]	49[b]	Trace Dtn	2	Trace
		4.27 x 10^{10}	Canal	450/500/R	150	0.00	900[b]	90[b]	None	0	0
		7.23 x 10^{10}	Gamma	450/500/R	150	0.00	900[b]	90[b]	None	0	0
J-R71	RAF 100-55, JP-5	0	-	450/500/R	50	25.00	140	15	50% Lt. Brown	4	2.02
		0.78 x 10^{10}	γ-n	450/500/R	150	0.05	860[b]	84[b]	25% V. Lt. Tan	1	1.42
		4.27 x 10^{10}	Canal	450/500/R	150	0.07	840[b]	82[b]	None	0	0
		7.23 x 10^{10}	Gamma	450/500/R	150	0.00	900[b]	90[b]	None	0	0
J-R4	RAF 99-55, JP-5	0	-	450/500/R	500	0.75	730	72	None	0	0
		0.87 x 10^{10}	γ-n	450/500/R	150	0.00	900[b]	90[b]	None	0	0
		4.35 x 10^{10}	Canal	450/500/R	150	0.00	900[b]	90[b]	None	0	0
		8.71 x 10^{10}	Gamma	450/500/R	150	0.07	840[b]	82[b]	None	0	0
J-111R	Highly Refined Kerosene - RF-1 (Circulated by pump 143 hours)	0	-	450/500/R	500	1.30	481	51	20% Very Lt. Tan	1	1.14
		0	-	450/500/R	180	0.50	840	67	5% Haze	1	0
		0	-	450/500/R	180	0.21	770	71	15% Slt. Disc.	2	Trace
		8.71 x 10^{10}	NAMP	450/500/R	5	25.00	47	14	50% Slt. Disc.	2	Trace
		8.71 x 10^{10}	NAMP	450/500/R	15	25.00	55	14	50% Slt. Disc.	2	Trace
		8.71 x 10^{10}	NAMP	450/500/R	45	25.00	51	20	50% Slt. Disc.	2	Trace
		8.71 x 10^{10}	NAMP	450/500/R	45	25.00	56	22	40% Haze	1	0
	normal air	8.71 x 10^{10}	Cobalt-60	450/500/R	180	0.40	770[b]	69[b]	10% Haze	1	0
	normal air both	8.71 x 10^{10}	Cobalt-60	450/500/R	180	25.00	1[b]	32[b]	10% Haze	1	0
	normal air tests on same sample	8.71 x 10^{10}	Cobalt-60	450/500/R	180	0.15	840[b]	82[b]	None	0	0
	normal air	8.71 x 10^{10}	Cobalt-60	450/500/R	180	0.70	470[b]	44[b]	20% Slt. Disc.	2	Trace
	normal air	8.71 x 10^{10}	Cobalt-60	450/500/R	180	0.40	620[b]	62[b]	5% Slt. Disc.	2	Trace
	normal air	8.71 x 10^{10}	Cobalt-60	450/500/R	180	24.0	240	42	15% Very Lt. Tan	1	1.24
	excess air	8.71 x 10^{10}	Cobalt-60	450/500/R	180	0.50	460[b]	43[b]	25% Slt. Disc.	2	Trace
	helium scrubbed	8.71 x 10^{10}	Cobalt-60	450/500/R	180	0.00	900[b]	92[b]	20% Slt. Disc.	2	Trace
	helium scrubbed	8.71 x 10^{10}	Cobalt-60	450/500/R	180	0.55	470	54	15% Slt. Disc.	2	Trace
		8.71 x 10^{10}	γ-n	450/500/R	180	24.00	810	84	20% Slt. Disc.	2	Trace
		8.71 x 10^{10}	Canal	450/500/R	180	1.80	610[b]	84[b]	5% Very Lt. Tan	1	0.94
		8.71 x 10^{10}	Gamma	450/500/R	180	0.20	760[b]	76[b]	Tr. Discoloration	2	Trace

[1] Log of Deposit function compensates for run time differences. See "Report of the Panel on Data Analysis," CRC-APR Fuel Thermal Stability Group, Coordinating Research Council, dated January 24, 1956, for method of calculating.

[2] Goodness Ratings and Filter Merit Ratings extrapolated to 500 minutes where required.

[3] Combined reactor radiation in BTU No. 2, 50% of absorbed energy gamma radiation.

[4] First coker test made immediately after irradiation on July 18, 1957. Second test made on remainder of same sample on November 29, 1957.

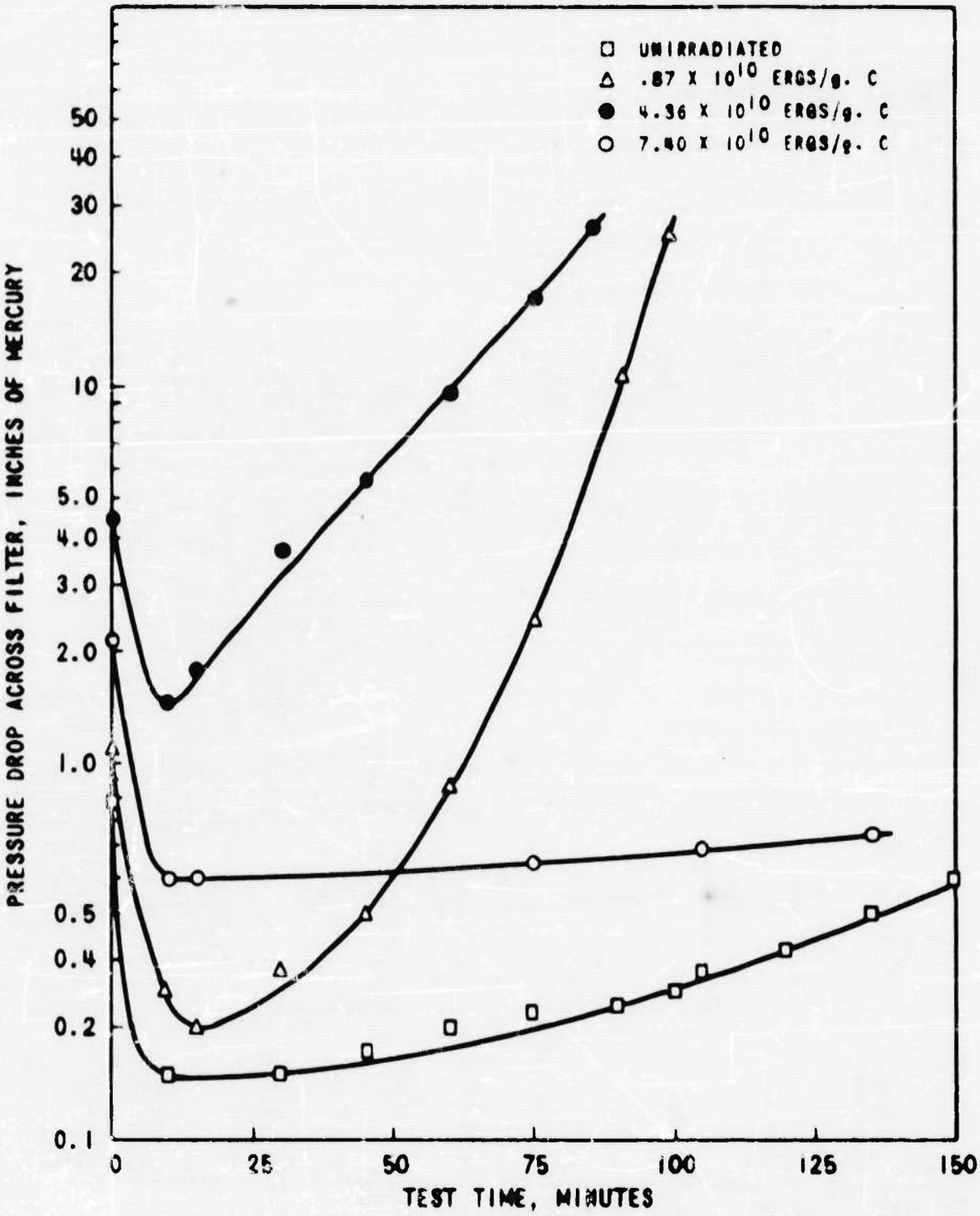


FIG. 29 - FILTER PRESSURE DROP AS A FUNCTION OF TIME-J-813 COKER TESTS
MODEL 03FC COKER: 400/400/6

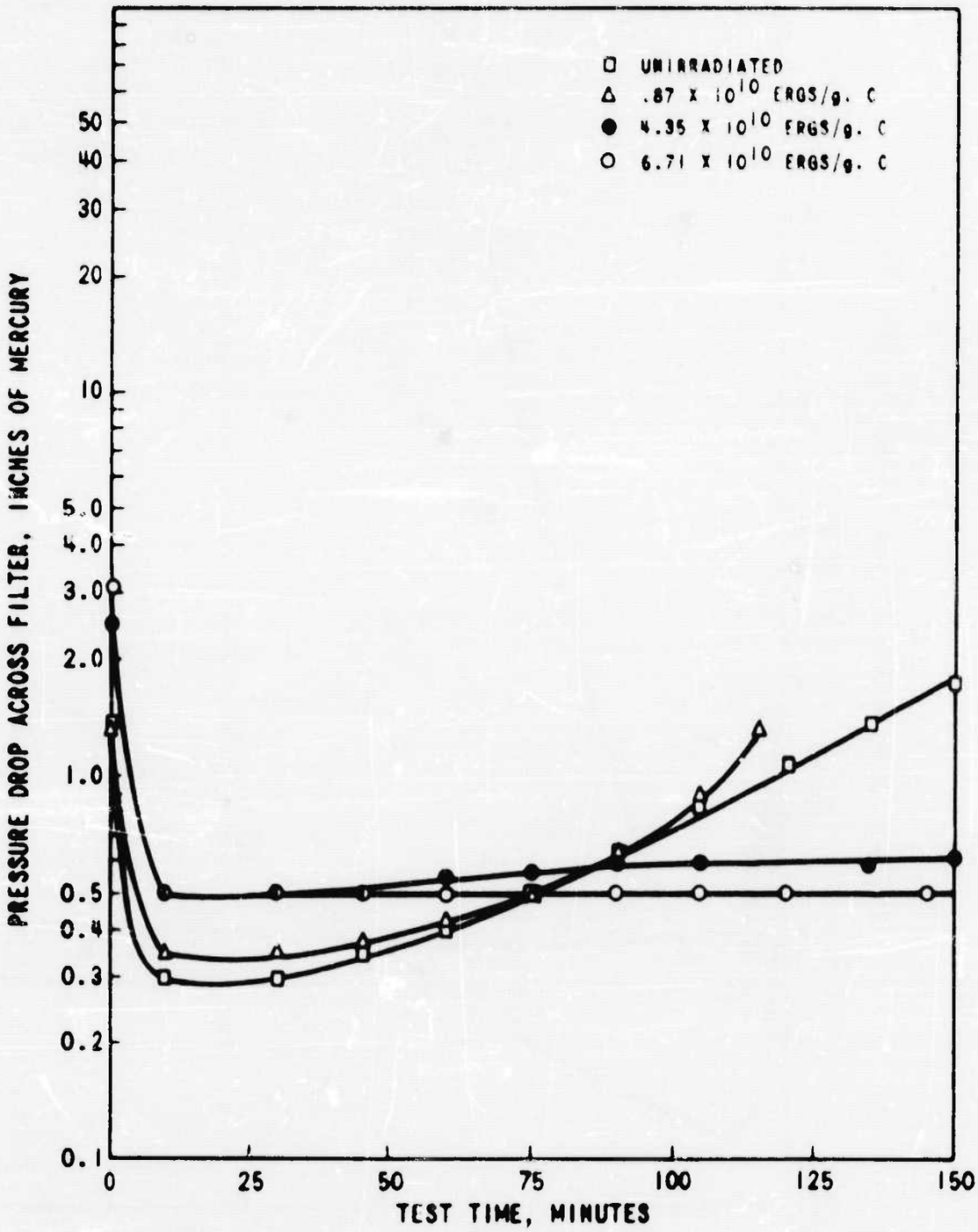


FIG. 30 - FILTER PRESSURE DROP AS A FUNCTION OF TIME-J-852 COKER TESTS

MODEL 03FC COKER: 400/400/6

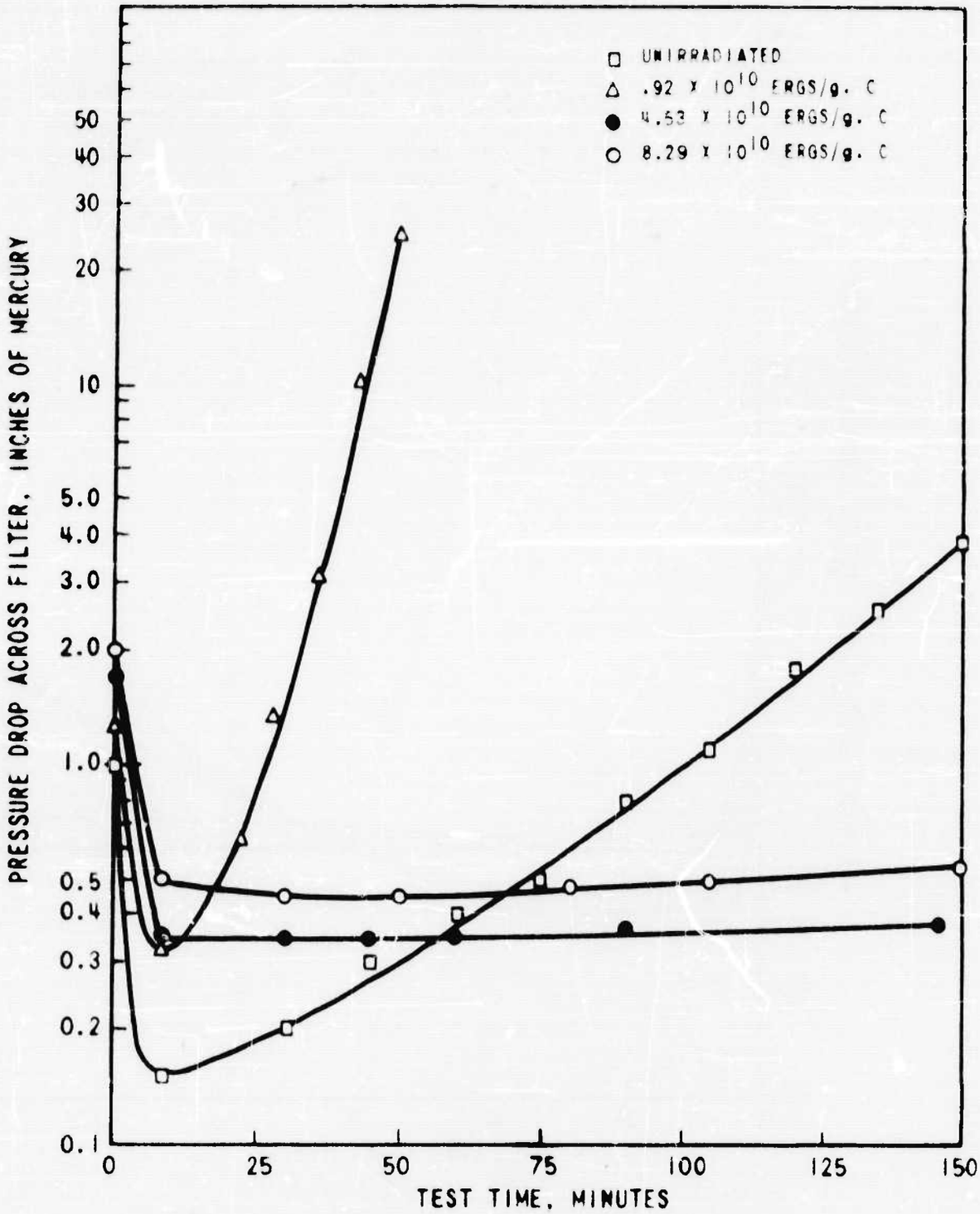


FIG. 31 - FILTER PRESSURE DROP AS A FUNCTION OF TIME-J-782 COKER TESTS

MODEL 03FC COKER: 350/400/6

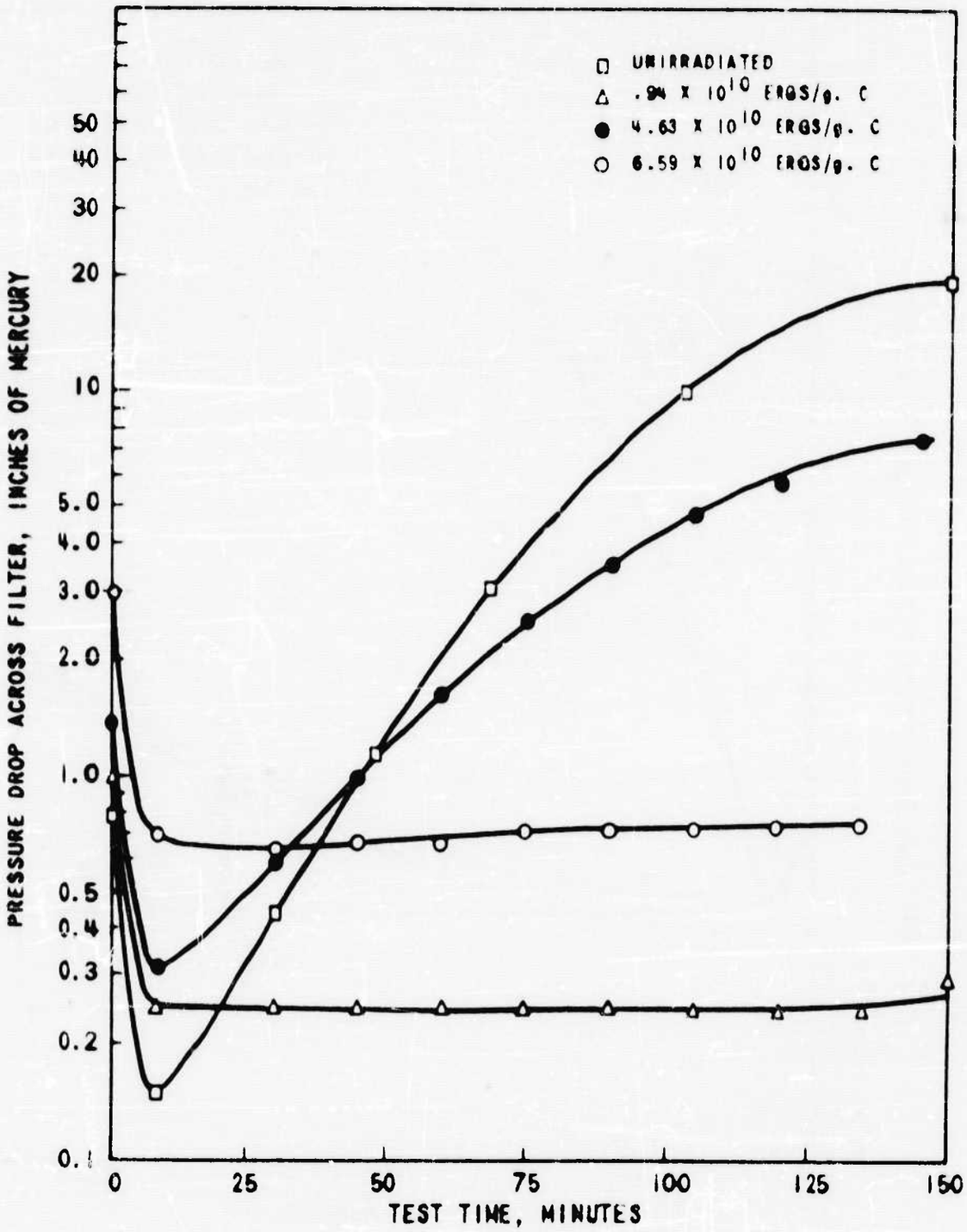


FIG. 32 - FILTER PRESSURE DROP AS A FUNCTION OF TIME-J-872 COKER TESTS

MODEL 03FC COKER: 350/400/6

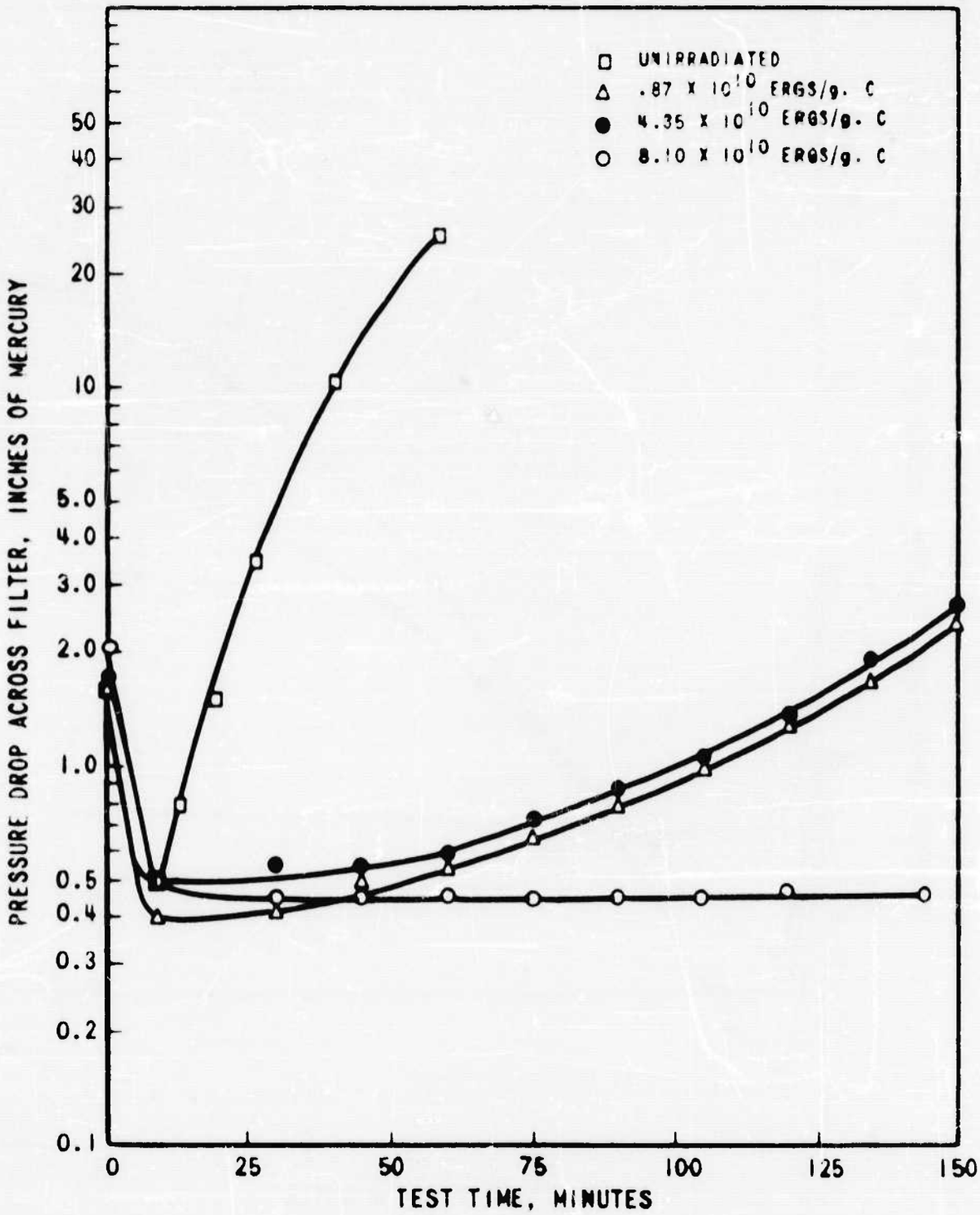


FIG. 33 - FILTER PRESSURE DROP AS A FUNCTION OF TIME-J-770 COKER TESTS

MODEL 03FC COKER: 375/400/6

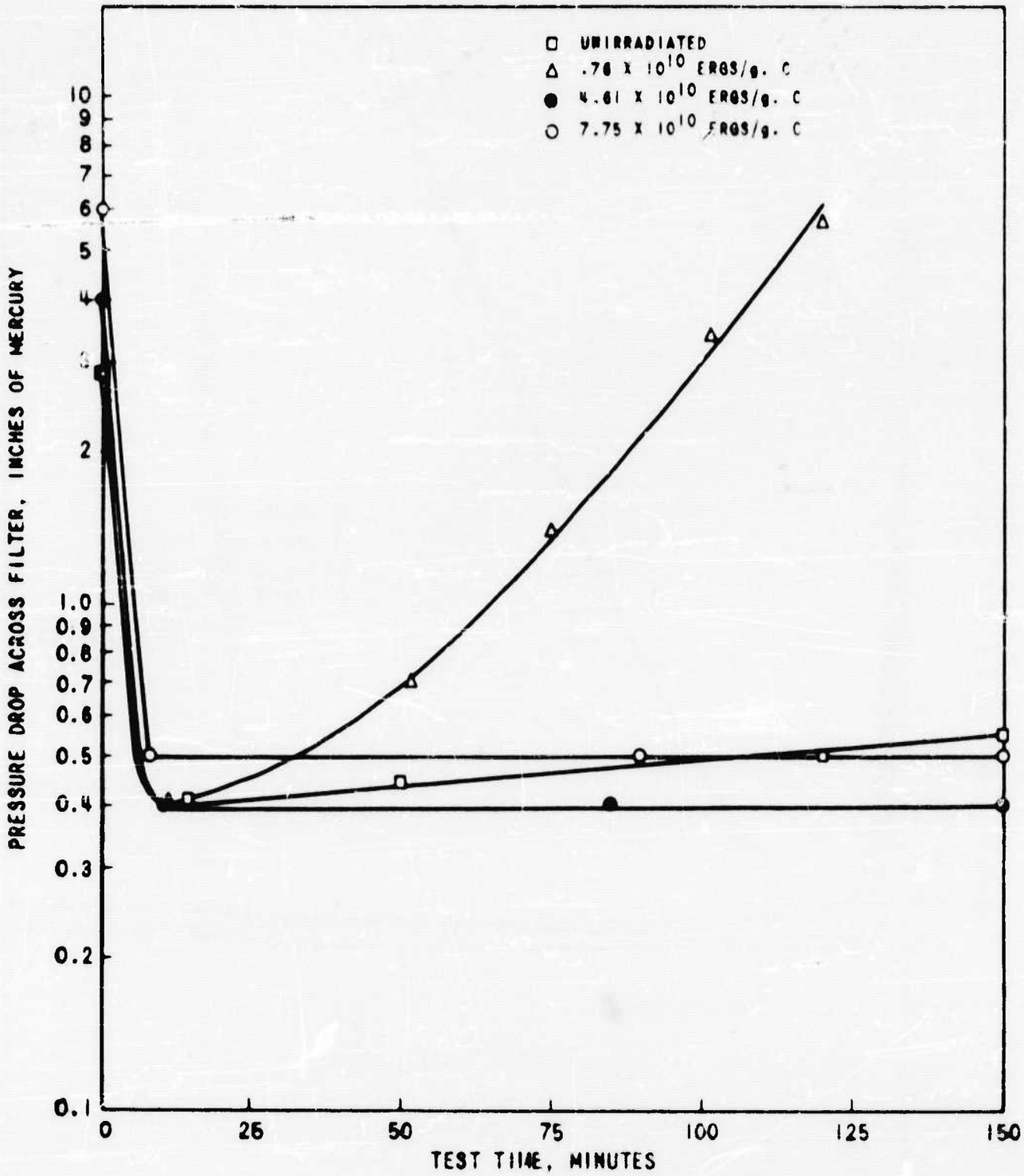


FIG. 34 - FILTER PRESSURE DROP AS A FUNCTION OF TIME-J-728 COKER TESTS

MODEL 03FC COKER: 450/500/6

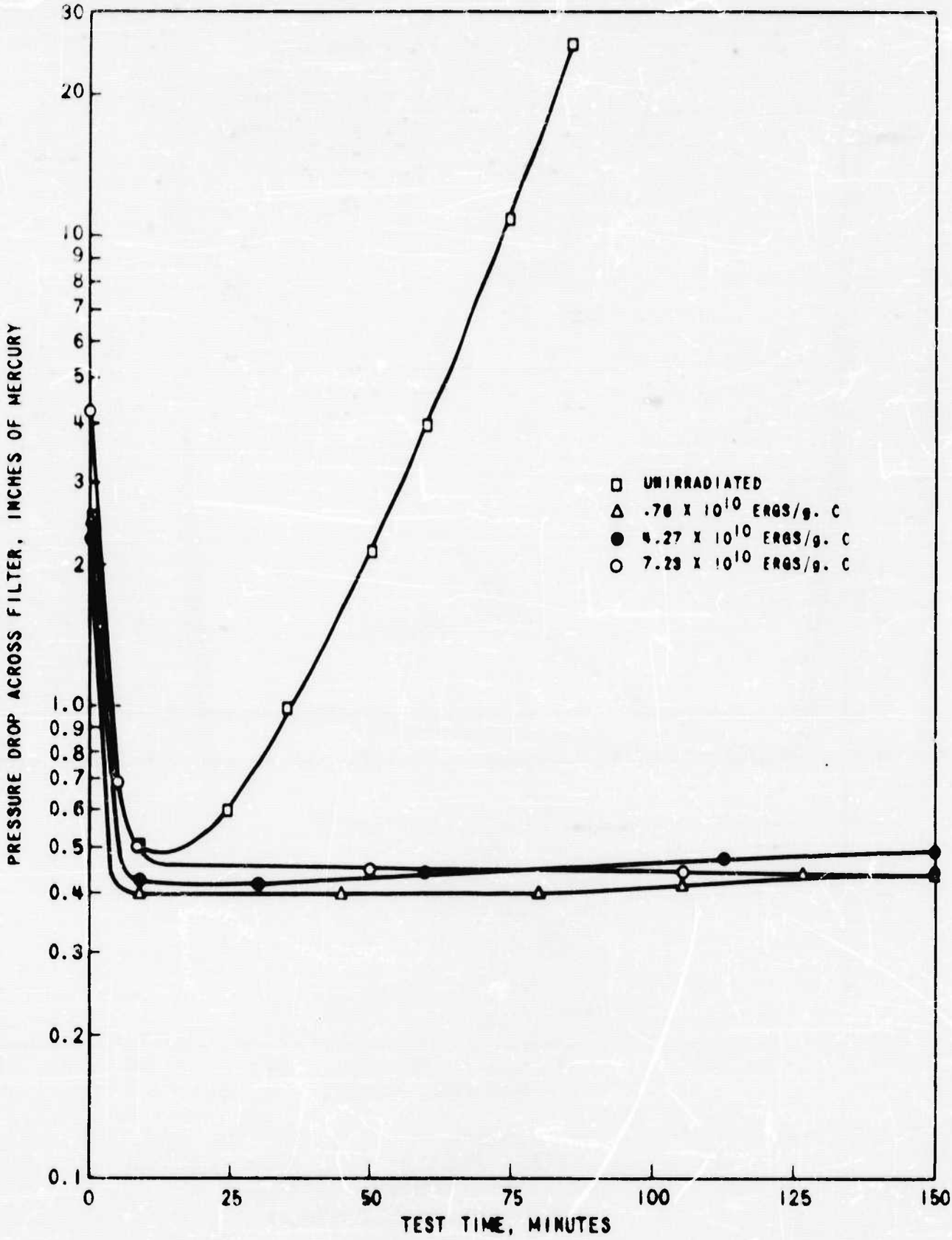


FIG. 38 - FILTER PRESSURE DROP AS A FUNCTION OF TIME-J-771 COKER TESTS

MODEL 03FC COKER: 400/500/6

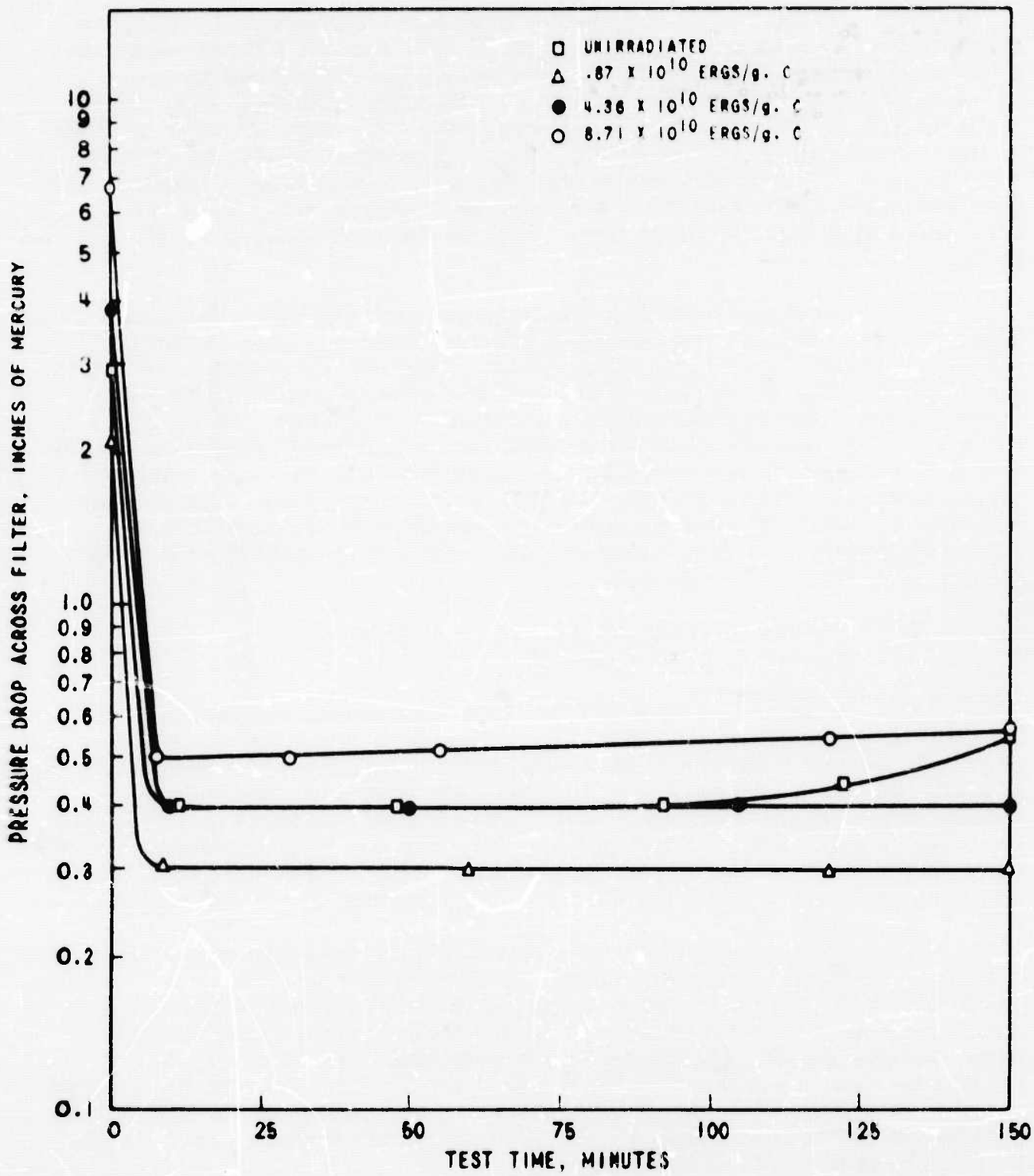


FIG. 38 - FILTER PRESSURE DROP AS A FUNCTION OF TIME-J-748 COKER TESTS

MODEL 03FC COKER: 450/500/6

Filter merit ratings and preheater deposits are plotted as a function of gamma dosage in Figures 37, 38, and 39. These show that gamma radiation in the dosage range investigated influenced jet fuel thermal stability measurably but not consistently. For example, three fuels (J-813, J-782, and J-728) showed reductions of 20 or more in FMR at the lowest dosage; while four showed improvements, and one changed very little. At the intermediate dosage, only one fuel had a lower FMR than its unirradiated sample. At the highest dosage, all FMR's on irradiated stocks were higher than those on the respective original fuels.

Preheater coating was not heavy for any of the fuels due partly to reduced test time and partly to the relatively good thermal stability of most of the fuels used. Four of the JP-4's showed a tendency for more deposits at the lowest dosage, and all five were as good as or better than the original samples at the highest dosage. Of the three JP-5's, J-771 was least stable; and tests were conducted at 400/500/6 for this fuel. Radiation improved both filterability and preheater coating to a marked degree. Neither J-728 nor J-746 formed preheater deposits at 450/500/6, relatively severe coker test conditions, irrespective of radiation dosage. J-728, however, did show a drop in FMR at the low dosage of 0.76×10^{10} ergs/g C.

7.4.5 Thermal Stability of J-1118, A Highly Refined Kerosene (RP-1)

A barrel sample of this stock was exposed to reactor irradiation at NARF in SPIT No. 2[1]. A dosage of about 87.1×10^7 ergs/g C gamma equivalent[2] was received, approximately 80% of which was gamma radiation. As predicted for this relatively low dosage, no measurable changes were observed in any physical tests made. However, contrary to expectations, thermal stability was appreciably reduced. CFR coker tests made at 400/500/6 showed a reduction in FMR from 67 for the unirradiated sample to 20 for the irradiated sample.

This finding led to a more extensive program with J-1118. A total of 19 coker tests was made. These are summarized in Table LXXXIX. Initially, three samples were irradiated in the Cal Research cobalt-60 source and two in the MTR Gamma Canal Source. Five dosages varying 10,000 fold were obtained. All of these five irradiated samples had lower FMR's than the base fuel except the sample exposed to 8.7×10^9 ergs/g C at the MTR. The minimum FMR of 32 was obtained at 8.7×10^6 ergs/g C. None of these irradiations produced the instability of the SPIT-2 sample.

[1] Nuclear Aircraft Reactor Facility, Systems Panel Irradiation Test No. 2.

[2] Sample received 8×10^6 roentgens of gamma, 3×10^{14} neutrons/sq cm (epithermal), and 5×10^{14} neutrons/sq cm thermal.

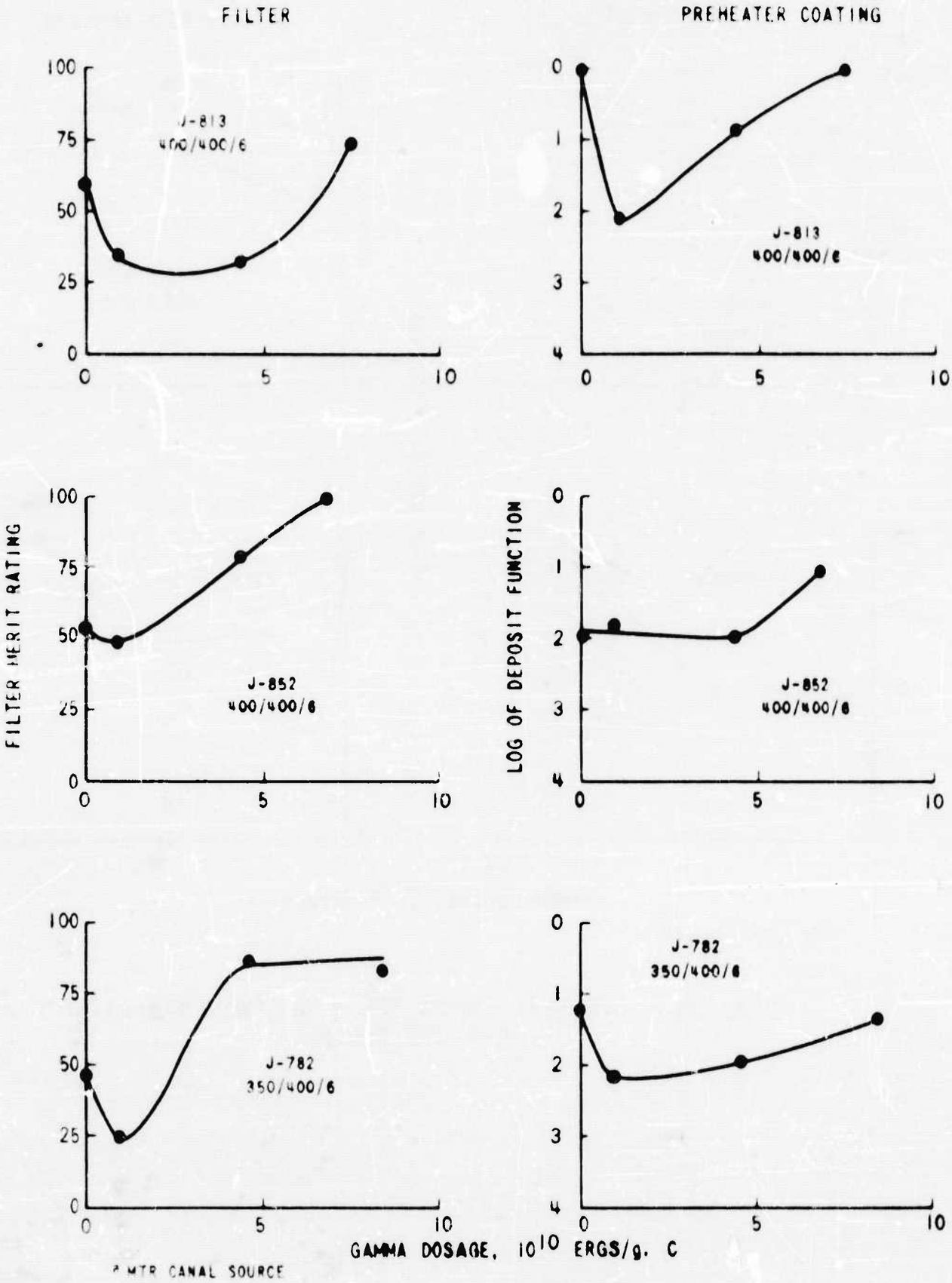


FIG. 37 - CFR FUEL COKER TESTS OF THREE IRRADIATED* JP-4 JET FUELS

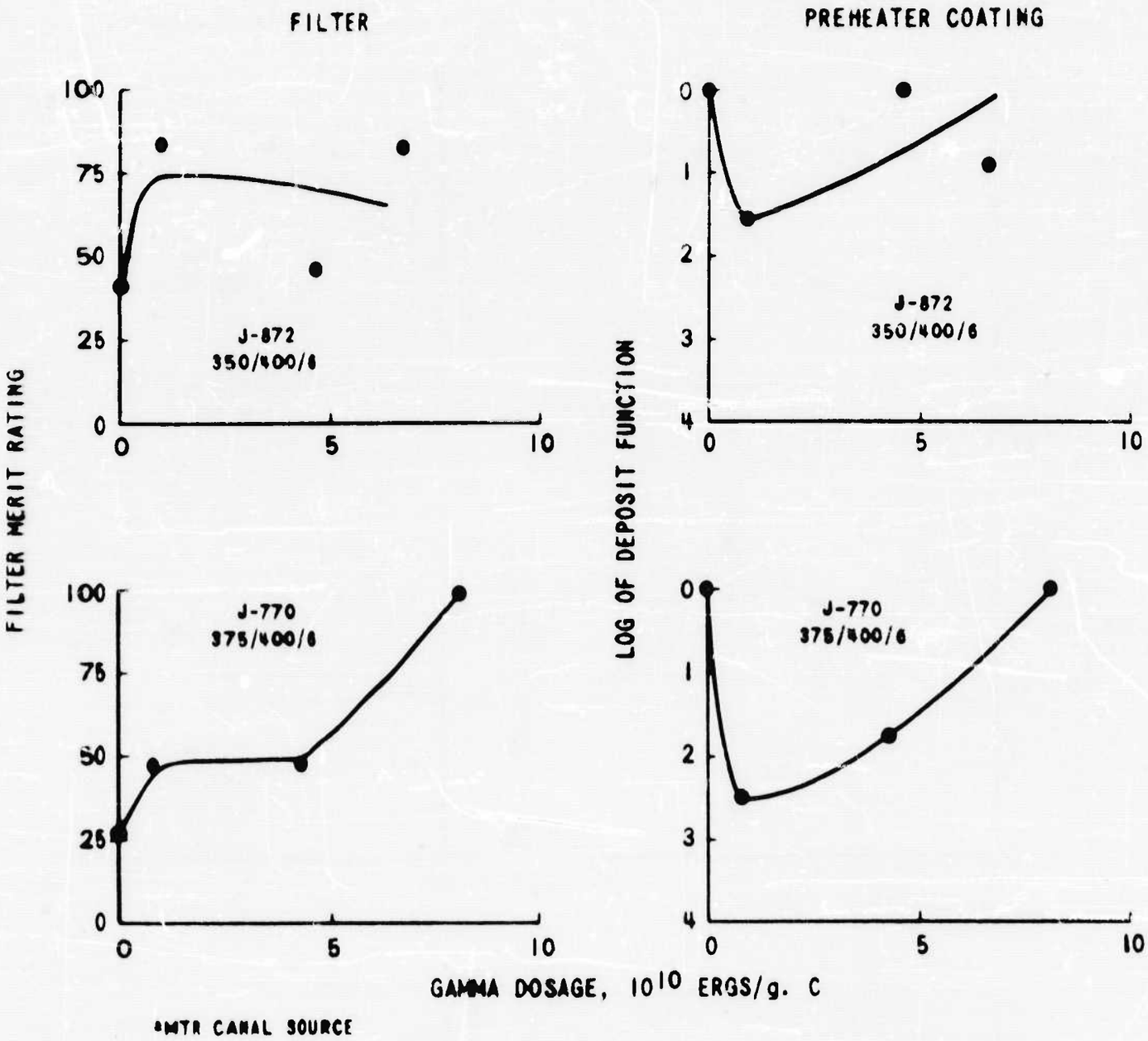


FIG. 38 - CFR FUEL COKER TESTS OF TWO IRRADIATED*
JP-4 JET FUELS

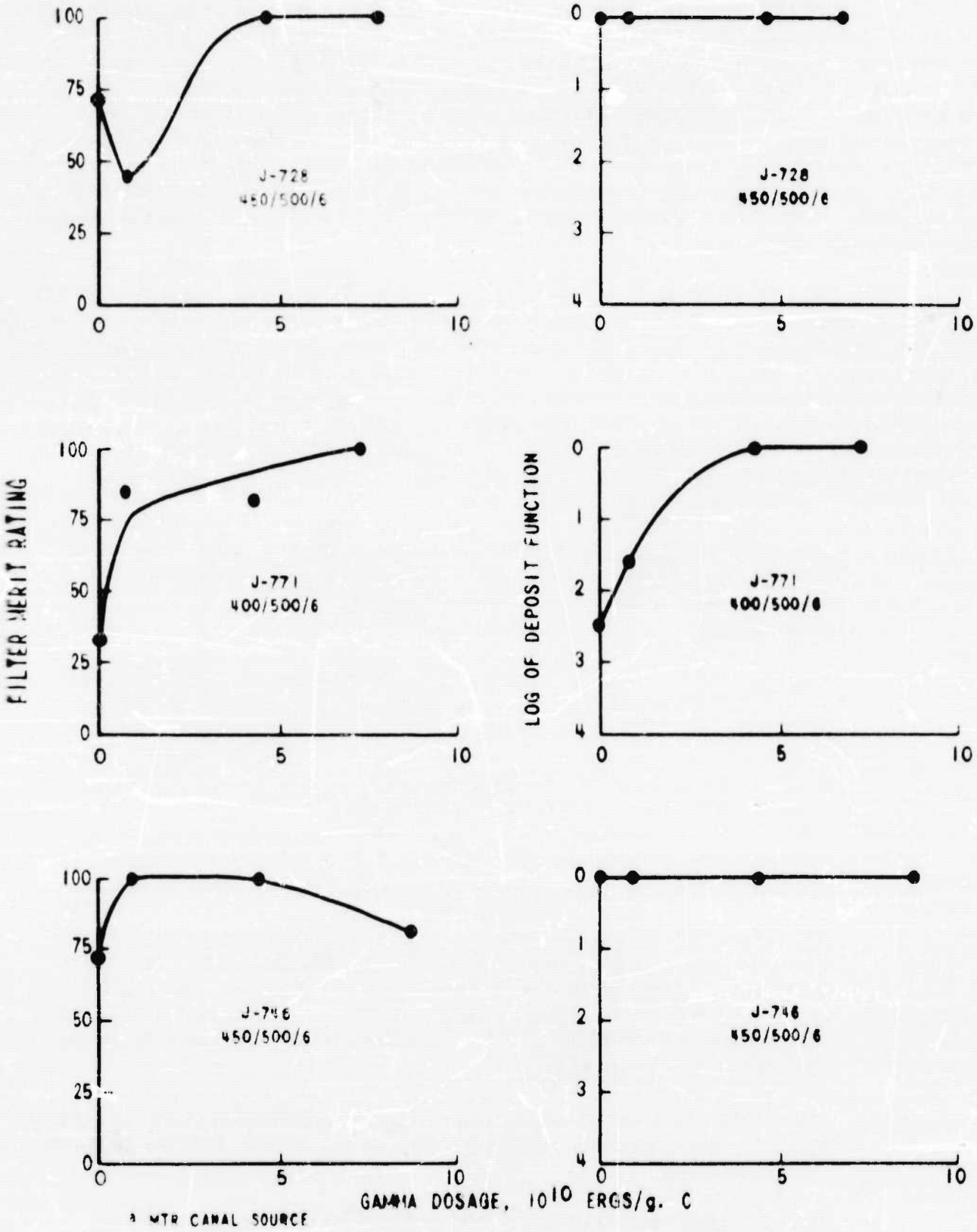


FIG. 38 - CFR FUEL COKER TESTS OF THREE IRRADIATED[a] JP-5 TYPE JET FUELS

Infrared spectra were obtained on these samples in an attempt to find differences in constituents resulting from different radiations and radiation environments. The resulting absorption traces were all practically identical. This showed that no change in composition, measurable by this technique, had occurred in any of the samples. The sample irradiated at 8.7 x 10^7 ergs/g C, however, did show slight additional adsorption at 13.1μ. This was interpreted as the presence of peroxide. Accordingly, peroxide numbers were obtained by titration on all samples. These are given in Table XC together with additional peroxide numbers on all samples of irradiated J-1118.

The data from the first five gamma irradiations and the SPIT-2 irradiation indicated a good relationship between peroxide number and thermal stability: the higher the peroxide number, the lower the stability. Data obtained from subsequent samples, however, did not confirm this relationship. Figure 40 shows peroxide numbers plotted against filter merit ratings for J-1118. Also shown is a scale giving the approximate parts per million of oxygen content as peroxide. Figure 41 shows filter merit ratings plotted as a function of gamma dosage for all the samples of J-1118. The following observations were derived from this work:

a. Gamma irradiations performed either statically at the MTR or by loop circulation in the cobalt-60 source were about equivalent in effect on thermal stability (dosage 8.7 x 10^7 ergs/g C).

b. Reactor radiation (in NARF) at the same equivalent dosage was more damaging than pure gamma radiation to thermal stability.

c. Helium scrubbing of the fuel during gamma irradiation did not consistently improve thermal stability.

d. Introduction of excess air into the fuel during irradiation did not increase filter plugging or increase peroxide number.

e. The effect of gamma radiation on thermal stability appeared transitory in a sample irradiated to a dosage of 8.7 x 10^6 ergs/g C. The first coker test made 24 hours after exposure gave a 32 FMR, a second test of the same sample five months later gave a 69 FMR. No aging effect was observed with the unirradiated material.

f. The effect of radiation in this range on preheater tube deposits was not well defined. Differences were noted, but no pattern was apparent.

It was suggested that iron contamination was primarily responsible for the loss in thermal stability of the SPIT-2 samples. An iron analysis showed 0.2 ppm of iron present in the sample. There is no information available on the effect of iron in either soluble or suspended form on thermal stability. This quantity of iron in a fuel of this type after undergoing considerable handling and storage does not appear unusual.

TABLE XC

COMPARISON OF IRRADIATION DOSAGES, PEROXIDE NUMBERS, AND COKER FILTER MERIT RATINGS FOR J-1118

Source of Irradiation	Dosage	Peroxide Number	Filter Merit Rating (Coker Conditions 400/500/6)
None (Base Fuel)	None	0.1	67
	None	-	75[a]
Cal Research Cobalt-60	8.71×10^5 ergs/g C gamma	1.1	46
Cal Research Cobalt-60	8.71×10^6 ergs/g C gamma	1.4	32
Cal Research Cobalt-60	8.71×10^6 ergs/g C gamma	0.5	68
Cal Research Cobalt-60	8.71×10^6 ergs/g C gamma[b]	0.6	99
Cal Research Cobalt-60	8.71×10^6 ergs/g C gamma[c]	0.7	63
Cal Research Cobalt-60	8.71×10^7 ergs/g C gamma	2.0	42
MTR Canal Gamma	8.71×10^7 ergs/g C gamma	2.0	39
MTR Canal Gamma	8.71×10^8 ergs/g C gamma	0.1	49
NARF	8.71×10^8 ergs/g C gamma[d]	4.0	20
MTR Canal Gamma	8.71×10^8 ergs/g C gamma	0.5	76

[a] Circulated without irradiation for 143 hours in same pumping apparatus used in cobalt-60 exposures. Note: 10^6 ergs/g C sample also circulated for 143 hours.

[b] Helium scrubbed during exposure.

[c] Clean, dry air bubbled into fuel during exposure.

[d] Figure given is energy equivalent. Sample received 8×10^6 roentgen gamma, 3×10^{14} neutrons/cm^2 epithermal, and 5×10^{14} neutrons/cm^2 thermal.

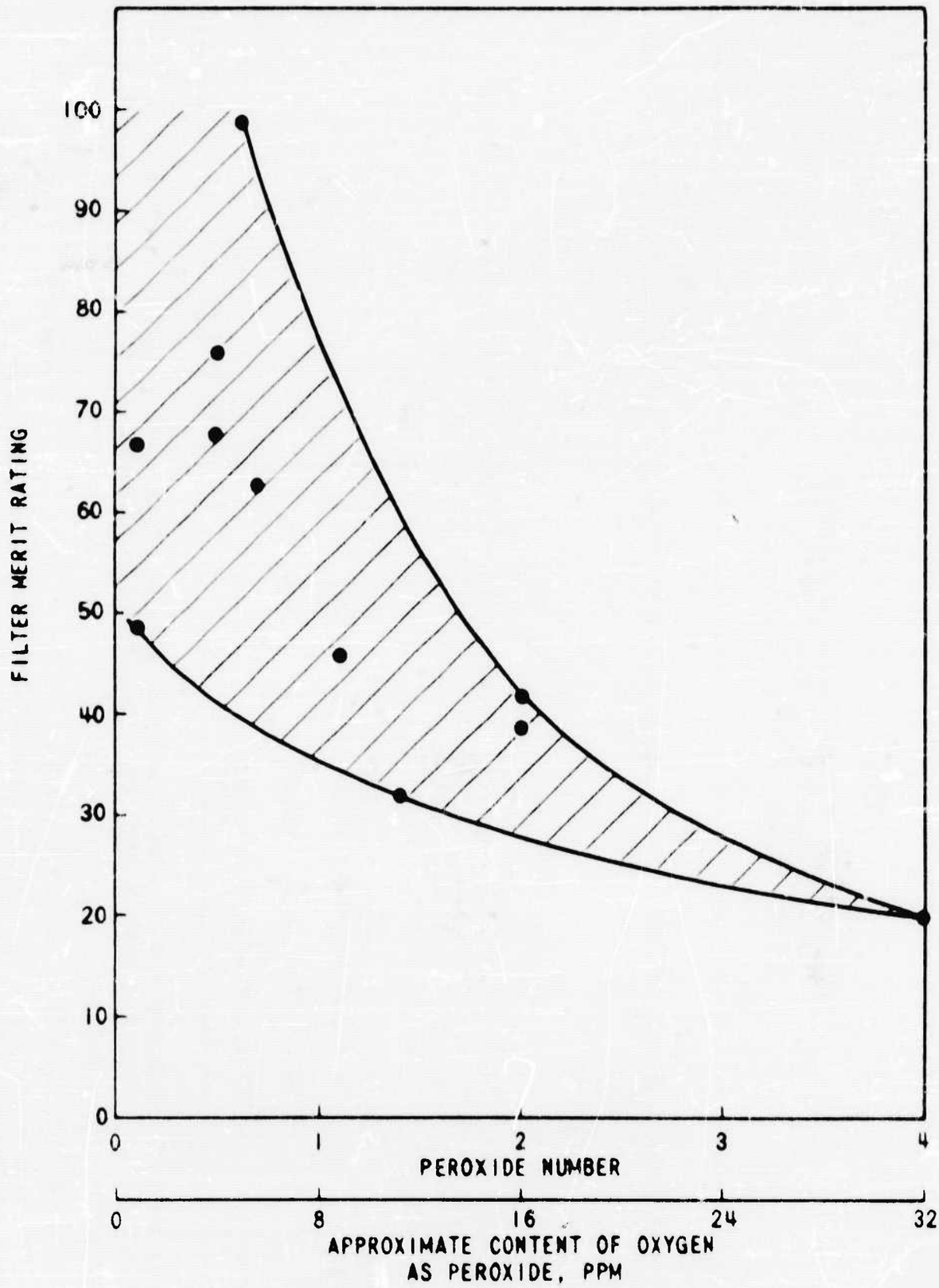


FIG. 40 - RELATIONSHIP BETWEEN PEROXIDE NUMBER AND THERMAL STABILITY (IRRADIATED SAMPLES OF J-1118)

AS MEASURED BY CFR FUEL COKER FILTER MERIT RATINGS AT 400/500/6

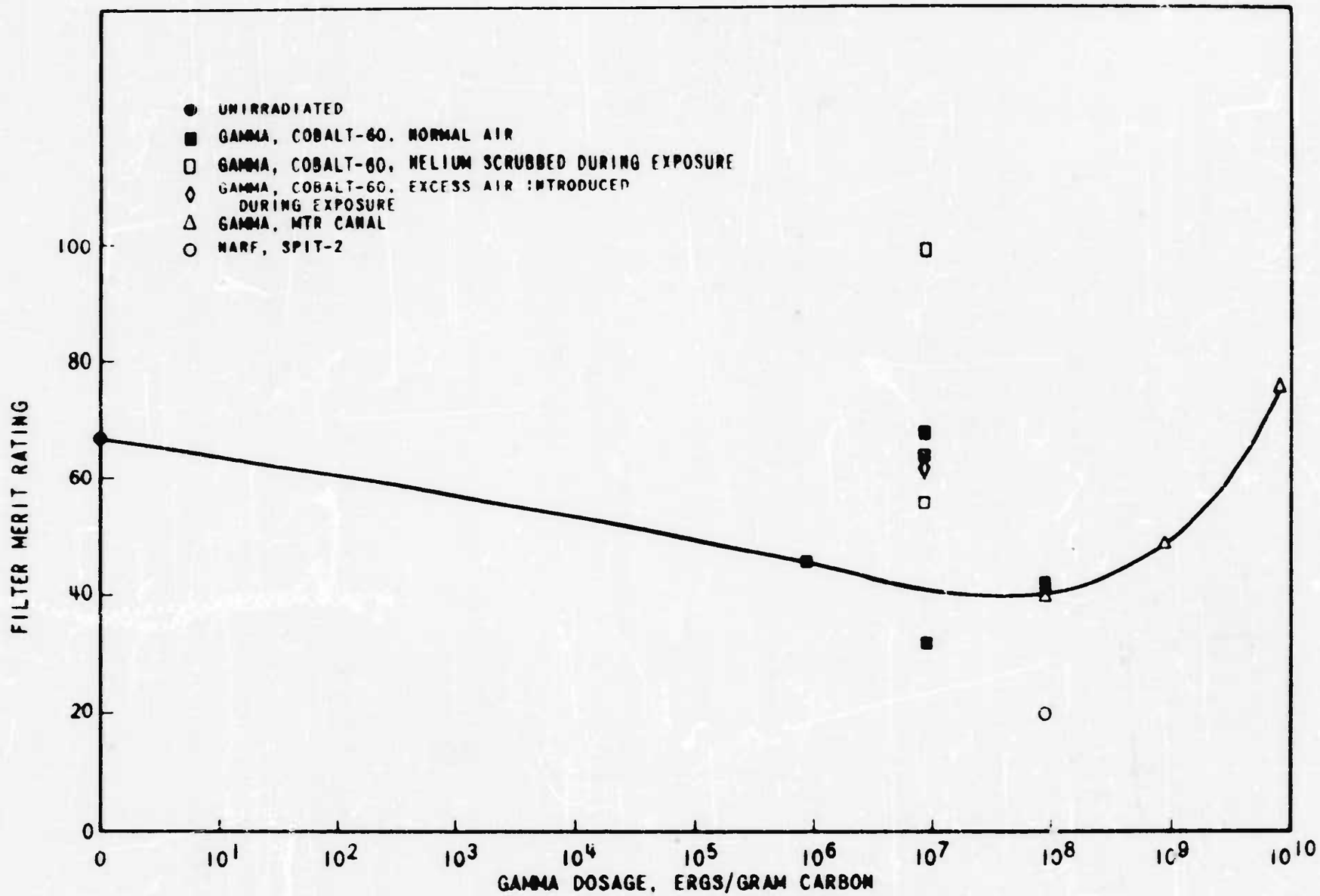


FIG. 41 - EFFECT OF IRRADIATION ON THERMAL STABILITY

CFR FUEL COKER TESTS ON KEROSENE (J-1118)
TEST CONDITIONS: 400/500/6

7.5 Status

It was found that both gamma and reactor irradiation can be damaging to jet fuel thermal stability at dosage levels too low to cause noticeable changes in other fuel properties. It appears that different fuels may have different critical dosages in this regard. No information was obtained which explained the reduced thermal stability. At this time, it appears that combined reactor radiation is more damaging to thermal stability than gamma irradiation at the same dosage level. The part played by oxygen in reducing thermal stability of irradiated fuels is not yet understood, but it appears important.

The change in fuel characteristics at higher dosages of 87×10^8 to 87×10^9 ergs/g C is now well defined. Viscosity increase appears to be the limiting property in this radiation range, while thermal stability will generally be as good as or better than that of unirradiated fuel. Initial fuel composition and crude source do not appear to influence the magnitude of change in physical properties brought about by irradiation.

7.6 Conclusions

a. Gamma irradiation in the dosage range of 8.7×10^5 to 8.7×10^9 ergs/g C reduces fuel thermal stability.

b. Reactor irradiation reduces thermal stability more than equivalent gamma dosage.

c. At high gamma dosages (above about 40×10^9 ergs/g C), fuel thermal stability is usually unchanged or improved.

d. Viscosity increase is the major problem at higher radiation dosages.

e. Peroxidation may be important in thermal instability resulting from irradiation.

7.7 Recommendations

This program showed that work is needed in the following areas to overcome the problems of jet fuel radiolysis:

a. The mechanism of the changes in thermal stability brought about by irradiation.

b. The influence of hydrocarbon type on thermal stability changes caused by irradiation.

c. The performance of additives in protecting fuels from loss in thermal stability on irradiation.

d. The effect of reactor irradiation.

e. The effect of time between exposure and testing for thermal stability.

APPENDIX I

TEST METHODS (S. R. CALISH)

This section describes the test methods used to evaluate the physical and chemical properties and the performance of materials studied under this contract. Whenever applicable, methods described in either the Federal Test Method Standard No. 791, dated December 15, 1955, or the ASTM Standards for Petroleum Products and Lubricants, dated November 1956, were used. Short descriptions of the "Special Tests" employed follow the tabulation of methods.

I. Applicable Tests

A. Greases

Test	Method
Dropping Point	ASTM D 566-42
ASTM Worked Penetration	ASTM D 217-52T
Norma Hoffman Bomb	
Copper Corrosion	FSM No. 5314
Oxidation	ASTM D 942-50
Dirt Content	FSM No. 3005.1
Bearing Performance	FSM No. 331.1
Work Stability	FSM No. 313.1
Evaporation	ASTM D 972-51T
Apparent Viscosity	ASTM D 1092-55
Low Temperature Torque	Special Test
Navy Gear Wear Test	FSM No. 335-T

B. Hydraulic Fluids

Test	Method
Viscosity	ASTM D 445-53T
Pour Point	ASTM D 97-47
Flash Point	ASTM D 92-52
Spontaneous Ignition Temperature	Special Test
Bulk Modulus (Adiabatic)	Special Test

Test	Method
Shear - Sonic Oscillator	Special Test
Hydraulic Pump	Special Test
Foaming	FSM No. 3212
Thermal Decomposition	Special Test
Gassing During Irradiation	Special Test
Density	ASTM D 941-49
Acid No.	ASTM D 664-54
Vapor Pressure	Special Test
Oxidation-Corrosion	
347° F	FSM No. 5308.4
400° F	FSM No. 5308.4
500° F	Special Test
Hydrolytic Stability	Special Test

C. Engine Oils

Test	Method
Viscosity	ASTM D 445-53T
Pour Point	ASTM D 97-47
Flash Point	ASTM D 92-52
Spontaneous Ignition Temperature	Special Test
Foaming	ASTM D 892-46T
Evaporation	ASTM D 972-51T
SOD Lead Corrosion	Special Test
Shell Four-Ball Wear	Special Test
Ryder Gear Test	Special Test
Panel Coking	Special Test
Oxidation-Corrosion	
347° F	FSM No. 5308.4
400° F	FSM No. 5308.4
500° F	Special Test
Mean Hertz Load(Screening Test)	Special Test
WADC Deposition Test	Special Test

D. Gear Oils

Test	Method
Viscosity	ASTM D 445-53T
Flash Point	ASTM D 92-52
Pour Point	ASTM D 97-47
Acid No.	ASTM D 664-54
Oxidation-Corrosion	FSM No. 5308.4
Load Carrying Ability	
Ryder Gear Test	Special Test
Mean Hertz Load	FSM No. 6503 (Also Special Test)

E. Fuels

Test	Method
Distillation	FSM No. 1001.8
Gravity, °API	FSM No. 401.4
Existent Gum	FSM No. 3302.4
Reid Vapor Pressure	FSM No. 1201.4
Thermal Value	FSM No. 2502.3
Viscosity	FSM No. 305.3
Aromatics	FSM No. 3701.2
Olefins	FSM No. 3701.2
Flash Point	FSM No. 1102.7
Thermal Stability (CFR Coker)	Special Test
Filter Residue	Special Test

II. Special Tests

A. Greases

1. Low Temperature Torque - This method is described in Section 4.5.3 of Military Specification MIL-G-3278A for Grease, Aircraft, and Instrument, dated March 23, 1956.

B. Hydraulic Fluids

1. Spontaneous Ignition Temperature - A controlled temperature vertical muffle furnace is used. A stainless steel plate is heated in 10°F steps in the furnace. One drop of the test fluid is dropped onto the plate through an opening in the door at each step. The temperature at which the fluid first flashes is the spontaneous ignition temperature. The furnace is air purged between each 10°F, and the flash temperature is rechecked as temperature is decreased.

2. Bulk Modulus (Adiabatic) - In an appropriately instrumented apparatus, the velocity of a 500 kc/sec ultrasonic wave through the test liquid is measured at atmospheric pressure and 76° F. The adiabatic bulk modulus is the product of the density of the liquid times the square of the velocity.

3. Shear - Sonic Oscillator - About 50 ml of the test fluid is exposed to a Raytheon 10-kc sonic oscillator. The change in viscosity is the test criterion. Test duration can be varied as desired, usually 0.5 to 4 hours. In the past[1], fair to good correlation was established with shear breakdown experienced in the testing of fluids in aircraft piston pumps.

4. Hydraulic Pump Test[2] - A simple hydraulic circuit was used to evaluate fluids for shear and for wear. Mounts are provided for a 15 horsepower electric driving motor to accommodate piston pumps of either Vickers PF-3911 or New York Airbrake 66WA300 type. From the pump discharge, fluid flowed through an orifice, a pressure relief valve, heat exchanger, sump, and filter and back to the pump inlet. The Model 66WA300 pumps are run at constant delivery with the bypasses blocked with a socket screw. Tests are generally for 150 hours at 160° F, followed by 100 hours at 275° F. Parts are inspected and weighed at the start, at 150 hours, and at 250 hours. Interim inspections are made if anything unusual occurs.

5. Thermal Decomposition - Ten milliliters of test fluid is placed in a Type 410 stainless steel capsule[3] under a helium atmosphere. The capsule is welded shut and heated for a specified period in a muffle furnace set at the desired temperature. Gas evolution is determined by venting the gas to a vacuum flask[3] at the conclusion of the test. The effect upon fluid viscosity is also determined.

6. Gassing During Irradiation - Ten milliliter samples of test fluid are sealed into a Type 410 stainless steel[3] capsule under helium. The capsule is subjected to the desired radiation dosage and then vented to a vacuum flask[3] for determination of evolved gas.

7. Vapor Pressure - This method uses a vacuum-jacketed boiling point apparatus in which the pressure of an inert atmosphere is varied by means of a slow leak. The vapor pressure of the boiling fluid is the pressure of the inert atmosphere. Provision is made to measure the pressure by way of a direct connection to the boiling chamber. An oil manometer is used for measuring vapor pressures in the range of 0.1-15 mm mercury, while a mercury manometer is used for higher pressures. The apparatus may be used over the temperature range from 70-550° F.

[1] Unpublished work, California Research Corporation.

[2] "Effects of Radiation on Aircraft Lubricants and Fuels," (California Research 1956 Summary Report on Contract AF 33(616)-3184) WADC Technical Report 56-646, p. 110.

[3] N. P. Shiells, R. O. Bolt, and J. G. Carroll, "Safe Containers Hold Organics for Irradiations," Nucleonics 14, No. 8, 54 (1956).

8. Oxidation-Corrosion at 500°F - This test is conducted in an apparatus designed to one-fourth scale the Federal Standard Method No. 5308.4. A temperature controlled aluminum block is used for heating purposes. Glassware is designed for 25 ml (one-fourth scale) of test fluid. Metal specimens are in the form of washers which fit about the air bubbling tube and are separated by glass collars. An air flow rate of 1.25 liters/hour is maintained. Various metal specimens can be used, and standard inspections are run on the residues.

9. Hydrolytic Stability - Ten milliliters of test fluid, 0.6 ml of water, and a weighed piece of polished copper are placed in a 22-ml Parr[1] peroxide bomb. The bomb and contents are weighed before and after test to determine leakage. The bomb is rotated at 5 rpm in a 400°F oven in the "coke bottle" rig of Specification MIL-H-8446A for 20 hours. The fluid is tested for viscosity, neutralization number, and insolubles. Weight loss of the copper strip is also determined.

C. Engine Oils

1. Spontaneous Ignition Temperature - See section on hydraulic fluids, page 213.

2. SOD Lead Corrosion - This method is described in Section 4.5.13 of Military Specification MIL-L-7808C for Lubricating Oil, Aircraft, Turbine Engine, Synthetic Base, dated November 2, 1955.

3. Shell Four-Ball Wear - The average scar diameters[2] from runs at 4, 10, and 40-kg jaw load on the Shell Four-Ball Wear Tester are used to indicate the antiwear properties of engine and hydraulic oils. In this machine, 4-1/2 inch balls of 52100 steel are mounted in a tetrahedral arrangement. The lower three are loaded against the upper ball which rotates at a preset speed. After a specified time, wear spots on the lower three balls are measured with the aid of a Filar eyepiece on a microscope.

4. Ryder Gear Test - This method is described in Section 4.5.7 of Military Specification MIL-L-7808C.

5. Panel Coking - This method is described in Section 4.5.10 and reference literature of Military Specification MIL-L-7808C.

6. Oxidation-Corrosion at 500°F - See Item 8 above.

[1] Parr Instrument Company, Moline, Illinois.

[2] Average of diameter perpendicular to and parallel to the direction of rotation.

7. Mean Hertz Load (Screening Test) - The procedure, equipment, and techniques are identical to those described in Federal Standard Method No. 6503. Sufficient loads are used to determine the load in kg required to give a 1.0 mm scar. This value is related to the Mean Hertz Load obtained from a full-scale test as shown in Figure 42, this curve was obtained from many runs over a long period. Correlation with the full-scale test is sufficiently accurate for screening test work[1].

8. WADC Deposition Test - This method is a later development of the panel coking test. The latter has a questionable correlation with engine service. It is designed to evaluate the deposit and sludge-forming tendencies of jet engine oils. The oil system is composed of a "chicken-feeder" type reservoir, a pump, a 200-mesh screen filter, an oil cooler, and a Pyrex coking furnace in which is immersed a heater tube. The system oil temperature is maintained at 300° F "oil-in," and the heater tube at 590° F. A value of ten times the weight of coke formed on the heater tube added to the weight of sludge on the filter screen yields a number known as the "Deposit Rating", this is the criterion of excellence.

This method is described in detail in a Southwest Research stitute Report No. AVD 224-18, dated March 12, 1957, covering Project No. 6-(1-3044) under WADC Contract AF 33(616)-3529.

D. Gear Oils

1. Ryder Gear Test - This method is described in Section 4.5.7 of Military Specification MIL-L-7808C.

E. Fuels

1. Thermal Stability Test (CFR Coker)[2,3] - This device is proposed by the CFR-AFD Fuel Thermal Stability Group for testing the thermal stability of jet fuels[3]. In the test, the fuel is preheated to a desired temperature (e.g., 400° F), and then pumped through a filter (maintained at a selected temperature (e.g., 500° F) at a given rate (e.g., 6 pounds per hour). The criterion of the test is the degree of filter plugging by the flue. Filter plugging is manifested by a pressure drop across the filter. Test conditions are typically written 400/500/6, indicating the fuel temperature in °F, the filter temperature in °F, and the flow rate in pounds per hour.

[1] Unpublished work, California Research Corporation.

[2] "A Survey of the Radiation Stability of Jet Fuels," (California Research-AEC Report No. 9, Contract AT(11-1)-174) TID 5366, June 30, 1956 (SECRET - RESTRICTED DATA).

[3] "Instructions for Operation and Maintenance of CFR Fuel Coker," Coordinating Research Council Manual No. 3, March 1957.

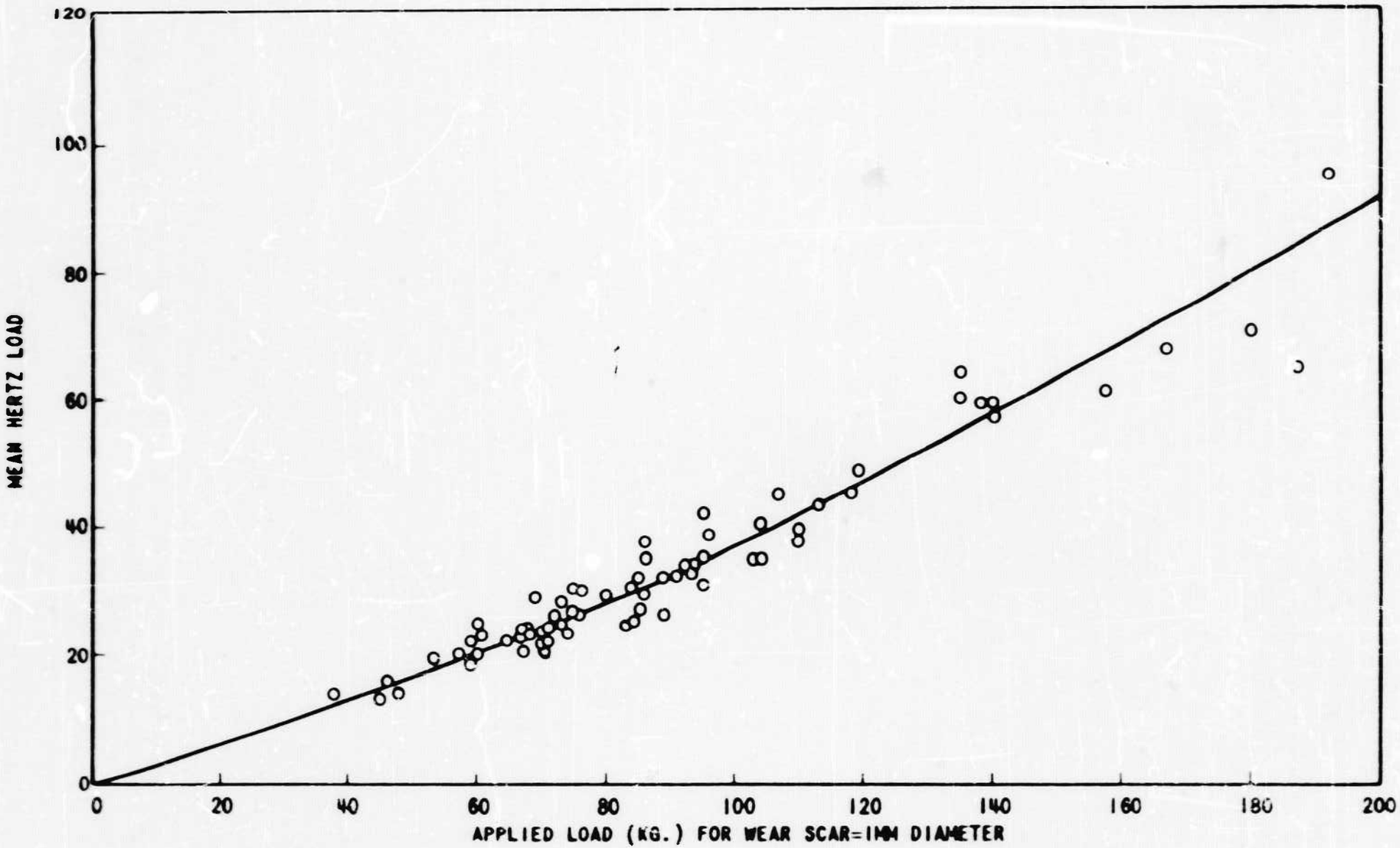


FIG. 42 - CORRELATION OF MEAN HERTZ LOAD WITH SCREENING TEST

2. Filter Residue Test[1] - 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 crucible is washed, dried, cooled, and weighed. The filter residue, corrected for adsorption, is calculated as mg per 500 ml.

[1] "Effects of Radiation on Aircraft Lubricants and Fuels," (California Research 1956 Summary Report on Contract AF 33(616)-3184) WADC Technical Report 56-646, p. 178.

APPENDIX II

SYNTHESIS OF DIARYLALKANES (A. C. ETTLING)

Example - Synthesis of Phenyl n-Nonylphenylisodecane

A. Preparation of the Diphenyl Diketone

Nine hundred nine grams (4.5 moles) isosebacic[1] acid, 1.5 liters benzene, and about 415 grams (3 moles) phosphorus trichloride were stirred and warmed to 120° F in a large flask. Stirring was continued for 30 minutes and the mixture allowed to cool and settle. The benzene solution of isosebacic acid chloride was decanted from the orthophosphorus acid into a large separatory funnel. The acid chloride solution was added over a period of three hours to a stirred mixture of 3 liters benzene and 1.2 kilograms (9 moles) anhydrous aluminum chloride contained in an enamel pail. The mix was stirred at ca. 167° F for two more hours before pouring onto a mix of ice and hydrochloric acid. The benzene solution was washed with dilute hydrochloric acid and with water. After solvent removal, the diketone was distilled through a 6-inch Vigreaux column, collecting the fraction boiling at 390-441° F at 0.4 millimeters.

B. Reduction of Diketone to Diphenylisodecane

A mixture of 1.025 kilograms (3.18 moles) diketone, 1600 milliliter triethylene glycol, 340 grams (10 moles) 95% hydrazine, and 160 grams (2.85 moles) potassium hydroxide was stirred and heated at 200° F in a 5-liter monel flask for one hour. The temperature was slowly raised to 274° F at which temperature much foaming and evolution of gas occurred. Water was collected in a Stark and Dean trap. The stirring and heating was continued at 274° F for about two hours. The temperature was gradually raised to 420° F and the mix stirred for 12 hours. After cooling, water and benzene were added. The aqueous layer was discarded. The benzene solution was water washed, dried, filtered, and the solvent was then removed. The diphenylisodecane was distilled through a 6-inch Vigreaux column, and the fraction boiling 330-370° F at 0.15 mm was collected.

C. Acylation and Reduction to Obtain the n-Nonyl Alkyl Group

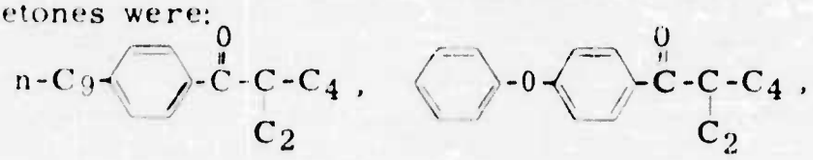
One and one-half moles of diphenylisodecane was acylated with 0.5 mole pelargonyl chloride as in Step A, and the excess diphenylisodecane was removed by distillation. The ketone was reduced as in Step B using 2 moles hydrazine hydrate per mole ketone and the product distilled.

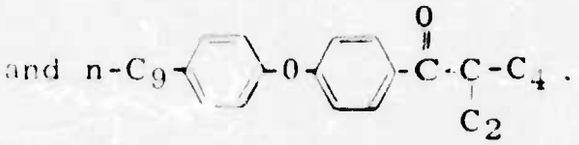
[1] U.S. Industrial Chemicals Co.

Approximate Composition	72-80% 2-ethyl suberic acid 12-18% 2,5-diethyl adipic acid 6-10% sebacic acid

In some syntheses, n-heptane was used as an inert diluent to facilitate mixing in Step A. The temperature of acylation (120-170° F) was not critical. In the Wolff-Kischner reduction, hydrazine hydrate could be substituted for 95+% hydrazine. Also, the amount of alkali was varied without adverse effect. The temperature at which rapid hydrazone decomposition occurred varied with the particular compound being reduced.

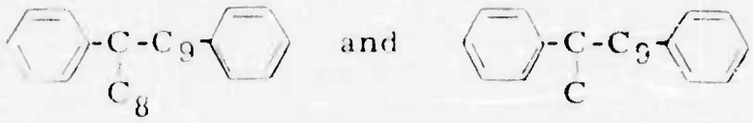
Several attempts were made to introduce a 2-ethylhexyl group into an aromatic nucleus by acylation with 2-ethylhexoyl chloride. Reduction of the ketone by the Wolff-Kischner method failed. The unsuccessfully reduced ketones were:



and 

Recovery of the unchanged ketones was surprising in view of the similarity between these structures and the diketone precursor of diphenylisodecane.

Two attempts to prepare diarylalkanes by reacting terminal-dihaloalkanes with alkylbenzenes in the presence of aluminum chloride were unsuccessful. Similarly, two attempts to prepare the following diarylalkanes from oleic acid and undecylenic acid failed:



Arylation of the double bond followed by conversion to the acid chloride, acylation of benzene, and reduction of ketone were to be followed. The synthesis of these compounds was not pursued in view of the unpromising initial results.

APPENDIX III

SYNTHESIS OF 500-POUND BATCH OF C_{14-16}-ALKYL DIPHENYL ETHER (A. C. ETTLING)

A Pfaudler glass-lined kettle was charged with 895 pounds diphenyl ether, 9 pounds chloroform, and 20 pounds anhydrous aluminum chloride. The temperature was kept at 130°F while charging. Three hundred pounds C_{14-16} alpha-olefins (Archer-Daniels-Midland) was then added over a period of two hours while the temperature was held at 130-150°F. Stirring at 130-150°F was maintained for an additional two hours. The mix was washed with dilute acid, water, and dilute sodium bicarbonate solution. After filtering, the yield was 1133 pounds. Crude alkylate, in the amount of 1118 pounds, was topped to 375°F at 9 mm pressure to remove excess diphenyl ether. The yield of bottoms product was 467 pounds. Samples of the bottoms product were distilled in laboratory equipment. Physical data are in Table VIII and yield data in Table XCI.

The olefin used for this batch contained a large amount of hexadecene, unlike earlier samples used. The viscosity index and pour point of the final product were, therefore, slightly higher than the values previously reported for laboratory samples as follows:

	Laboratory Sample[1]	Appendix III Sample[2]
Viscosity Index	112	114
Pour Point	-45	-15

[1] "Effects of Radiation on Aircraft Lubricants and Fuels," (California Research 1956 Summary Report on Contract AF 33(616)-3184) WADC Technical Report 56-646, p. 21.

[2] See Table VIII, p. 11.

TABLE XCI

DIPHENYL ETHER ALKYLATION WITH C_{14-16} ALPHA-OLEFINS (LARGE SCALE)

Experiment No.	4658-21		
	Pounds	Pound Moles	Mole Ratio
Reactants			
1. Diphenyl Ether	895	5.26	3.9
2. C_{14-16} Alpha-Olefins	300	1.35	1
3. Aluminum Chloride	20	0.15	0.12
4. Chloroform	9	0.075	0.06
Reaction Conditions			
Temperature, °F	120-150		
Total Time, Hours	4		
Procedure:	Reactant 4 followed by 3 added to 1 at 130° F (10 minutes) 2 added with stirring at 130-150° F (2 hours) Stirring continued at 120-150° F (2 hours)		
Product			
Alkylate[a], Pounds	467		
Theory for Monoalkyl Diphenyl Ether, Pounds	530		
Handling Loss, %	6.5		
Yield, % of Theory	88		

[a] After removing solvents, unreacted starting material, and light ends.

APPENDIX IV

TEN-POUND PREPARATION OF POLY-DODECYL DIPHENYL ETHER (D. R. WILGUS)

Two simultaneous experiments were conducted using the following procedure. A 3-1/2 gallon enamel pail was charged with 2.2 kg (6.5 moles) mono-sec-dodecyl diphenyl ether (boiling range 358-412° F/0.5 mm), 217 g (1.6 moles) anhydrous aluminum chloride (Merck), and 65 ml (0.8 mole) chloroform (Baker). The mixture was stirred and heated to 140° F. 1-Dodecene (Humphrey-Wilkinson), 2.735 kg (16.25 moles), was added from a dropping funnel at such a rate that a reaction temperature of 140-167° F could be maintained. After completion of monomer addition (approximately three hours), the reaction mixture was stirred at 140° F for an additional three hours. A sufficient volume of benzene was then added to facilitate transfer and workup of the product. Washings of the benzene solution were made with dilute hydrochloric acid, dilute sodium bicarbonate, and water. The solvent was removed under reduced pressure, and the product was topped to 590° F overhead and 642° F bottoms at about 1/2 mm pressure. The bottoms product, 57% of total, was filtered through Celite. Properties are summarized in Table VIII, Reference 5158-36.

APPENDIX V

SYNTHESIS OF BIS(TRIDECYL) SELENIDE (A. C. ETTLING)

Using the following procedure, about 3 pounds of bis(tridecyl) selenide can be prepared per run. This is as large a scale as is convenient for working in a 12-liter flask (Experiment 5136-6).

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

Selenium metal powder (410 g, 5.2 moles) was added with stirring to a hot solution of 2000 g (50 moles) of sodium hydroxide dissolved in 8 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 950 g (6 moles) of "Rongalite CX" (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 pure 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 which are difficult to separate and wash.) After standing for 12 to 48 hours, the mother liquors were decanted. The crystals were washed by decantation with about 3 liters of absolute alcohol. A nitrogen stream was maintained in the apparatus during these operations to avoid air oxidation of the sodium selenide.

B. Reaction of Oxo-Tridecyl Bromide and Sodium Selenide to Give Bis(tridecyl) Selenide

The flask containing the sodium selenide, prepared as described, was fitted with a reflux condenser, dropping funnel, and stirrer. Absolute alcohol (6 liters) was added, the mixture heated to reflux temperature, and 2176 g (8.28 moles) of Oxo-tridecyl bromide[1] added over a period of two hours. To insure completion of the reaction, the mixture was refluxed with stirring for four hours. After cooling, the liquid was decanted into a separatory funnel. The inorganic salts in the flask were washed with benzene several times, with the benzene solutions being added to the material in the separatory funnel. Water was then added to the separatory funnel and the aqueous alcohol layer discarded. The benzene solution of the crude product was water washed, dried over sodium sulfate, and filtered. The crude product was topped in a simple still to a bottoms temperature of 350° F at 1 mm. (Higher temperature causes decomposition.) The bottoms product was treated with Norite "A" to improve its color. Yield of product containing 16.9% selenium was 1415 g, 77% of theoretical.

[1] From Enjay Oxo-tridecyl alcohol by the method of Organic Syntheses, Coll. Vol. p. 246; b.p. 210-230° F at 2 mm.

APPENDIX VI

POLYMERIZATION OF ALPHA-METHYLSTYRENE (D. R. WILGUS)

The apparatus used for homopolymerization of alpha-methylstyrene consisted of a 2-liter resin flask fitted with a condenser, stirrer, and thermometer. A slurry of Dry Ice and acetone was employed as an external cooling medium. A catalyst tube (100-300 ml) was placed alongside the reactor and connected to it to inject catalyst solution under slight nitrogen pressure. Adequate circulation of coolant was maintained by a separate stirrer. The general procedure for polymerization was as follows. The monomer (Dow Chemical) and methyl chloride (Du Pont) were charged to the resin flask and cooled to the desired temperature. Methyl chloride (100-300 ml) was also charged to the catalyst tube. After cooling it to the reaction temperature, boron trifluoride (Matheson) was bubbled in at a moderate rate for a period of 20 minutes partially to saturate the solvent. The precooled catalyst solution was then pressured through a small glass orifice to produce a spray on the rapidly agitated reaction mixture. The injection jet was placed about 1 inch above the surface of the mixture. The feed rate of catalyst solution varied with the polymerization temperature. After polymerization, the reaction mixture was poured into precooled methanol to precipitate the polymer. The recovered product was dissolved in benzene. The solution was filtered, and the polymer was again precipitated with methanol. The recovered poly(alpha-methylstyrene) was then dried to constant weight in a vacuum oven at 212° F.

Polymerizations involving the use of concentrated sulfuric acid were conducted in a similar manner. A microburette was substituted for the catalyst tube previously described, and the acid (General Chemical, 95.5-96.5%) at room temperature was added to the precooled mixture of monomer and solvent.

APPENDIX VII

ALKYLATION OF POLY(ALPHA-METHYLSTYRENE) (D. R. WILGUS)

A solution of 10 g of polymer in 225 g of o-dichlorobenzene (Eastman 99+%) was charged to a 1-liter copper reaction vessel equipped with an inlet tube at the top, an outlet valve at the bottom, and a stainless steel stirrer. Fifty ml of propylene tetramer (molecular weight 168 by bromine number determination) was added and the mixture cooled to 41° F in an ice bath. Liquid hydrogen fluoride (General Chemical), 75 ml, was added to the rapidly agitated mixture, and stirring was continued for a period of one to six hours.

The polymer solution was separated from the hydrogen fluoride via the drainoff valve at the bottom of the reactor and poured into a cold caustic solution with good stirring to neutralize any residual catalyst. The organic layer was separated and water washed. The alkylated polymer was then precipitated with methanol and redissolved in benzene. The benzene solution was filtered and the polymer reprecipitated with methanol. This procedure was repeated. The product was dried to constant weight in a vacuum oven at 212° F.

APPENDIX VIII

PREPARATION OF ALKYLPHENOXYETHYL METHACRYLATE (D. R. WILGUS)

A. Oxyethylation of Alkylphenol

The alkylphenol was obtained locally at California Research and was prepared by alkylating phenol with an equimolar amount of propylene tetramer. A 12-liter capacity, high pressure Aminco rocker bomb was charged with 1.3 kg of the alkylphenol and 20 g sodium hydroxide. A total of 399 g ethylene oxide (Carbide and Carbon) was pressured into the vessel at such a rate that the reaction temperature could be maintained at 248-266° F. The pressure of the system did not exceed eight atmospheres. The mixture was held at reaction temperature for four hours after all oxide had been added to insure complete reaction. The product was discharged from the vessel after suitable cooling.

A solution of 400 g of product in 1 liter of benzene was treated with hydrochloric acid to neutralize the caustic. The solution was dried by azeotropic distillation and filtered through Celite. Hydroxyl determination of an aliquot of the filtrate indicated slightly more than 1 mole of ethylene oxide per mole of alkylphenol.

B. Reaction of Alkylphenoxyethanol With Methacrylyl Chloride

The monomer was prepared by dropwise addition of 10% excess of theory methacrylyl chloride (Monomer-Polymer) to a stirred 40% benzene solution of the alkylphenoxyethanol containing a 10% excess of triethylamine (Eastman). The temperature rose from room temperature to 135° F. Quinone inhibitor (Eastman), 0.14% by weight (based on monomer), was added after completion of the methacrylyl chloride addition. The mixture was maintained at 135-140° F for five hours. A small amount of methanol was then added, and heating was continued for another hour to insure complete reaction of the monomeric chloride. Methyl methacrylate and excess methanol were removed by azeotropic distillation under reduced pressure. The solution was filtered to remove the amine hydrochloride. The filtrate was washed with 2% caustic solution and with water. It was then concentrated to give approximately a 50% solution of the alkylphenoxyethyl methacrylate. Analysis by saponification and hydroxyl numbers indicated a monomer purity of 83%.

APPENDIX IX

POLYMERIZATION OF ALKYLPHENOXYETHYL METHACRYLATE (D. R. WILGUS)

The following procedure was adopted for the solution polymerization of alkylphenoxyethyl methacrylate. A 500-ml three-neck flask fitted with a stirrer, thermometer, and reflux condenser was charged with a 50% benzene solution containing 100 g of monomer. The solution was swept with nitrogen and the appropriate amount of α,α'-azodi-isobutyronitrile (Eastman) catalyst added. The mixture was stirred and heated at reflux, 204° F, under a nitrogen blanket for eight hours. The polymer was precipitated twice from benzene with methanol. It was redissolved in benzene and the solution filtered. The solvent was stripped off, and the residual polymer was dried to constant weight in a vacuum oven at 212° F.

APPENDIX X

ISOTHERMAL BULK MODULUS OF HYDRAULIC FLUID-HYDROGEN MIXTURES*

(R. L. PEELER AND H. S. YAPLEE, CALIFORNIA RESEARCH CORPORATION, RICHMOND AND LA HABRA, CALIFORNIA)

Pressure-volume-temperature measurements were made on three aircraft hydraulic fluids, both alone and with added hydrogen. Apparatus in which mercury was the pressurizing medium was used. Pressures ranged from atmospheric to 5000 psi and gas-liquid ratios from 0 to 25. Measurements were taken at 80° F with MIL-O-5606 fluid and at 80° F, 200° F, and 300° F with Oronite 8200 fluid and C_{14-16}-alkyl diphenyl ether.

Isothermal bulk modulus was calculated for both the one- and two-phase regions. Separation of even a small gaseous phase caused a large decrease in bulk modulus. Hydrogen saturation pressures were determined from the inflection points of the pressure-volume curves. The solubility of hydrogen in the fluids is proportional to pressure and increases with increasing temperature.

INTRODUCTION

Bulk modulus is one of the critical design parameters affecting the performance of hydraulic servomechanisms. On exposure of a hydraulic system to nuclear radiation, evolution of gas by the hydraulic fluid is one of the major problems. The low bulk modulus of gas compared to the hydraulic fluid may cause the system to become unstable or otherwise adversely affect performance. The object of this investigation was to determine the relationship between the amount of gas present and the bulk modulus of the gas-hydraulic fluid system.

A study of the effect of entrained air on isothermal compressibility of AN-O-366 fluid at 68° F was made by Campbell[1]. Calculated and measured compressibilities were found to be in good agreement. Wood[2] had calculated the bulk modulus of a mixture of two fluid phases in the region well below the resonant frequency to be:

$$B = \frac{B_1 B_2}{(1-X) B_1 + X B_2}$$

where B = bulk modulus of mixture
B_1, B_2 = bulk modulus of the two components
X = volume fraction of first component.

* Paper presented at the Second WS 125A Symposium on Radiation Effects, Columbus, Ohio, October 23, 1957.

[1] Numbers refer to bibliography at end of paper.

This expression has been found to be highly accurate for sonic velocity measurements in a liquid-liquid emulsion[3] and to be within the rather large experimental error for air bubbles dispersed in water[4]. Tangren, et al[5], have studied flow of air-water mixtures through a de Laval nozzle. Equations of state and motion were derived assuming negligible compressibility of the water phase and were compared with experimental results.

Propagation of pressure impulses through a gas-liquid mixture has been shown to be dependent on both the degree of dispersion of the two phases and the frequency of the input signal. A dispersion of gas bubbles in liquid was calculated by Minnaert[6] to have a characteristic resonant frequency given approximately by the expression:

$$f_o = \frac{1}{2\pi R_o} \left(\frac{3\gamma P_o}{d}\right)^{1/2}$$

where f_o = resonant frequency

R_o = radius of bubble

γ = ratio of specific heat at constant pressure to specific heat at constant volume

P_o = static pressure of bubble

d = density of liquid

Meyer and Tamm[7] measured these resonant frequencies for several gas-liquid combinations, while Meyer and Skudrzyk[8] derived equations for the complex compressibility of the resonant region. Fox, et al[4], have confirmed these equations by measuring phase velocity through an air-water mixture over a wide frequency range. Fortunately, the resonant frequencies for expected conditions are above those usually encountered in hydraulic systems. Therefore, compressibility measured under static conditions, even in the presence of gas, is applicable to almost all hydraulic system calculations.

IDENTIFICATION OF RADIOLYSIS GASES

Three hydraulic fluids, MIL-O-5606 fluid, Oronite High Temperature Hydraulic Fluid 8200, and C_{14-16}-alkyl diphenyl ether, were selected for use in this investigation. These are typical of petroleum, silicate ester, and alkyl aromatic fluids, respectively. The last material is representative of a promising class of radiation resistant, high-temperature base stocks.

To determine the nature of the volatile radiolysis products, 10-ml samples were irradiated in the Materials Testing Reactor gamma facility at Arco, Idaho. The samples were contained under a helium atmosphere in Type 410 stainless steel capsules. Following irradiation, gases were bled off to a final pressure less than atmospheric and analyzed by mass spectrograph. Results are shown in Table XCII. Hydrogen is by far the most prominent product. Therefore, in the bulk modulus work, only hydrogen was added to the hydraulic fluids to simplify the procedure.

Table XCII

Composition of Radiolysis Gas From Hydraulic Fluids

	MIL-O-5606 Fluid	8200 Fluid	C_{14-16}-Alkyl Diphenyl Ether
Dosage, r	3.4×10^8	3.0×10^8	3.4×10^8
Temperature of Irradiation, °F	80	80	400
ml Gas Evolved/ml Fluid at STP	13.4	12.2	3.2
Composition of Gas, Mole %			
Hydrogen	91.2	83.6	95.5
Methane	-	2.8	1.4
Ethane	0.5	4.0	1.3
Ethylene	0.1	-	0.6
Propane	-	-	0.4
Propylene	0.1	-	0.2
Butanes	0.1	0.5	0.2
Butenes	-	-	0.2
Pentanes	-	0.5	-
Pentenes	-	-	0.1
Carbon Monoxide	3.7	8.3	-
Carbon Dioxide	1.3	0.3	-
Other	3.0	-	-

DESCRIPTION OF APPARATUS

Pressure-volume-temperature measurements were made in the apparatus described by Standing[9]. This equipment, shown diagrammatically in Figure 43, consists of a pressure cell equipped with an induction stirrer where equilibrium can be obtained between gas and liquid phases, a controlled temperature oven, a pressurizing system for injecting mercury into the cell, a traveling rod carrying an electrical contact to determine the location of the mercury-fluid interface, and appropriate gages, connections, etc. After the fluids were degassed by vacuum evacuation, mercury was pumped in under pressure, the location of the fluid-mercury interface being measured by position of the traveling rod.

Where the bulk modulus of gas-liquid mixtures was to be measured, the maximum hydrogen-fluid ratio was introduced into the cell and pressure-volume measurements made after stirring at each pressure to establish equilibrium. Measured quantities of hydrogen were removed in a stepwise manner to obtain lower ratios. Because of the relatively high volatility of MIL-O-5606 fluid, removal of hydrogen at 200°F and 300°F would have resulted in loss of fluid, vitiating subsequent volume measurements. Therefore, measurements were not made of bulk modulus of MIL-O-5606 fluid-hydrogen mixtures at these two temperatures.

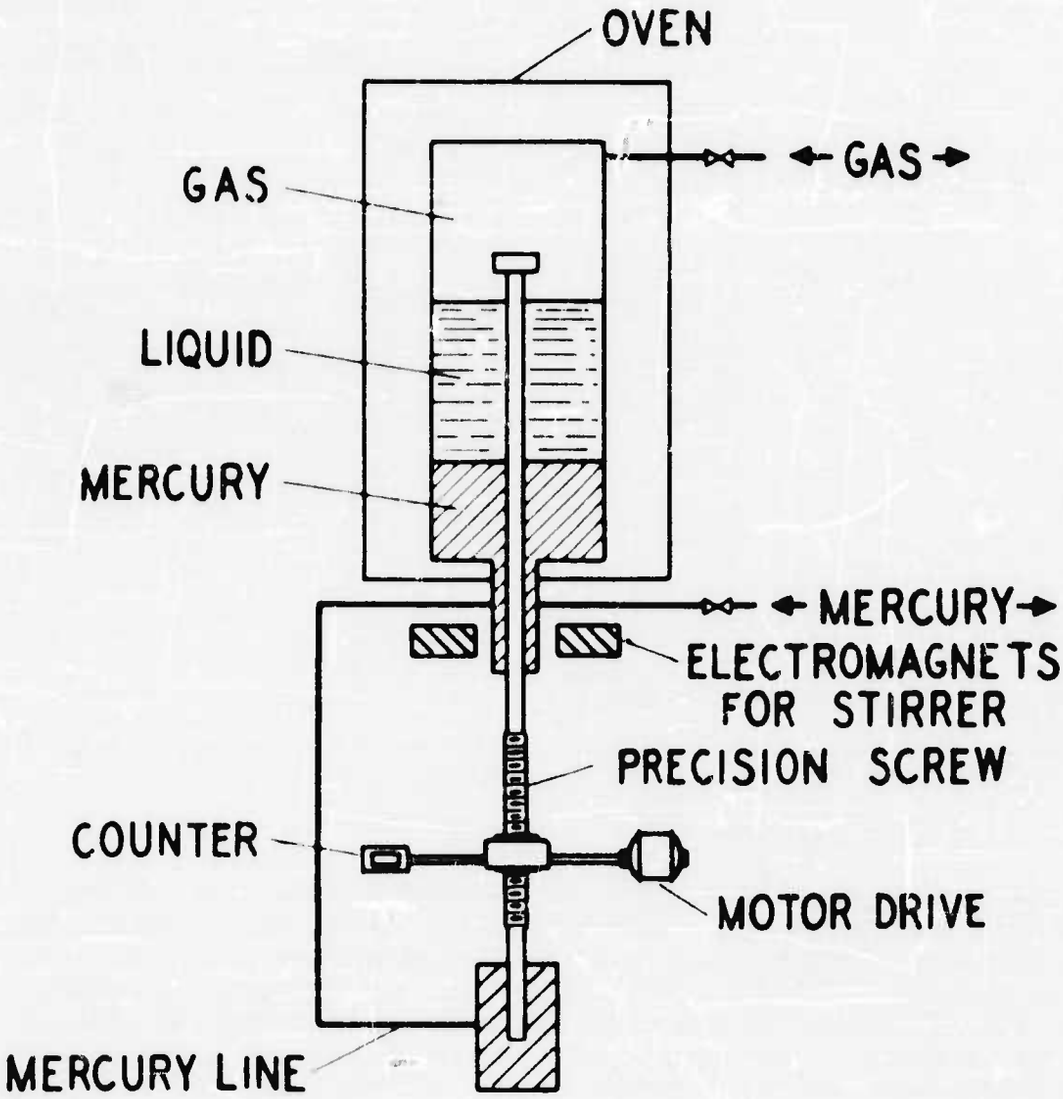


FIG. 43 - SKETCH OF P-V-T CELL

In the first series of measurements, that of 8200 fluid at 80° F, the positions of the traveling rod were calibrated using the average of two previously reported values for the isothermal bulk modulus of gas-free 8200 fluid. The average value was within 3% of the individual values which were: (1) P-V-T data from Boeing Airplane Company[10] and (2) values calculated from the adiabatic bulk modulus obtained from ultrasonic velocity measurements[11]. For all other runs, a subsequent calibration based on measurements at 80° F on degassed, distilled water compared with the known bulk modulus of water[12] was used.

EXPERIMENTAL RESULTS

Pressure-volume measurements were made on MIL-O-5606 fluid, Oronite 8200 fluid, and C_{14-16}-alkyl diphenyl ether at 80° F, 200° F, 300° F, and on mixtures of hydrogen with 8200 fluid and C_{14-16}-alkyl diphenyl ether at 80° F, 200° F, and 300° F and with MIL-O-5606 fluid at 80° F. The pressure range covered was from atmospheric to 5000 psi, and the hydrogen-fluid ratio, from about 2 to 25, was arbitrarily chosen to cover a wide range of conditions. Typical pressure-volume data for 8200 fluid at 200° F are shown in Figure 44. The gas-liquid ratio is defined as the volume of hydrogen corrected to 0° C and 760 mm divided by the volume of the fluid at the test temperature and atmospheric pressure. The bubble point of the hydrogen-fluid system can be easily determined from the point of inflection of the pressure-volume curve.

Isothermal bulk modulus, defined as

$$B_T = -v \left(\frac{\partial p}{\partial v}\right)_T$$

where B_T = isothermal bulk modulus

v = volume

p = pressure,

was determined by measuring graphically the slope of the smoothed pressure-volume curves and substituting in this equation. Results are given for 8200 fluid in Figures 45, 46, 47, for C_{14-16}-alkyl diphenyl ether in Figures 48, 49, and 50, and for MIL-O-5606 fluid in Figure 51. The data can be summarized as follows:

1. Separation of a gaseous phase causes a very large reduction in bulk modulus even at pressures only slightly below the saturation pressure. Thus, in Figure 45, at a 5.6 gas:liquid ratio, the bulk modulus drops abruptly from 183,000 psi to 29,000 psi when the pressure is decreased through 1525 psia.

2. Dissolved gas decreases bulk modulus as the quantity of gas increases. This effect is small compared to the reduction caused by the presence of a gas phase.

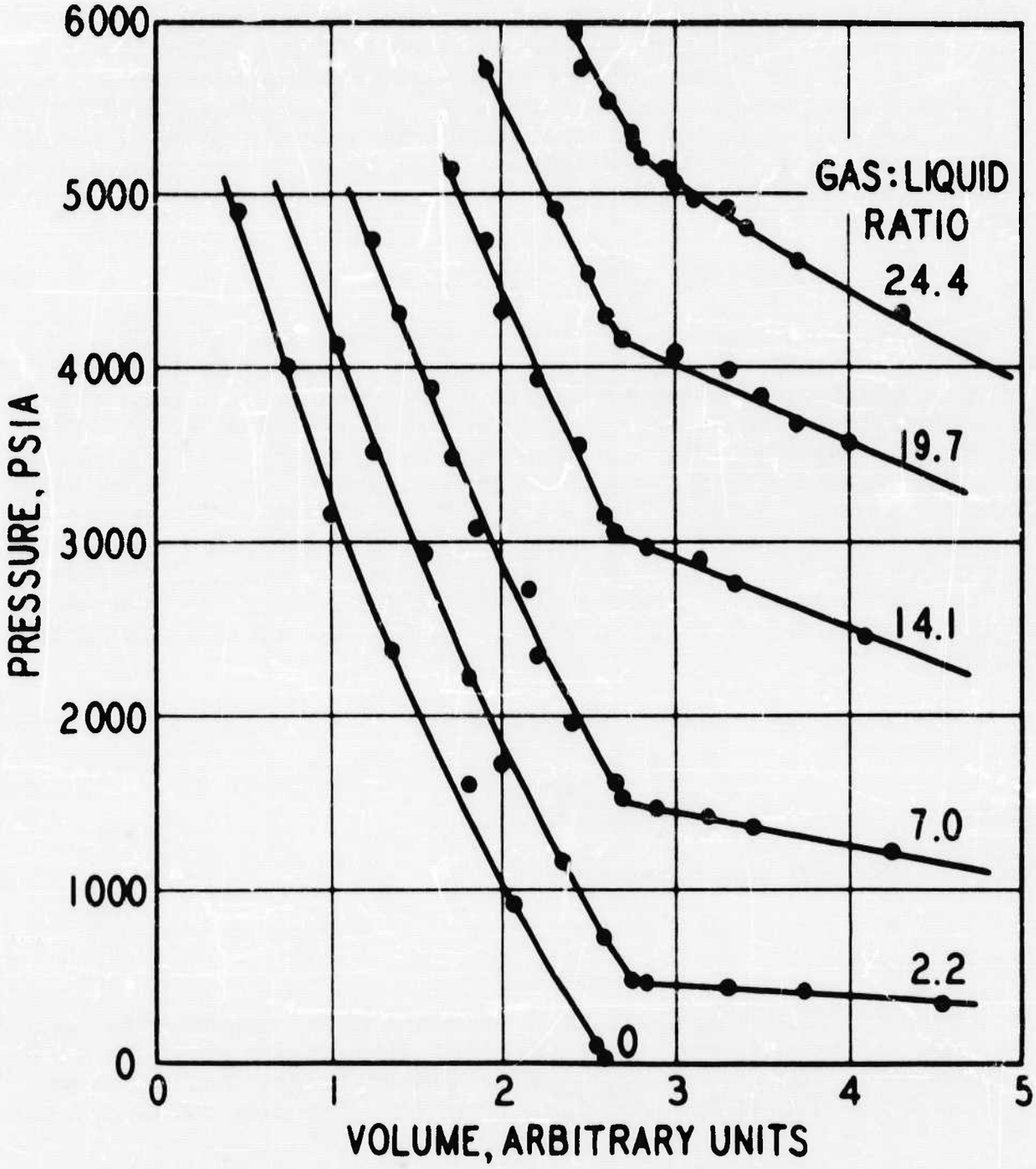


FIG. 44 - PRESSURE-VOLUME MEASUREMENTS FOR HYDROGEN
8200 FLUID MIXTURES AT 200°F

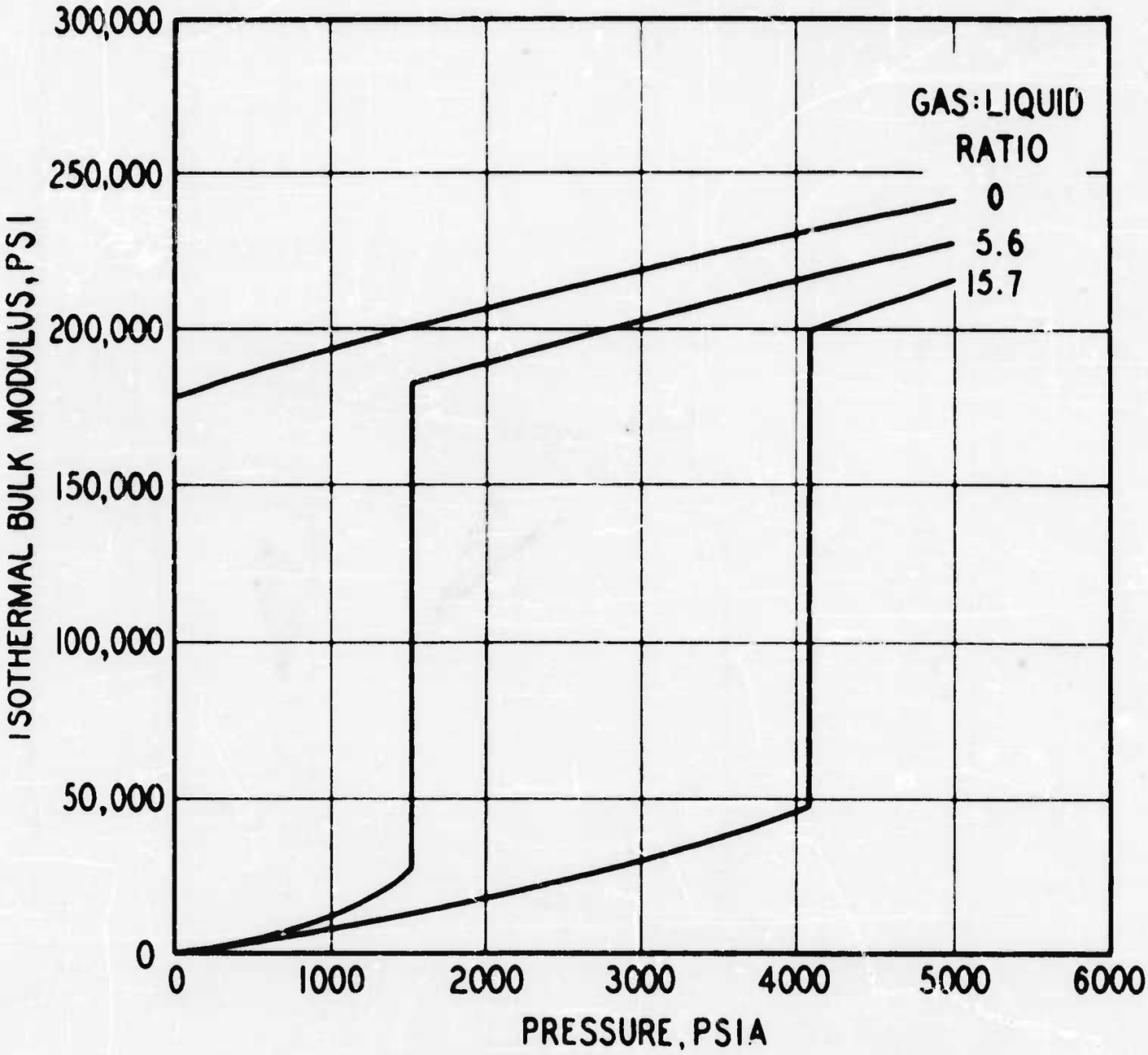


FIG. 45 - ISOTHERMAL BULK MODULUS OF HYDROGEN
8200 FLUID MIXTURES AT 80°F

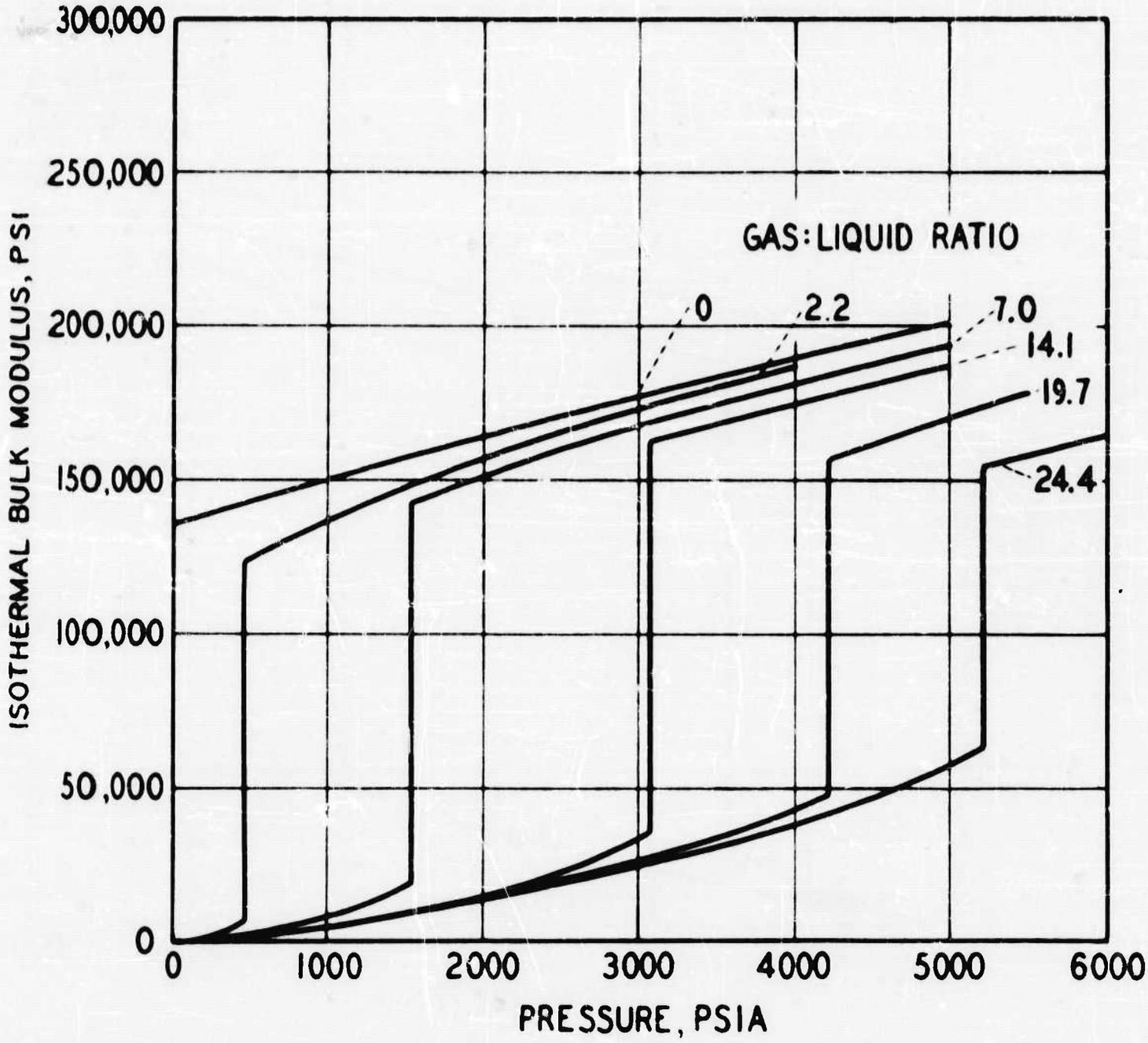


FIG. 48 - ISOTHERMAL BULK MODULUS OF HYDROGEN
8200 FLUID MIXTURES AT 200°F

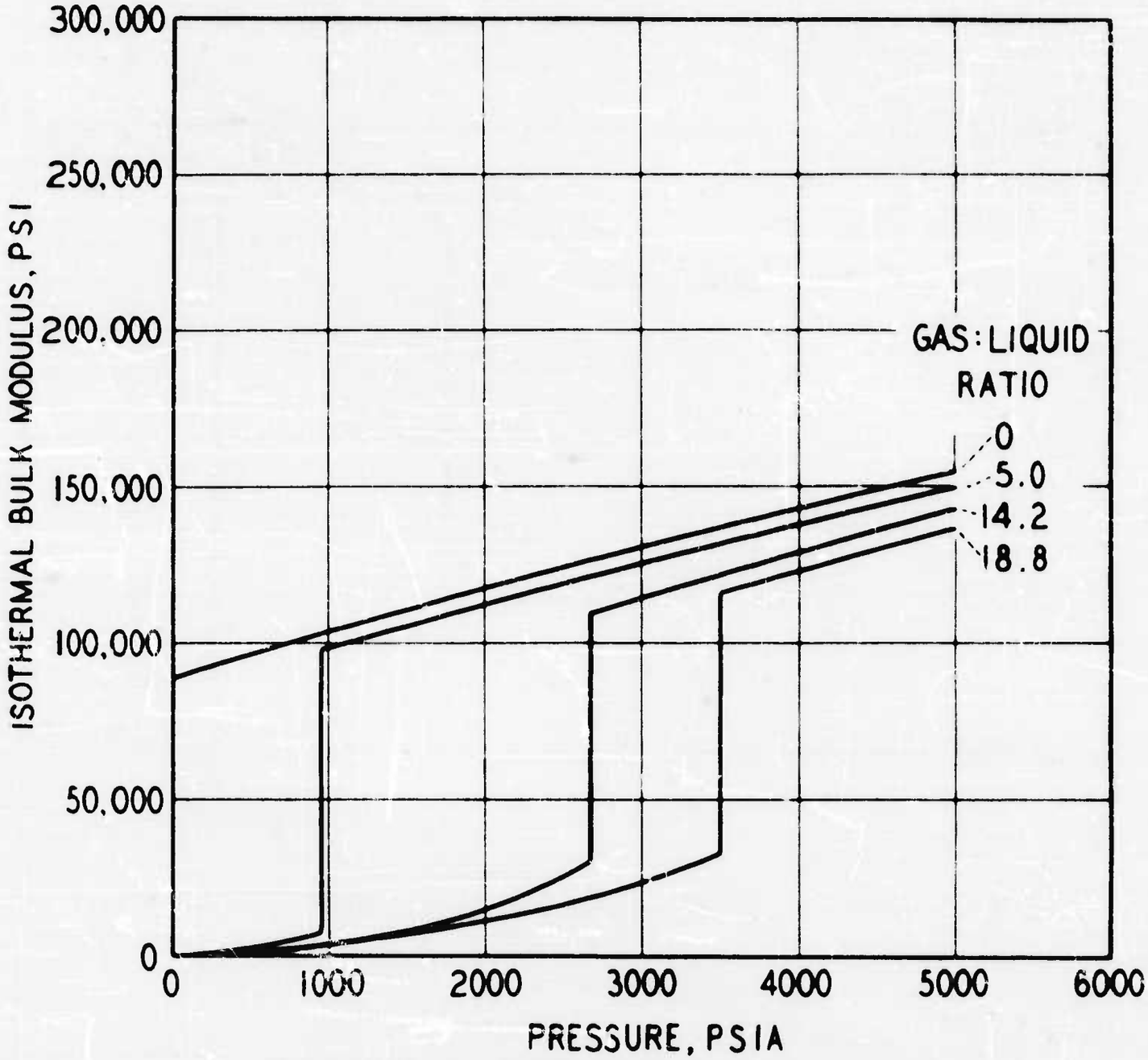


FIG. 47 - ISOTHERMAL BULK MODULUS OF HYDROGEN
8200 FLUID MIXTURES AT 300°F

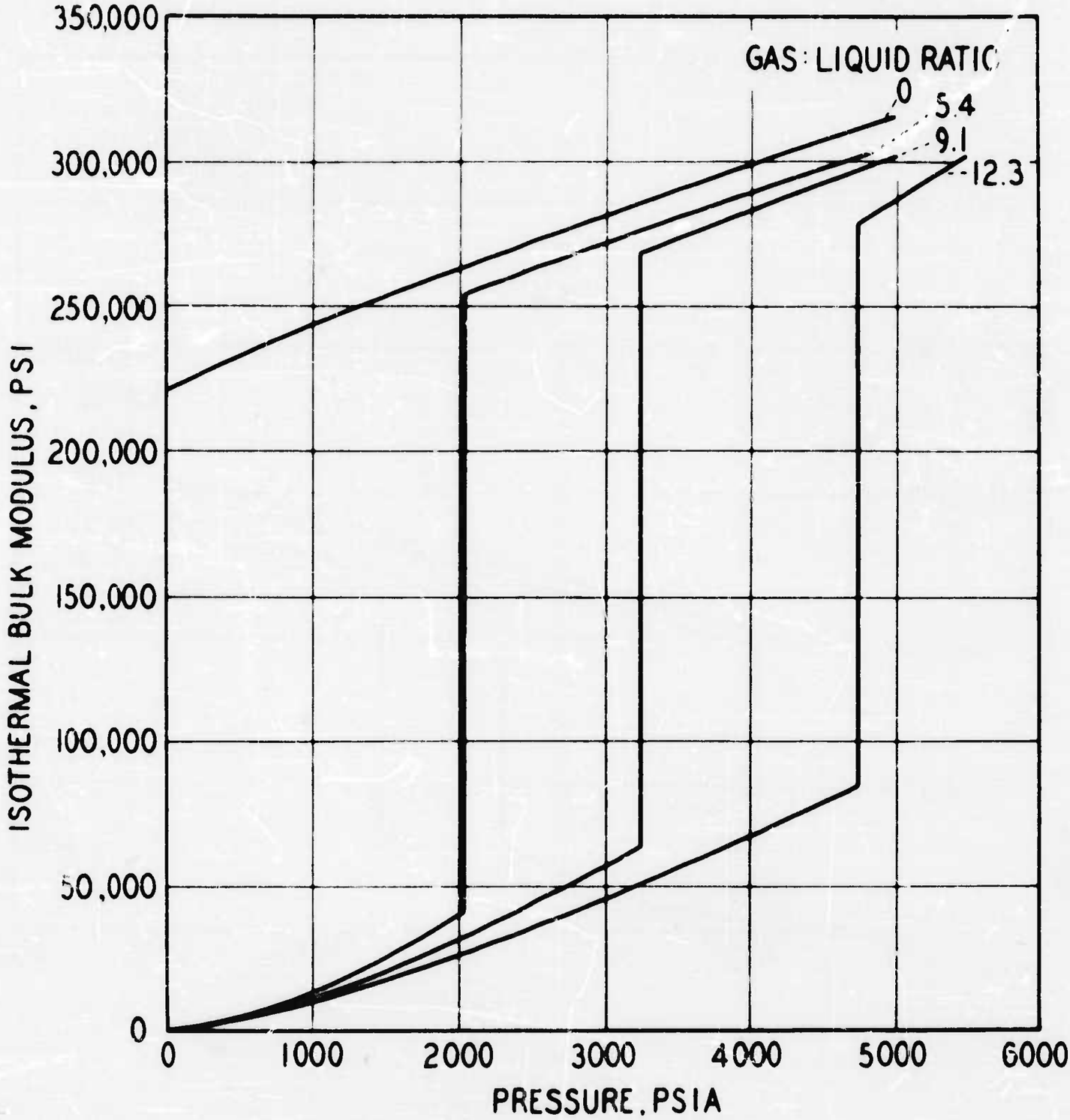


FIG. 48 - ISOTHERMAL BULK MODULUS OF HYDROGEN C_{14-18}-ALKYL DIPHENYL ETHER MIXTURES AT 80°F

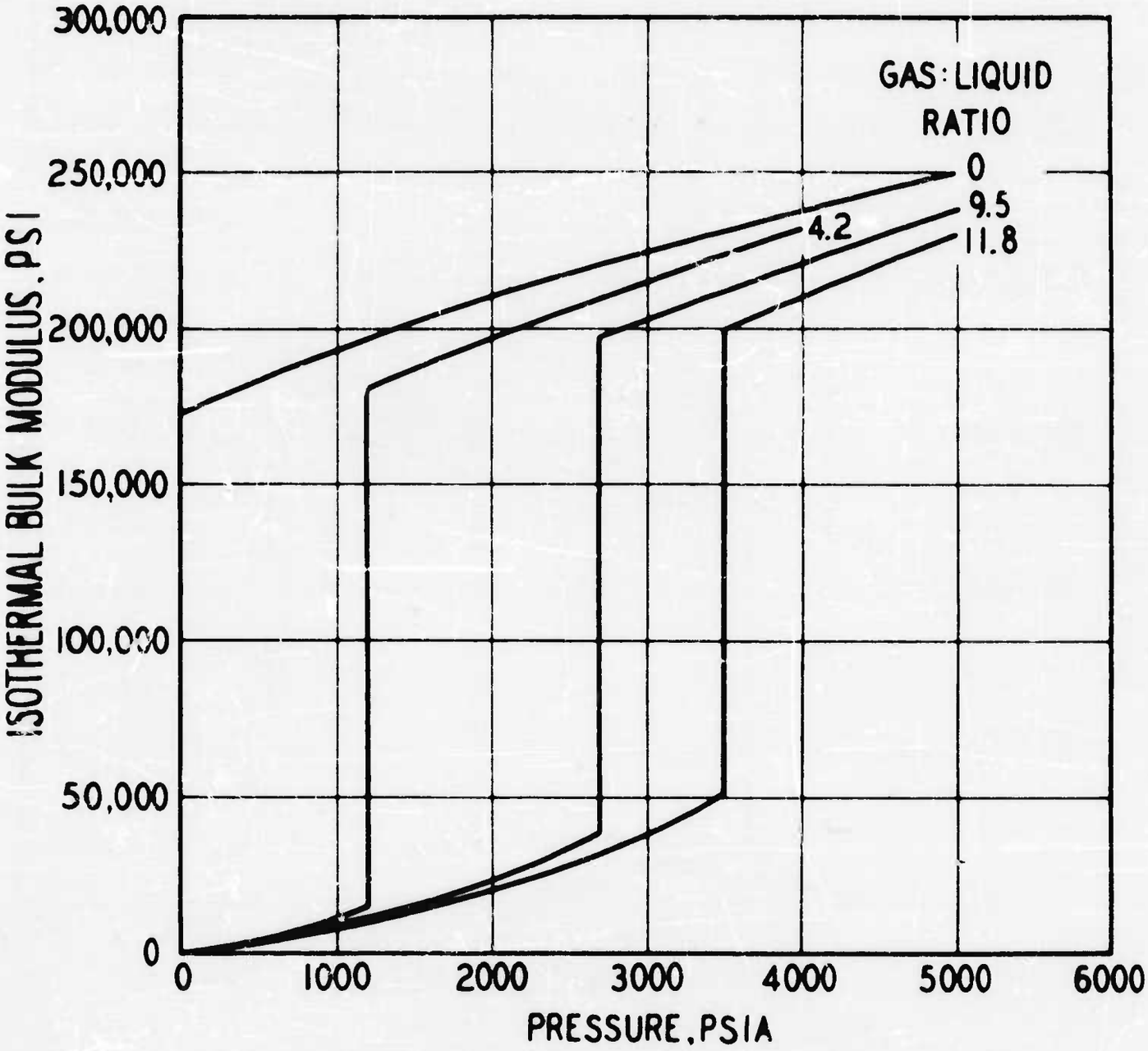


FIG. 49 - ISOTHERMAL BULK MODULUS OF HYDROGEN C_{14-18}-ALKYL DIPHENYL ETHER MIXTURES AT 200°F

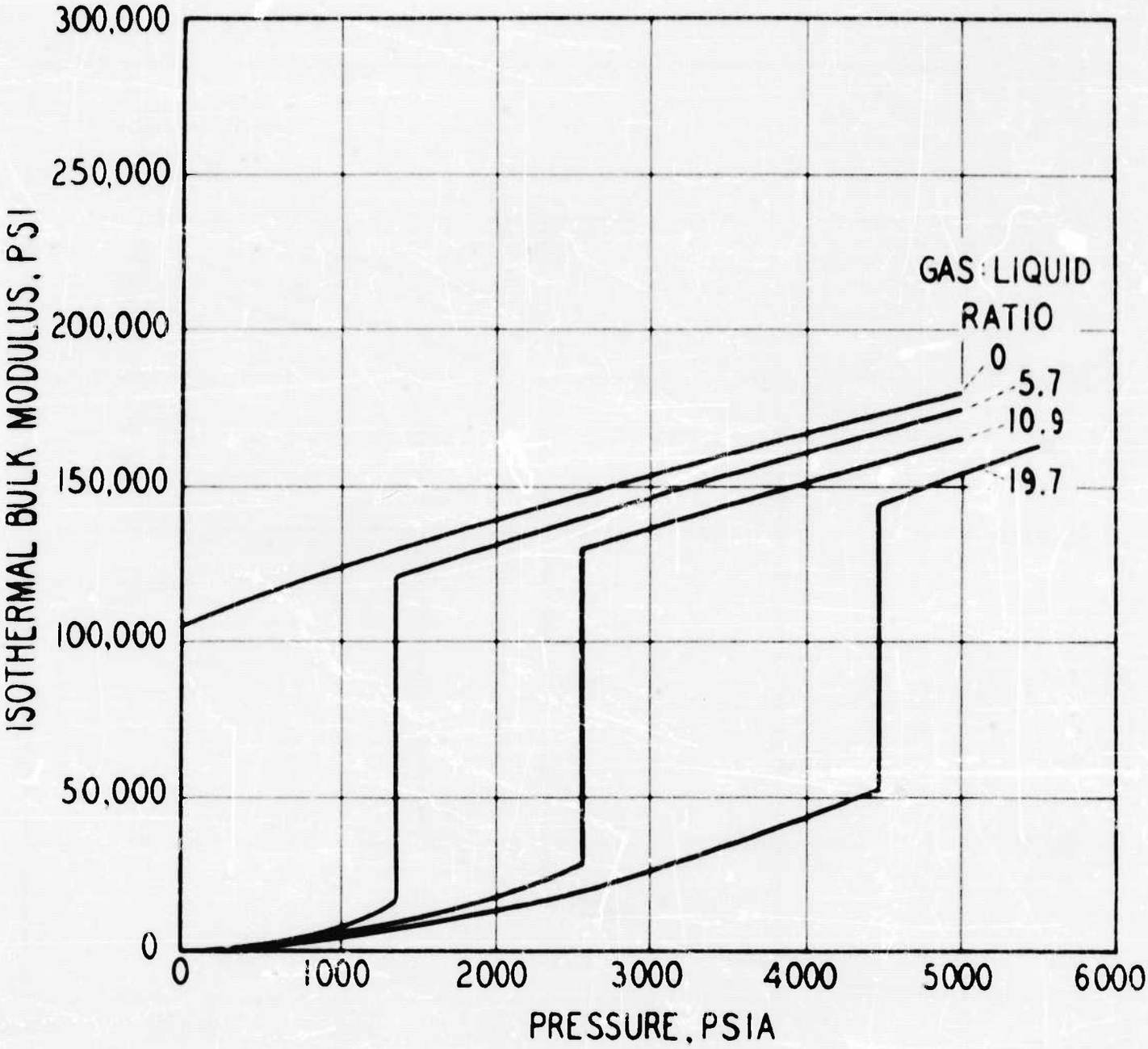


FIG. 50 - ISOTHERMAL BULK MODULUS OF HYDROGEN C_{14-16}-ALKYL DIPHENYL ETHER MIXTURES AT 300°F

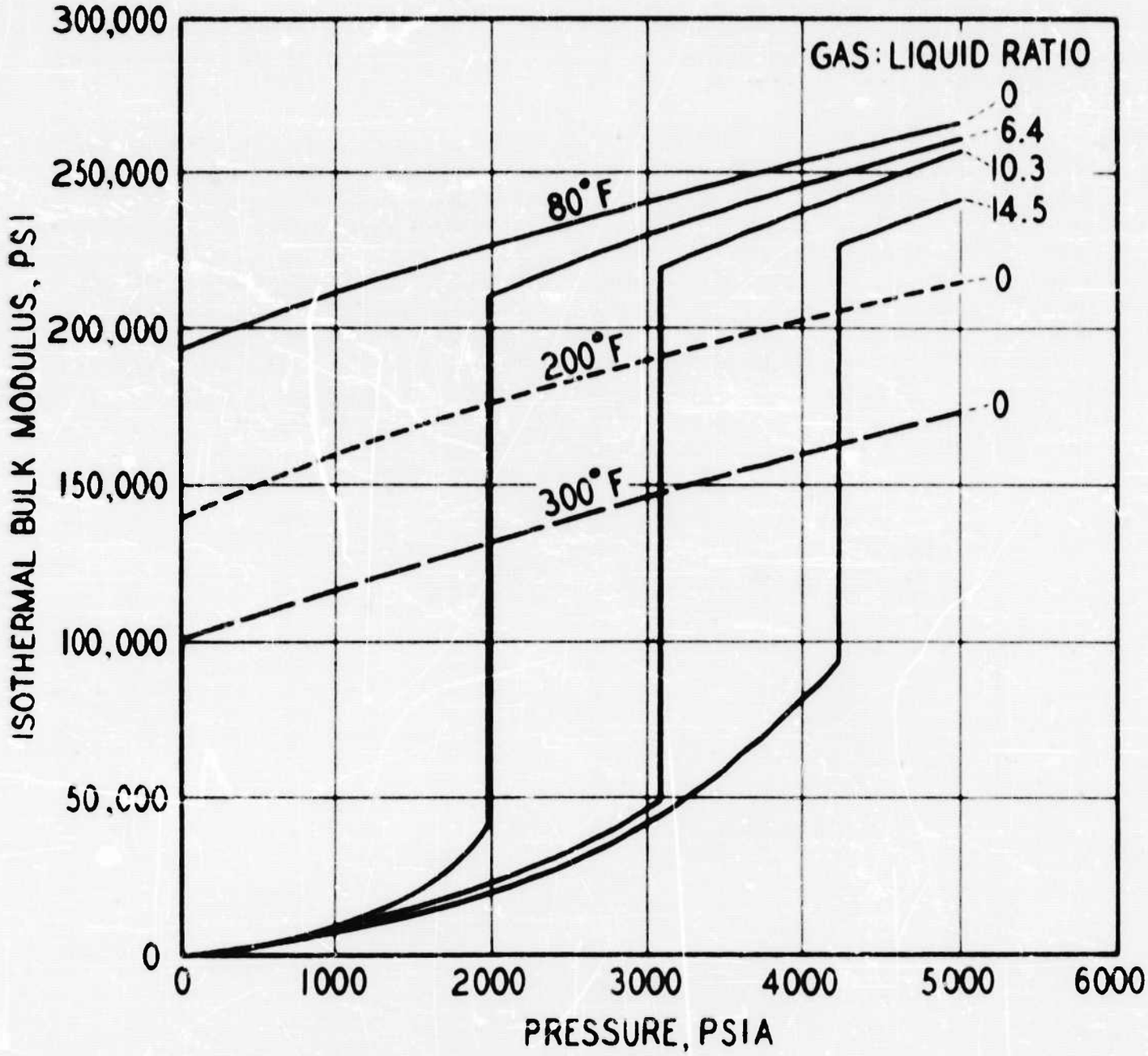


FIG. 51 - ISOTHERMAL BULK MODULUS OF HYDROGEN MIL-O-5608 FLUID MIXTURES

3. Over the temperature range measured, the degassed fluids in order of decreasing isothermal bulk modulus are: C_{14-16}-alkyl diphenyl ether, MIL-O-5606 fluid, and 8200 fluid. Earlier adiabatic bulk modulus measurements[11] have also shown 8200 fluid to be more compressible than MIL-O-5606 fluid at 80-300° F but to be less compressible at temperatures above 400° F.

Saturation pressures for each hydrogen hydraulic fluid ratio were determined from the bends in the pressure-volume curves. The data are plotted in Figure 52. The solubility of hydrogen is directly proportional to pressure, within experimental error, showing conformity to Henry's law. The solubility of hydrogen increases in 8200 fluid and C_{14-16}-alkyl diphenyl ether as the temperature increases. This result is in agreement with the known behavior of hydrogen in lubricating oils[13] and organic solvents[14]. The Bunsen solubility coefficients (volume of gas corrected to 0° C and 760 mm for each volume of liquid at the test temperature under a 760 mm partial pressure of gas) have been calculated and are listed in Table XCIII and plotted in Figure 53. The order of decreasing solvency for hydrogen is: 8200 fluid, MIL-O-5606 fluid, C_{14-16}-alkyl diphenyl ether.

Table XCIII

Bunsen Solubility Coefficient α for Hydrogen Dissolved in Hydraulic Fluids

Fluid	Solubility Coefficient, Vol Gas*/Vol Liquid/Atm at		
	80° F	200° F	300° F
8200 Fluid	0.052	0.068	0.077
C_{14-16}-Alkyl Diphenyl Ether	0.041	0.051	0.063
MIL-O-5606 Fluid	0.049	-	-

* Corrected to 0° C and 760 mm.

CONCLUSIONS

Hydrogen, the principal radiolysis product of three representative hydraulic fluids, causes a large reduction in bulk modulus if present in sufficient quantity to form a separate gaseous phase. Dissolved hydrogen causes only a small reduction in bulk modulus. Therefore, it is highly desirable to keep the lowest pressure in the operating portion of the hydraulic system above the saturation pressure of the quantity of hydrogen expected to be evolved. Increasing the temperature of the hydraulic fluid and, thus, increasing the solubility of hydrogen (within the range covered in this work) is one means of reducing the minimum pressure allowable. For prolonged operation or use in strong radiation fields, bleeding of dissolved hydrogen from the system appears essential.

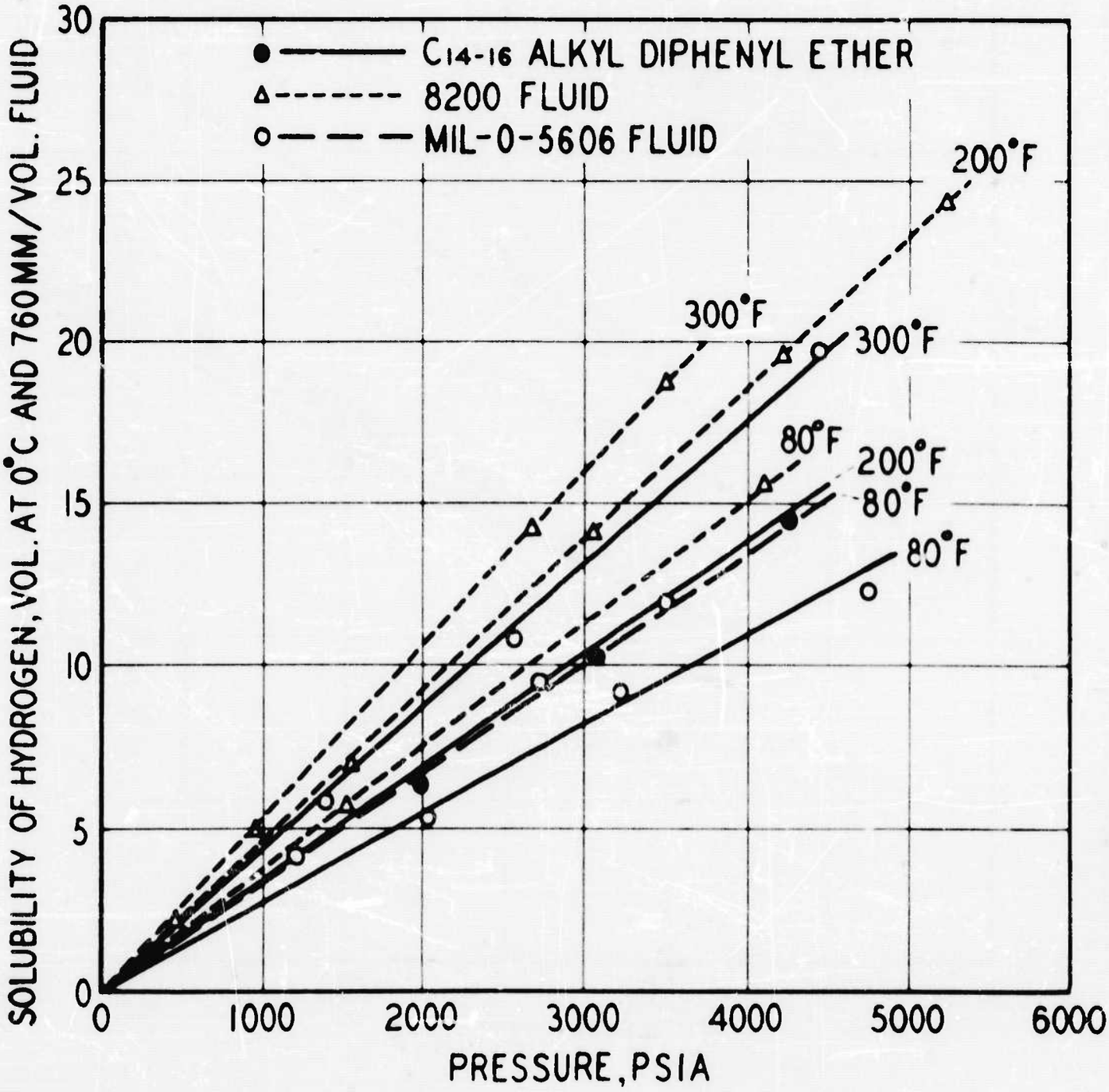


FIG. 52 - SOLUBILITY OF HYDROGEN IN HYDRAULIC FLUIDS

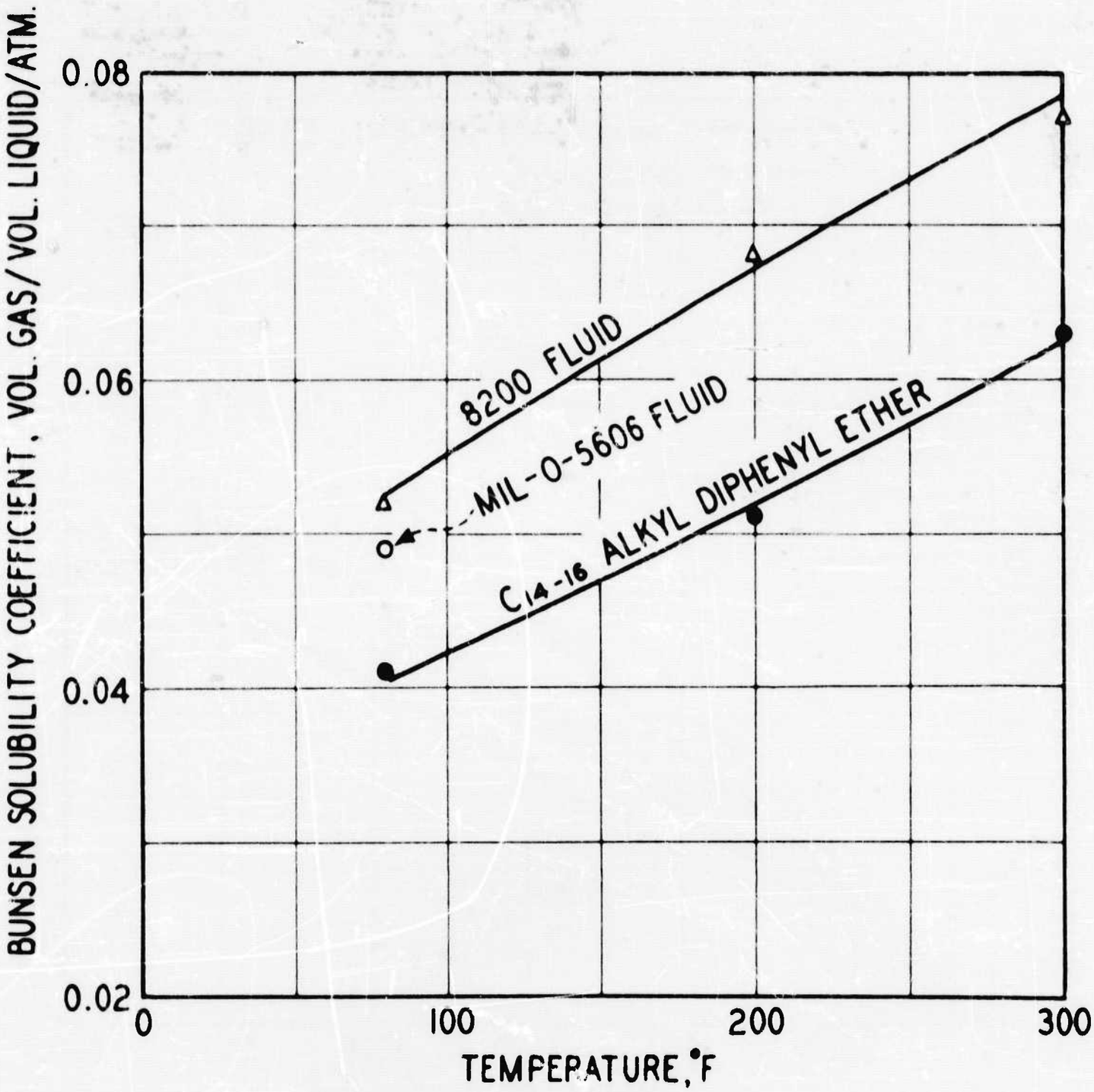


FIG. 53 - BUNSEN SOLUBILITY COEFFICIENT FOR HYDROGEN DISSOLVED IN HYDRAULIC FLUID

The C_{14-16}-alkyl diphenyl ether has a much lower gas evolution rate and higher initial bulk modulus than the 8200 or MIL-O-5606 fluids, and this more than compensates for a slightly lower solubility for hydrogen in the ether. The use of alkyl aromatic hydraulic fluids, such as one based on C_{14-16}-alkyl diphenyl ether, offers an opportunity for substantially extending the radiation dosage which the hydraulic system can tolerate before bulk modulus drop limits system performance.

ACKNOWLEDGMENT

This work was performed in part under Air Force Contract No. AF 33(616)-3181 administered by the Materials Laboratory, Directorate of Research, Wright Air Development Center.

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APPENDIX XI

CALCULATION OF BULK MODULUS
(R. L. PEELER)

Because of the importance of the two-phase region in limiting hydraulic system performance, a comparison of calculated and measured bulk modulus was desirable. Equations for isothermal compressibility in the two-phase region were derived using the following nomenclature:

B = isothermal bulk modulus of system
B_l = isothermal bulk modulus of liquid phase
P = pressure of system
P_a = atmospheric pressure
P_s = saturation pressure for complete solution of gas in liquid
V = total volume of both phases
V_g = volume of gas phase
V_l = volume of liquid phase
V_a = volume of total gas (including dissolved gas) in system corrected to atmospheric pressure
Z = compressibility factor for hydrogen at pressure P

At constant temperature in the two-phase region, assuming gas solubility proportional to pressure,

$$V_g = V_a (1 - P/P_s) \frac{P_a Z}{P}$$

$$V = V_l + V_g$$

$$\frac{\partial V}{\partial P} = \frac{\partial V_l}{\partial P} - \frac{V_a P_a Z}{P^2} - \frac{V_a P_a}{P_s} \frac{\partial Z}{\partial P}$$

Comparison of the second and third terms, at pressures and temperatures covered in the experimental work, indicates that the third term will always be less than 2% of the second. Therefore, to simplify computations the third term will be neglected.

$$\frac{1}{V} \frac{\partial V}{\partial P} = \frac{1}{V} \left(\frac{\partial V_l}{\partial P} - \frac{V_a P_a Z}{P^2} \right)$$

$$= \frac{1}{V_l + V_a (1 - \frac{P}{P_s}) \frac{P_a Z}{P}} \left(\frac{\partial V_l}{\partial P} - \frac{V_a P_a Z}{P^2} \right)$$

$$= \frac{1}{1 + \frac{V_a}{V_l}\left(1 - \frac{P}{P_s}\right)\frac{P_a Z}{P}} \left(\frac{1}{V_l}\frac{\partial V_l}{\partial P} - \frac{V_a P_a Z}{V_l P^2}\right)$$

But $B = -V\frac{\partial P}{\partial V}$,

Therefore, $B = \left[1 + \frac{V_a}{V_l}\left(1 - \frac{P}{P_s}\right)\frac{P_a Z}{P}\right] \times \frac{B_l}{1 + B_l \frac{V_a}{V_l}\frac{P_a}{P^2} Z}$

At $P \xrightarrow{\lim} P_s$, this reduces to,

$$B = \frac{B_l}{1 + B_l \frac{V_a P_a Z}{V_l P_s^2}}$$

Calculations were made for the two-phase region of 8200 fluid-hydrogen mixtures at 200° F. The following simplifying assumptions were made:

$\frac{V_a}{V_l}$ is independent of pressure and equal to its value at P_a.

B_l is equal to B for the degassed liquid. Although this is not correct, the liquid makes only a small contribution to the total compressibility of the system, and the error introduced is correspondingly small.

Values of Z for hydrogen were taken from the literature[1,2].

[1] W. F. Hoot, Petrol. Refiner 35, No. 3, 150 (1956).

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APPENDIX XII

CALCULATION OF RADIATION-INDUCED VISCOSITY CHANGE FOR JET FUELS (J. A. BERT)

The following empirical equation was developed to relate initial viscosity to viscosity after irradiation:

$$\text{Log}(\eta_y - C) = my + \log(\eta_0 - C)$$

or

$$my = \log \frac{(\eta_y - C)}{(\eta_0 - C)}$$

where η_y = viscosity in centistokes after exposure to dosage y in 10^8 r

y = gamma dosage divided by 10^8 r

η_0 = viscosity in centistokes before exposure

m = index of susceptibility of the fuel to viscosity change caused by irradiation

C = a constant for a particular fuel at the particular temperature at which the viscosity is determined.

The equation was derived for a given base fuel by plotting viscosities measured at one temperature versus radiation dosage on semilogarithmic coordinates. The resulting curve was converted to a straight line by subtracting a suitable constant from each viscosity measurement. Figure 54 shows this for fuels J-746 and J-770 (see page 185) for viscosities measured at 100°F. The slope of a given line is exponent "m" in the equation, and the constant subtracted from the viscosities for each fuel is "C."

The constant "C" was found to be directly proportional to the 10% distilled point divided by the API gravity of the original fuel. Plots of "C" values versus 10% points divided by API gravities gave the following relationships for 100°F and 0°F viscosities:

$$C_{100°F} = 0.165 \frac{(10\% \text{ Point})}{(°\text{API})} - 0.21$$

$$C_{0°F} = 0.41 \frac{(10\% \text{ Point})}{(°\text{API})} - 0.39$$

The slope, "m," can be considered an index of susceptibility to change in viscosity caused by irradiation; the greater the slope the greater the susceptibility. Attempts were made to develop an expression giving approximate values of "m" in terms of fuel properties, e.g., aromatic content, which are related to radiation resistance. However, this was unsuccessful.

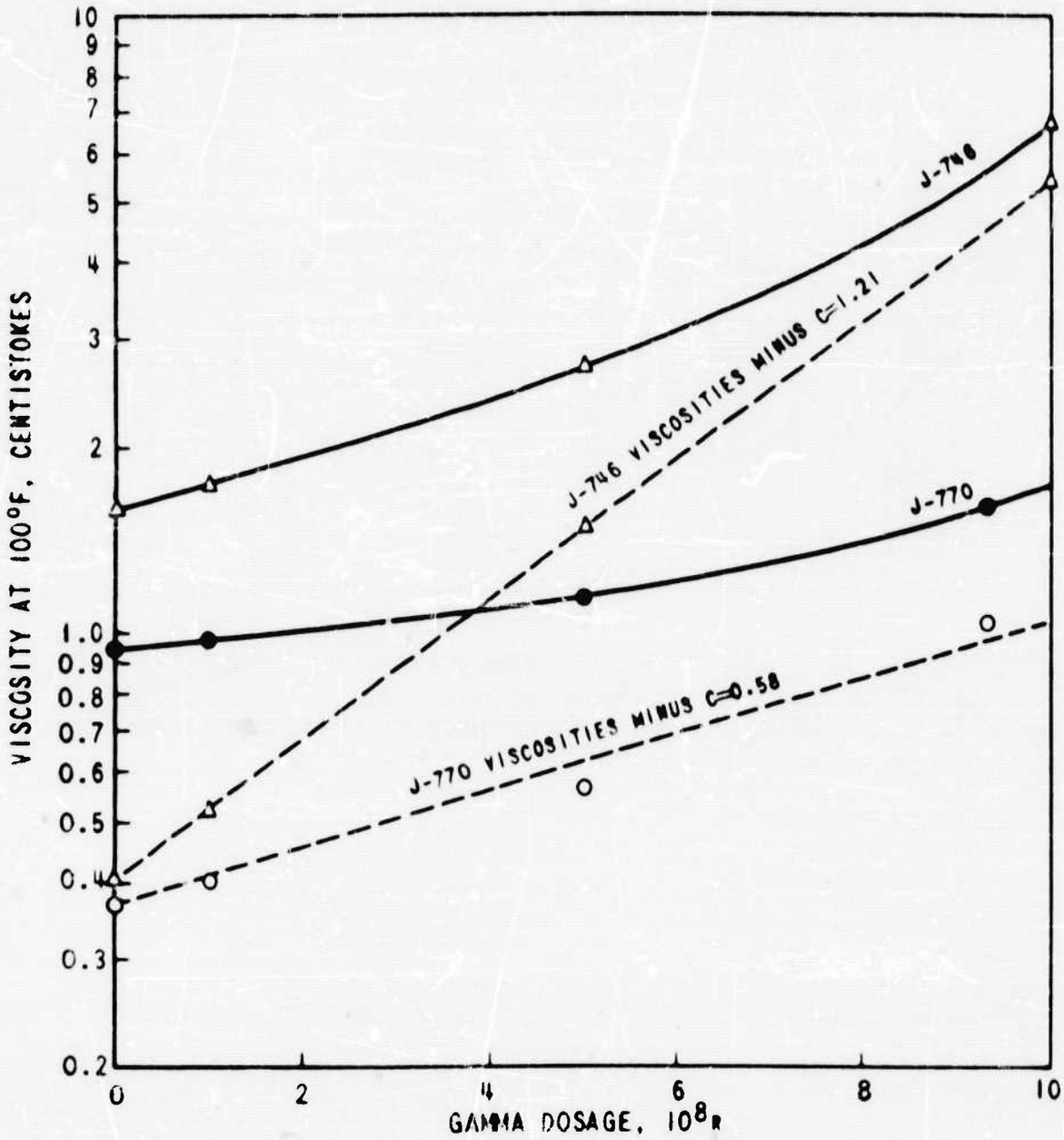

FIG. 54 - VISCOSITIES AT 100°F AS A FUNCTION OF RADIATION DOSAGE

ILLUSTRATING DEVELOPMENT OF EQUATION FOR RELATING VISCOSITY TO DOSAGE

Difficulties here may be seen from the data of Table XCIV, where the 22% aromatic JP-5 (J-771) had an index not materially different from those found for the two zero aromatic JP-5 fuels, J-728 and J-746.

Table XCIV

Values of "m" and "C"

Fuel No.	100°F		0°F	
	m	C	m	C
J-813	0.0622	0.51	0.118	1.43
J-852	0.0540	0.47	0.0915	1.31
J-782	0.0442	0.45	0.0750	1.26
J-872	0.0802	0.50	0.147	1.37
J-770	0.0465	0.58	0.0923	1.58
J-728	0.0900	1.21	0.112	3.15
J-771	0.102	1.51	0.109	3.85
J-746	0.113	1.21	0.112	3.15

The data of Table XCV show good agreement between viscosities actually measured and those which were calculated from the values for "m" and "C" in Table XCIV. Correlation is shown graphically in Figure 55 for JP-4 fuels and in Figure 56 for JP-5 fuels.

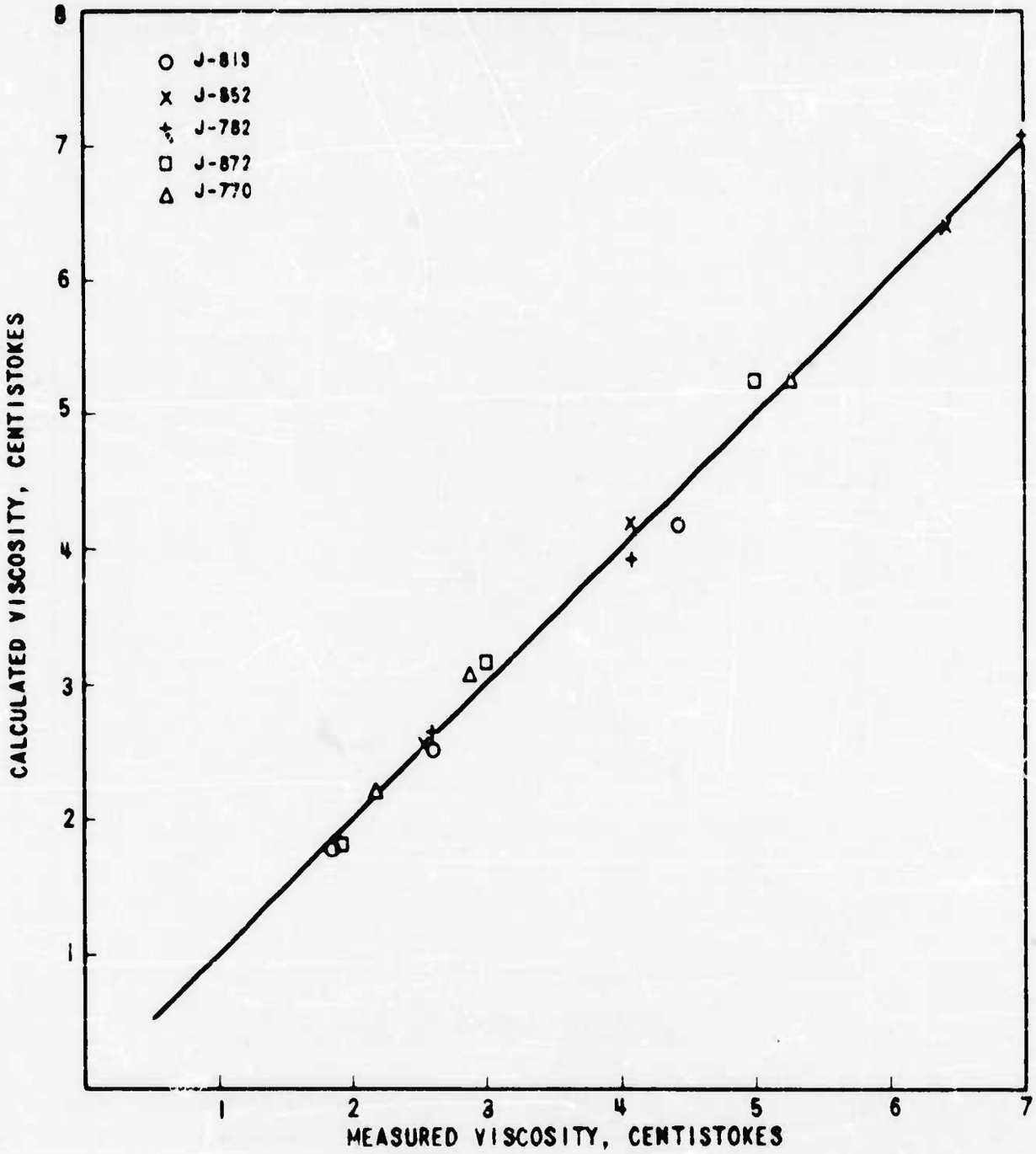

FIG. 55 - CORRELATION OF MEASURED AND CALCULATED VISCOSITY AT 0°F, JP-4 FUELS

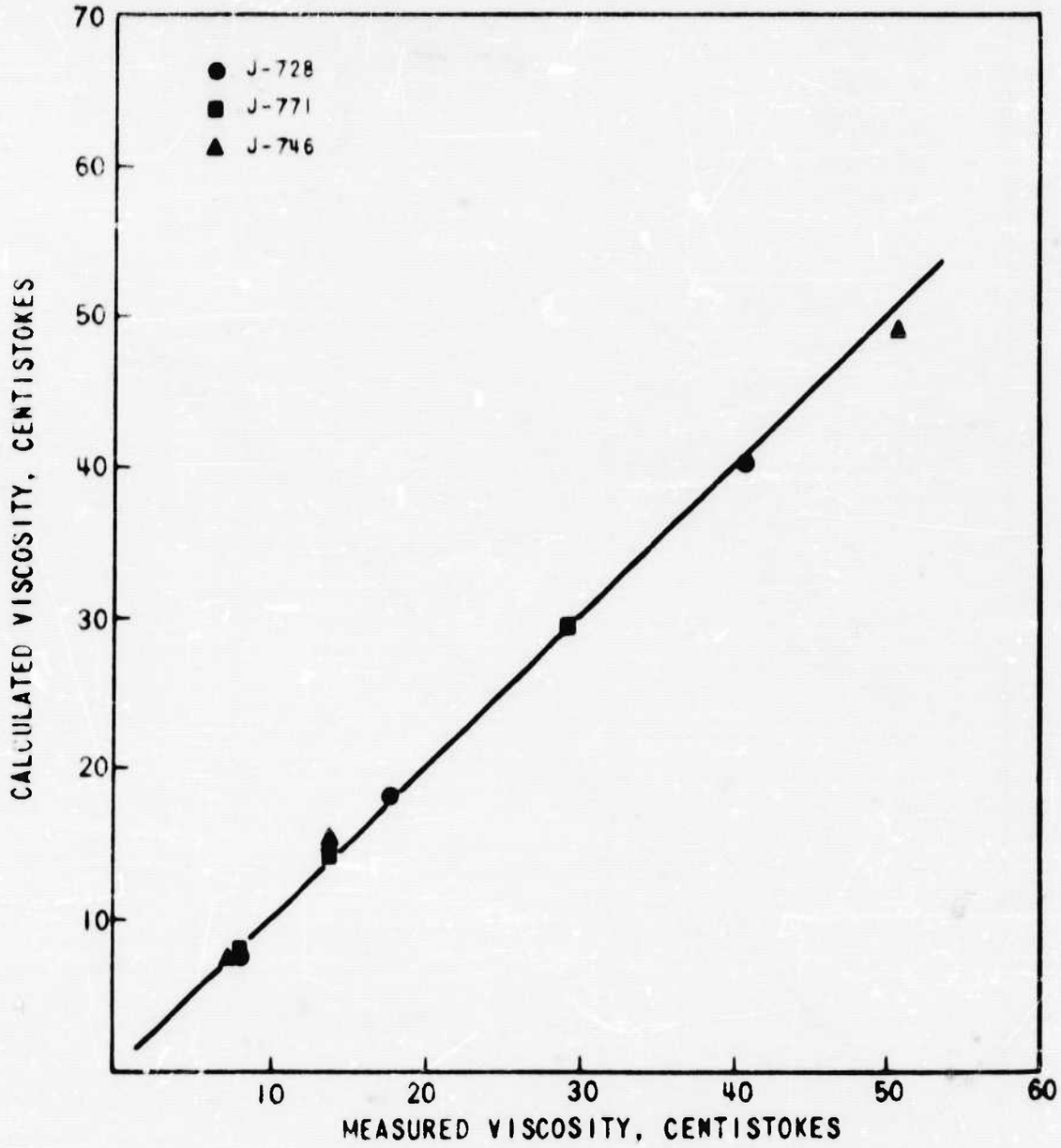

FIG. 58 - CORRELATION OF MEASURED AND CALCULATED VISCOSITY AT 0°F, JP-5 FUELS

TABLE XCV

COMPARISON OF MEASURED AND CALCULATED VISCOSITIES

Fuel	Gamma Dosage, 10^8 r	Viscosity at 100°F, cs		Viscosity at 0°F, cs	
		Measured	Calculated	Measured	Calculated
J-813	0	0.78	-	1.70	-
	1.0	0.84	0.962	1.86	1.79
	5.1	1.04	1.08	2.58	2.51
	8.5	1.51	1.44	4.44	4.20
J-852	0	0.96	-	2.31	-
	1.0	1.04	1.03	2.55	2.54
	5.0	1.38	1.38	4.06	4.18
	7.7	1.75	1.75	6.43	6.39
J-782	0	1.02	-	2.38	-
	1.06	1.06	1.09	2.60	2.61
	5.2	1.41	1.42	4.08	3.92
	9.52	2.00	1.95	7.02	7.07
J-872	0	0.78	-	1.67	-
	1.08	0.84	0.84	1.89	1.81
	5.32	1.16	1.26	3.00	3.18
	7.57	1.71	1.65	5.00	5.25
J-770	0	0.95	-	2.09	-
	1.0	0.98	1.01	2.17	2.22
	5.0	1.15	1.21	2.87	3.07
	9.3	1.64	1.58	5.26	5.25
J-728	0	1.86	-	6.94	-
	0.87	1.95	1.99	7.93	7.90
	5.29	3.28	3.15	17.7	18.2
	8.90	5.30	5.30	40.6	40.4
J-771	0	1.90	-	7.01	-
	0.9	1.97	2.00	7.99	7.82
	4.91	2.70	2.77	13.7	14.7
	8.31	4.26	4.29	29.4	29.5
J-746	0	1.62	-	6.60	-
	1.0	1.74	1.74	7.35	7.63
	5.0	2.74	2.70	13.7	15.7
	10.0	6.82	6.83	50.6	49.1