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NUCLEAR RADIATION RESISTANT LUBRICANTS

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MATERIALS LABORATORY

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FOREWORD

This report was prepared by the Organic Materials Branch, Materials Laboratory, Directorate of Research, Wright Air Development Center, with First Lieutenant William L. R. Rice acting as project engineer. It is a general summary of studies for nuclear radiation resistant lubricant development and research conducted by this Center. The work reported herein was initiated under Project Number 2133, "Radiation Effects," Task Number 73071, "Radiation Effects on Materials".

This report covers a period of work from January 1956 to May 1957.

All irradiations performed were under the supervision of Lt. William R. Daniels, Analysis and Measurements Branch, Materials Laboratory, Directorate of Research, Wright Air Development Center.

This report was presented at the First Semi-Annual 125A Radiation Effects Symposium sponsored by the United States Air Force, which was held in Fort Worth, Texas, on 22 and 23 May 1957.

ABSTRACT

This report presents a general summary of the state of the art of nuclear radiation resistant lubricant development. Data are presented on the effects of gamma radiation on currently available fluids and lubricants, showing the limitations of each. Development of advanced materials is discussed, with a general outline presented of the approach taken by the major support contractors.

It is estimated that on the basis of information to date, conventional ester type lubricants should prove operable to at least 1×10^7 roentgens of gamma radiation at temperatures from -65° to 350°F. Improved ester types, of the aromatic ester or complex ester variety, with proper additives, are expected to give suitable performance up to about 1×10^8 roentgens, operating in the temperature range -40° to 400°F or higher. Selected mineral oils, usable from about 0° to 400°F, may possibly be reliable to about 2 to 3×10^8 roentgens. The aromatic ethers, which are expected to be stable at temperatures well above 400°F (laboratory tests show thermal decomposition temperatures of 700° to 800°F), have not been evaluated for radiation resistance, but based on similar types of aromatic compounds they should be stable in the range 10^9 to 10^{10} roentgens. Much further work is required to verify this estimate.

A summary is presented of the future plans and major problem areas remaining in the fluid and lubricant development programs.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:

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I. INTRODUCTION

Successful development and utilization of nuclear powered aircraft depends, to a large extent, on the availability of materials of construction. The presence of nuclear radiation creates greater problems than in current non-nuclear systems, since materials must withstand both nuclear and thermal effects. A particularly critical type of material is one of organic composition, since the organics have radiation stability of comparatively low order. One must then question the use in a nuclear bomber of greases, hydraulic fluids, engine oils, gear oils, fuels, instrument oils, and any other lubricant or fluid of an organic nature. To determine the magnitude of the problem and find possible solutions, several steps must be taken. First, the limits of usability of current or conventional lubricants and fluids must be established. If they are not suitable for a particular application, one must either try to improve them or develop substitute materials of greater radiation resistance. As a last resort, if no other alternative is available, the problem component and its susceptible lubricant must be shielded or relocated to reduce the radiation to tolerance levels. This could result in a weight penalty, reduced system reliability, or both.

Rather than wait for final system design criteria, the Materials Laboratory of the Wright Air Development Center has been conducting extensive research on the development of nuclear radiation resistant fluids and lubricants. This program, which has been in effect for well over a year, is designed to provide organic materials of optimum stability to the combined effects of nuclear radiation, thermal breakdown, and oxidative degeneration. The research efforts have not been bound by specification requirements but have instead been aimed toward target properties. Such an approach does not limit the contractor to those materials meeting certain requirements, but allows him to find what fluids have the greatest number of desirable properties. In this manner he can follow a systematic approach to the final goal without being hampered by the necessity of meeting rigid end item specifications.

The target properties that have been established for the various development contracts are generally based on the most recent non-nuclear high temperature specifications, with the temperatures extended 50°F to 100°F or higher. Radiation levels that must be met are set in the range from 10^8 roentgens to 10^9 roentgens, the area

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in which all conventional lubricants show major property changes. All irradiations have been conducted in gamma sources thus far due to the lack of well calibrated reactor facilities capable of handling large volumes of test fluids and lubricants under the desired environmental conditions.

In essence, we are seeking at present materials that represent a major breakthrough in the state of the art of high temperature lubricants. These materials must also possess the quality of resistance to relatively high levels of nuclear radiation.

This report is intended to give a brief survey of the changes occurring in irradiated fluids and lubricants, the probable limitations on available materials, and the approach now being followed to develop advanced products.

II. RADIATION RESISTANT GREASES

Work on the development of radiation resistant greases has been conducted by the California Research Corporation since the early 1950's. This effort was initiated under the auspices of the Atomic Energy Commission (2, 3) and is now being sponsored by the Materials Laboratory of the Wright Air Development Center (7). A survey was recently completed by the Wright Air Development Center of the gamma radiation stability of a wide range of military specification greases (6). Additional unpublished work has been conducted by industrial research organizations.

The initial work by the California Research Corporation indicated extreme sensitivity of greases to the action of radiation. Conventional metallic soap-mineral oil greases showed excessive softening at gamma dosages of about 5×10^8 roentgens. Use of alkylaromatic fluids with selected thickeners gave improvement of the resistance to softening, but major change again took place in grease hardness at 5×10^9 roentgens (2). Further research led to the conclusion that the resistance of a grease to radiation depends strongly on the combination of thickener, base oil, and added inhibitors. It was found that compounding greases with special additives did not improve capabilities at high radiation levels, even though initial performance was increased. It was concluded that greases of improved stability to nuclear radiation can be formulated from alkylaromatic oils with selected gelling agents. Such greases could be expected to be comparable with present greases on the basis of non-nuclear performance and would probably still be useful at dosages above 1 x 10^9 roentgens (3). Testing of conventional greases showed that at dosages of 6 x 10^8 roentgens, bearing life can be reduced as much as 90%, bomb oxidation stability was impaired appreciably, low temperature torque showed a minor change, and evaporation showed only a slight increase. Copper corrosion did not appear to be markedly changed by dosages up to 3 x 10^9 roentgens. Wear properties appeared to show a slight improvement. Penetration increases with irradiation (indicating considerable softening) then decreases to eventual hardening of the grease to first a rubbery solid and finally a hard resin-like mass. Use of greases in neutron fields poses a special problem, due to neutron activation of high cross section elements. It was concluded that careful choice should be made of greases for such an application to minimize the hazards of radioactivity (3).

The grease development work of the California Research Corporation is now in effect under sponsorship of the Wright Air Development Center. Work during the first contract year verified earlier observations to the effect that conventional lubricating greases soften (to about 5 x 10^8 r.) and then harden (above from 5 to 10 x 10^8 r.) under gamma irradiation. It was also confirmed that properties such as bearing performance, corrosivity to copper, and bomb oxidation resistance suffer on irradiation. The initial softening on irradiation can be greatly reduced with the aid of an aromatic gelling agent, Sodium-n-octadecyl-terephthalamate, in place of conventional soaps. The hardening that takes place at higher dosages can be postponed by the use of an alkylaromatic oil, such as octadecyl biphenyl, in place of the usual mineral oils. The most promising type of grease for high temperature operation in the presence of nuclear radiation appears to be a C_{16}-C_{18} alkylbiphenyl gelled with a sodium terephthalamate and containing a selenide inhibitor (7). Future development efforts will be devoted to improving present experimental greases and conducting extensive evaluation of the more promising formulations.

A screening program was conducted by the Wright Air Development Center to determine the usability of currently available greases, both of specification and non-specification type. The greases were irradiated to gamma dosages of about 1 x 10^8 roentgens and subjected to specification type tests. The greatest changes took place in penetration, bomb oxidation, and bearing life, with relatively minor changes in properties such as oil separation, evaporation, gear wear, low temperature torque, dropping point, or copper corrosion (6). Table I gives a brief summary of test data of four of the greases studied. The Sinclair L-347 grease, a qualified MIL-L-3545 product, although showing a marked change in penetration, softening by 30 points on the worked penetration, gave excellent bearing performance at 250°F. The Master Lubricants Company grease M-3, a soap thickened mineral oil grease, showed little change in test properties and minor change in its 250°F bearing performance. The MLG 9307, an experimental MIL-G-3278 type grease, showed poor stability in the 350°F bearing test, while MLG 9305, an arylurea-silicone grease, showed no change in bearing life at 450°F after irradiation to 6.5×10^7 roentgens. Tables II and III give test data on the MLG 9305 and a copper phthalocyanine-DC 710 grease, illustrating changes taking place at comparatively low levels of gamma radiation. These two greases are being evaluated in the high temperature bearing test at 450°F for each dosage level to find the limits of usability of such types.

Summary

At comparatively low dosages of gamma radiation, from 10^7 to 10^8 roentgens, tests have indicated that conventional greases of the soap thickened mineral oil type should be satisfactory, within the temperature limitations of the grease. Greater trouble is expected with the higher temperature greases based on silicone fluids, since certain of these fluids solidify or gell at about 10^8 roentgens. The diester oil-soap thickened greases, such as those meeting Specification MIL-G-3278, could be expected to give trouble at about 10^8 roentgens, so careful selection of such a grease would be necessary.

When higher dosages are to be encountered, in the range 10^8 roentgens and higher, specialty greases of proven radiation resistance will be required. For such an application, it will be necessary to test the grease with and without nuclear radiation present, since the newer radiation resistant greases are not proven for lubricity or bearing performance capabilities under varying design conditions. Such greases are discussed in references (3) and (7).

For use at neutron exposures equivalent to the gamma dosages discussed above, the same limitations on grease types could be expected. The additional problem of neutron activation must be considered, since the more common greases with lithium or sodium soaps will become radioactive. So long as the induced radioactivity can be tolerated, greases appropriate for the specified bearing and temperature conditions can be used.

TABLE I - PROPERTIES OF SOME IRRADIATED GREASES

Grease	Dosage (R)	Dropping Point (°F)	Penetration		Bomb Oxid. Press. Drop (psi)	Bearing Life Hours at 10,000 RPM		
			Unworked	Worked		250°F	350°F	450°F
Sinclair L-347 (1)	0 10.2×10^7	394 408	272 268	339 369	< 4.0 4.0	692, 318 1014, 752		
Master Lub M-3	0 8.2×10^7	393 390	302 291	312 309	-11.0 1.0	1561, 520 1199, 419		
MLG 9307	0 8.6×10^7	500+ 500+	347 369	357 369	< 5.0 6.0		108 33, 66	
MLG 9305	0 6.5×10^7	500+ 500+	347 391	335 382	1.0 6.0			311, 387 429

(1) MIL-L-3545 Grease

TABLE II - EFFECT OF GAMMA RADIATION ON AN ARYLUREA-SILICONE GREASE (MLG 9305)

Dosage (Roentgens) MLG Number	0 9305	1 x 10^6 56-854	3 x 10^6 56-855	1 x 10^7 56-856	3 x 10^7 56-857	6.5 x 10^7 ——	1 x 10^8 56-858	3 x 10^8 56-859
Dropping Point (°F)	500+	500+	500+	500+	500+	500+	500+	Fluid
Penetration Unworked Worked	347 335	343 331	347 346	347 346	354 350	391 382	422 414	444 (1) 455 (1)
Bomb Oxidation Lb. Pressure Drop	1.0	3.0	0.0	2.0	2.0	6.0	20.0	7.0
Bomb Copper Corrosion Pressure Drop (psi) Appearance of Copper	0.0 Same	0.5 Same	0.0 Same	0.0 Same	0.0 Same	0.0 Same	15.0 Same	0.5 Same
Oil Separation (%) (30 hours at 212°F)	0.05	0.53	1.24	1.06	0.95	1.66	1.30	Fluid

(1) Soupy

TABLE III - EFFECT OF GAMMA RADIATION ON A COPPER PHTHALOCYANINE - DC 710 GREASE

Dosage (Roentgens) MLG Number	0 56-863	5 x 10^6 56-849	1 x 10^7 56-850	5 x 10^7 56-851	1 x 10^8 56-852	5 x 10^8 56-853
Dropping Point (°F)	500+	500+	500+	500+	500+	500+
Penetration Unworked Worked	 276 282	 287 290	 291 293	 295 297	 332 327	 Rubbery Rubbery
Bomb Oxidation, Lb. Pressure Drop	1.0	0.0	0.0	7.0	3.0	2.0
Bomb Copper Corrosion Pressure Drop (psi) Appearance of Copper	 0.5 1A	 0.5 1A	 0.0 1A	 0.0 1A	 0.5 1A	 0.5 1A
Oil Separation (%) (30 hours at 212°F)	0.40	0.31	0.63	0.45	0.57	0.00

III. RADIATION RESISTANT GEAR OILS

A minor portion of the California Research Corporation research effort on the current Air Force contract is devoted to development of a gear lubricant. The work to date has been limited to investigation of extreme pressure (EP) compounds, since the engine oil base fluid development under the contract is expected to produce the most suitable base fluid for the finished gear oil. In preliminary studies of EP additives blended in a polyglycol fluid and two aromatic fluids, it was found that the additives adversely affect radiation stability. In some cases, the blends showed lower radiation stability than the base oil alone. Viscosity increases ranged from about 30% to 300%. A sulfurized olefin appeared to have the least effect on the radiation stability. Preliminary studies have led to the conclusion that a probable candidate for a radiation resistant gear oil would be composed of a C_{16}-C_{18} alkylbiphenyl containing a selenide inhibitor and a sulfurized olefin EP agent. Future studies will be directed along this line (7).

Two qualified MIL-L-6086 petroleum base gear lubricating oils were drawn from Air Force stock and tested for resistance to gamma radiation. The light grade oil data are summarized in Table IV, the medium grade oil data are given in Table V. In the range of gamma dosages up to 1×10^9 roentgens, the light grade gear oil showed major changes in most of its properties. The viscosities at 100° and 210°F increased approximately 100% and the flash point dropped over 60 degrees. The autogenous ignition temperature was unchanged, actually showing a slight improvement. Evaporation appeared to show a minor improvement, with a smaller percentage loss occurring for the test on the oils exposed to the higher levels. Gas evolution showed the usual rise with dosage. The oxidation-corrosion test at 250°F, which is not a specification requirement, indicated that up to about 1×10^8 roentgens the metal corrosion did not worsen. Copper corrosion for the control was excessive, but it did not worsen appreciably. In fact it was smaller at the highest dosages. However, in light of the excessive copper corrosion at all levels and the increasingly severe magnesium and cadmium corrosion at the higher levels, it is obvious that even under the relatively light test conditions the oil does not possess resistance to oxidative deterioriation and attack on metals.

The medium grade gear oil, shown in Table V, was irradiated over a wider range of gamma dosages and tested under more severe conditions. The oil showed the same attack on copper as the lighter grade, the test in this instance being conducted at 400°F for 72

TABLE IV - EFFECT OF GAMMA RADIATION ON A SPECIFICATION MIL-L-6086A (GRADE L) PETROLEUM BASE GEAR LUBRICATING OIL

Dosage (Roentgens) (1)	0	1.1 x 10^7	1.0 x 10^7	3.0 x 10^7		1.0 x 10^8		3.0 x 10^8		1.0 x 10^9	
Viscosity (centistokes)											
210°F	2.92	4.37	4.37	4.38	4.44	4.51	4.43	4.88	4.87	6.48	6.57
100°F	24.9	24.0	24.2	24.3	24.5	25.2	24.7	28.5	28.0	42.5	42.9
Pour Point (°F)	-20	-25	-35	-20	-20	-25	-20	-20	-20	-20	-20
Flash Point (°F)	380	365	375	375	365	365	350	300	335	230	320
Autogenous Ignition (°F)	750	760	765	760	770	770	775	765	770	760	770
Evaporation, % (6½ hrs., 400°F)	33.1	31.9	33.5	29.0	30.0	26.5	24.6	29.5	26.5	15.6	27.1
Gas Evolution, ml/ml (STP)	0	0.20	0.18	0.64	0.71	2.28	1.82	7.95	7.49	18.4	18.2
Oxidation-Corrosion (2)											
Metal Wt. Loss (mg/cm^2)											
Aluminum	0.00	0.00	-0.10	-0.04	-0.04	-0.08	-0.16	0.20	-0.12	-0.26	-0.34
Steel	-0.02	-0.04	-0.02	-0.02	0.00	0.00	-0.06	0.06	-0.12	-0.26	-0.28
Cadmium	0.08	0.20	0.22	0.00	0.06	0.20	0.92	1.14	1.08	0.60	0.92
Copper	7.04	3.54	0.06	10.76	2.64	6.04	9.98	4.12	4.06	1.50	1.56
Magnesium	-0.14	-0.14	-0.14	0.28	-0.10	-0.12	-0.82	-2.20	2.28	-4.28	-1.58
Neutralization Number											
Before	0.00	0.00	0.00	0.47	0.47	0.47	0.95	0.95	0.95	0.00	0.00
After	0.95	0.47	0.47	0.47	0.71	0.71	0.47	0.47	0.47	0.47	0.47
Change	0.95	0.47	0.47	0.00	0.24	0.24	-0.48	-0.48	-0.48	0.47	0.47
Viscosity at 100°F (cs)											
Before	24.9	24.0	24.2	24.3	24.5	25.2	24.7	28.5	28.0	42.5	42.9
After	23.9	24.6	24.6	25.2	25.4	25.2	24.7	27.8	28.9	46.9	43.3
Increase (%)	-4.0	2.4	1.5	3.8	3.6	0.0	0.0	-2.5	3.2	10.3	0.9

(1) Irradiated in MTR Gamma Canal
(2) 168 hours at 250°F
Note: Oil was a qualified product from Air Force stock.

TABLE V - EFFECT OF GAMMA RADIATION ON A SPECIFICATION MIL-L-6086A (GRADE M) PETROLEUM BASE GEAR LUBRICATING OIL

Dosage (Roentgens) (1)	0	1.0 x 10^7	3.0 x 10^7	1.0 x 10^8	3.0 x 10^8	1.0 x 10^9	3.0 x 10^9
Viscosity (centistokes)							
400°F	1.78	1.66	1.74	(2)	1.97	2.48	(2)
210°F	8.98	8.50	8.74	9.23	10.30	15.68	72.0
100°F	77.04	71.26	74.52	81.69	93.97	176.6	1487
Pour Point (°F)	-25	-25	-25	-25	-25	-15	0
Flash Point (°F)	430	430	435	375	375	280	290
Fire Point (°F)	465	475	465	485	480	420	335
Autogenous Ignition (°F)	760	750	745	750	775	750	695
Evaporation, % (6½ hrs., 400°F)	9.49	9.59	10.22	9.17	9.69	10.81	11.25
Gas Evolution, ml/ml (STP)	0	0.5	0.5	2.2	5.4	18.4	32.2
Oxidation-Corrosion (3)							
Metal Wt. Loss (mg/cm^2)							
Aluminum	-0.016	0.016	0.033	-0.084	0.050	0.016	-0.016
Copper	7.361	8.334	8.876	6.572	7.487	7.809	2.371
Silver	-0.169	0.423	-0.287	-0.389	1.304	0.000	-0.076
Steel	0.033	0.118	0.237	0.186	0.525	0.762	0.186
Neutralization Number							
Before	0.19	0.19	0.25	0.28	0.16	0.39	0.08
After	2.80	2.30	4.53	0.50	0.70	0.56	0.50
Change	2.61	2.11	4.28	0.22	0.54	0.17	0.42
Viscosity at 210°F (cs)							
Before	8.98	8.50	8.74	9.23	10.30	15.68	Not
After	(4)	(4)	(4)	(4)	34.24	(4)	Run
Increase (%)					233		
Evaporation Loss (%)	0.82	0.93	0.75	0.70	0.49	0.50	0.78

(1) Irradiated in MTR Gamma Canal
(2) Oil volatility interfered with test
(3) Miniaturized, 72 hours at 400°F (as in MIL-H-8446)
(4) Sludge prevented determination
Note: Oil was a qualified product from Air Force stock.

hours. Silver corrosion was significant at 1 x 10^7 roentgens and all metals except aluminum showed attack at 1 x 10^8 and higher. Although the metals were actually less corroded at the highest dosage, 3 x 10^9, this does not constitute an improvement in oil qualities, since in any application this level would not be reached until the corrosion of the intermediate levels was experienced. Physical properties showed the usual change. Viscosity increased after a minor decrease at the lower levels, pour point increased at 1 x 10^9 roentgens, and flash point dropped drastically starting at about 1 x 10^8 roentgens. Fire point followed the change in flash point, while the autogenous ignition temperature fell by over 50 degrees between 3 x 10^8 and 3 x 10^9 roentgens. Evaporation was essentially unchanged. Gas evolution showed the usual increase with irradiation.

Summary

Information to date on radiation effects on gear lubricants is insufficient to justify conclusions as to usability under different conditions. Changes in lubricity following irradiation have yet to be determined. Extensive testing and evaluation is necessary before gear lubricant limitations will be fully known.

IV. RADIATION RESISTANT HYDRAULIC FLUIDS

Development of a nuclear radiation resistant hydraulic fluid is being conducted by the California Research Corporation under Air Force sponsorship. This development effort is a major portion of the overall contract and is divided into two general categories, evaluation of the limitations of presently available fluids and formulation of improved hydraulic fluid blends.

Studies are almost completed on the evaluation of silicate base hydraulic fluids, particularly MLO 8200 fluid, after exposure to gamma radiation. California Research Corporation has concluded that the maximum permissible gamma dosage for MLO 8200 fluid appears to be about 10^8 roentgens or slightly higher. At this level they feel that there is negligible viscosity change. Gas evolution, predominantly hydrogen, amounts to about 1 ml of gas per ml of fluid per 2 x 10^7 roentgens (7). In addition to laboratory testing of silicate fluids, pump testing of the 8200 fluid has been conducted before and after exposure to 7.85 x 10^8 roentgens. In brief, it was concluded that irradiation to this level triples the viscosity but that the fluid could still be used in hydraulic systems employing New York Air Brake pumps with some reduction in wear to be expected. It was felt that operation of pumps at temperatures much below 0°F would be impaired (7).

Laboratory testing of MLO 8200 and 8515 fluids has also been conducted at the Wright Air Development Center. Tables VI through IX give a summary of the test data for the control and irradiated fluids. Table VI gives the results of some preliminary irradiations in the WADC 8000 curie Co^{60} source, for which only gas evolution and viscosity were determined. Extensive testing was conducted on larger volumes of samples irradiated in the MTR gamma canal. These data are given in Tables VII and VIII for MLO 8200 fluid and in Table IX for 8515 fluid. As is usual for irradiated fluids, the 8200 fluid showed an initial minor decrease in viscosity with irradiation and then a very marked increase at the higher dosage levels. The flash and fire points were drastically reduced at the lowest dosage, 5×10^7 roentgens, and were even lower at the higher levels. Pour point and evaporation were not changed greatly. The neutralization number showed an increase with irradiation. Metal corrosion during the oxidation-corrosion test was particularly marked for copper but was also large for the steel. It is interesting to note that for some reason the two samples irradiated to a gamma dosage of 5×10^7 roentgens did not fall in line with the higher level irradiations. The reason for this is not at all apparent. This same inconsistency was noted for the hydrolytic stability tests, wherein the copper corrosion following the test was far higher for the lowest dosage than for the control or the higher levels of radiation. Further work will be necessary to establish why a nominally low dosage should cause such apparently radical loss in fluid stability.

The 8515 fluid, which is a blend of MLO 8200 with 15% di-2-ethylhexyl sebacate, gave similar property changes as the MLO 8200 fluid. It was again noted that the samples irradiated to 5×10^7 roentgens caused metal corrosion during the oxidation-corrosion test that exceeded the corrosion at higher dosages. In particular, steel showed a very large weight loss at the lower irradiation level as compared with the loss at the higher dosages. The unpleasant possibility exists that certain critical properties of fluids are more seriously affected at lower dosages and are improved by irradiation to such an extent that at higher levels it is not apparent that changes have taken place.

TABLE VI - COBALT-60 IRRADIATION OF MLO 8200 AND 8515 HYDRAULIC FLUIDS

Fluid	Dosage (Roentgens)*	Gas Evolution (ml/ml at STP)	Viscosity (cs) 100°F	210°F
MLO 8200	Control	0	34.0	12.08
MLO 8200	5.0×10^6	0.2	32.90	11.20
MLO 8200	1.0×10^7	0.4	32.83	11.17
MLO 8200	3.0×10^7	1.0	30.50	10.24
MLO 8200	1.0×10^8	Leak	32.41	10.17
8515	Control	0	23.80	8.20
8515	5.0×10^6	Leak	23.93	8.05
8515	1.0×10^7	0.4	23.90	7.99
8515	3.0×10^7	1.0	23.00	7.56
8515	1.0×10^8	Leak	24.66	7.51

* WADC 8000 Curie Co^{60} source

Note: MLO 8200 was from Batch 53406-R
8515 was from Batch 53685-R

TABLE VII - EFFECTS OF GAMMA RADIATION ON MLO 8200 HYDRAULIC FLUID - PHYSICAL PROPERTIES

Dosage (Roentgens) (1)	0	5.0×10^7		1.0×10^8		5.0×10^8		1.0×10^9
Viscosity (centistokes) 400°F 210°F 100°F	 3.80 12.08 34.0	 2.55 8.21 24.40	 1.63 5.04 15.32	 3.01 9.85 29.91	 3.01 9.81 29.83	 (2) 20.74 74.30	 (2) 14.47 50.41	 (2) 97.26 425.6
Pour Point (°F)	<-85	<-85	<-85	<-85	<-85	<-85	<-85	-75
Flash Point (°F)	405	250	245	235	280	170	170	120
Fire Point (°F)	460	400	420	450	435	220	230	190
Autogenous Ignition (°F)	775	755	745	750	760	760	750	810
Evaporation, % (6½ hrs., 400°F)	22.3	21.57	16.73	17.02	15.32	17.08	16.60	16.36
Neut. No. (mg KOH/gm oil)	0.01	0.42	1.17	0.03	0.02	0.19	0.11	0.26
Gas Evolution (ml/ml)	0	1.1	0.4	2.8	2.8	12.9	9.6	Leak

(1) Irradiated in MTR Gamma Canal
(2) Material is volatile at 400°F
Note: Sample MLO 56-1039-1 solidified at 1.2×10^9R (gas evolution was 27.2 ml/ml).
MLO 8200 fluid was from Batch 53406-R.

TABLE VIII - EFFECTS OF GAMMA RADIATION ON MLO 8200 HYDRAULIC FLUID - STABILITY TESTS

Dosage (Roentgens) (1)	0	5.0×10^7		1.0×10^8		5.0×10^8		1.0×10^9
Oxidation-Corrosion (2)								
Metal Wt. Loss (mg/cm^2)								
Aluminum	0.000	2.168	0.931	0.000	0.067	0.000	-0.033	-0.016
Copper	0.280	1.829	2.625	2.920	5.386	3.406	1.287	1.016
Silver	0.016	0.304	0.948	0.033	0.033	-0.016	0.033	0.000
Steel	0.012	0.674	2.761	0.033	0.101	0.321	-0.016	0.982
Neutralization Number								
Before	0.01	0.42	1.17	0.03	0.02	0.19	0.11	0.26
After	0.76	1.82	2.80	2.38	2.80	2.38	1.54	0.98
Change	+0.75	+1.40	+1.63	+2.35	+2.78	+2.19	+1.43	+0.72
Viscosity at 210°F (cs)								
Before	12.08	8.32	5.02	9.86	9.84	20.60	14.78	98.90
After	8.04	8.60	5.40	7.01	6.44	10.97	10.56	44.31
Increase, %	-33.4	3.4	7.6	-28.9	-34.6	-46.7	-28.6	-55.2
Evaporation Loss, %		17.20	14.85	8.33	8.36	10.73	10.15	14.84
Hydrolytic Stability (3)								
Copper Wt. Loss (mg/cm^2)	0.01	0.42	0.55	0.01	0.03	0.00	0.03	0.01
Viscosity at 210°F (cs)								
Before	12.08	8.32		9.86	9.84		14.78	
After	11.90	8.49	(4)	9.68	9.48	(4)	18.54	(4)
Increase, %	-1.5	2.0		-1.8	-3.7		25.4	
Neutralization Number								
Water Layer	0.01	0.75		0.21	0.15		0.17	
Oil Layer								
Before	0.01	0.42		0.03	0.02		0.11	
After	0.01	0.14		0.05	0.04		0.14	
Change	0.00	-0.28		0.02	0.02		0.03	
Insols. in Oil Layer, %		0.44		0.17	0.11		0.30	
Color (Union)		7.5		6	5.5		5	

(1) Irradiated in MTR Gamma Canal
(2) Miniaturized, 72 hours at 400°F, as in MIL-H-8446
(3) 48 hours at 200°F and 25% H_2O, as in MIL-H-8446
(4) Material formed gell, test could not be completed.
Note: MLO 8200 fluid was from Batch 53406-R.

TABLE IX - EFFECTS OF GAMMA RADIATION ON 8515 HYDRAULIC FLUID

Dosage (Roentgens) (1)	0	5.0 x 10^7		1.0 x 10^8		5.0 x 10^8		1.0 x 10^9	
Viscosity (centistokes)									
400°F	2.70	1.98	2.42	2.33	2.22	(2)	(2)	(2)	(2)
210°F	8.20	6.05	7.33	7.16	7.07	12.78	11.70	43.66	44.86
100°F	23.8	18.30	22.79	21.52	22.06	52.29	44.86	213.8	217.0
Pour Point (°F)	<-85	<-85	<-85	<-85	<-85	<-85	<-85	-80	-80
Flash Point (°F)	400	270	260	270	210	150	180	170	150
Fire Point (°F)	440	395	410	435	340	210	270	225	225
Autogenous Ignition (°F)	795	735	740	765	750	760	785	805	800
Evaporation, % (6½ hrs., 400°F)	28.0	24.63	16.71	17.53	17.58	22.23	21.36	22.73	22.79
Neut. No. (mg KOH/gm oil)	0.00	1.12	0.56	0.61	0.78	1.93	1.82	1.23	1.12
Gas Evolution (ml/ml)	0	1.1	1.1	1.8	2.0	9.5	7.8	Leak	Leak
Oxidation-Corrosion (3)									
Metal Wt. Loss (mg/cm^2)									
Aluminum	0.030	2.676	0.033	0.000	0.016	-0.016	0.033	0.016	-0.016
Copper	0.190	2.524	1.253	1.524	2.134	0.813	0.355	0.152	0.525
Silver	0.060	0.084	-0.016	0.016	0.033	-0.016	0.033	0.000	0.016
Steel	0.050	15.279	0.271	0.016	0.050	2.134	1.067	1.490	0.542
Neutralization Number									
Before	0.00	1.12	0.56	0.61	0.78	1.93	1.82	1.23	1.12
After	0.35	2.46	2.07	3.08	2.80	2.24	1.96	1.45	1.23
Change	0.35	1.34	1.51	2.47	2.02	0.31	0.14	0.22	0.11
Viscosity at 210°F (cs)									
Before	8.20	6.05	7.33	7.16	7.07	12.78	11.70	43.66	44.86
After	5.48	4.23	3.69	4.72	4.20	7.64	10.60	23.28	19.14
Decrease (%)	33.2	30.0	49.6	34.1	40.5	40.2	9.4	46.7	57.3
Evaporation Loss (%)		9.80	8.04	10.45	8.67	11.00	15.31	13.87	13.85

(1) Irradiated in MTR Gamma Canal
(2) Volatile, viscosity could not be determined
(3) Miniaturized, 72 hours at 400°F (as in MIL-H-8446)
Note: 8515 fluid was from Batch 53685-R.

Development of improved fluids is the second phase of the hydraulic fluid portion of the California Research Corporation contract effort. They have concluded that the alkyl aromatics and alkyl diphenyl ethers offer the best possibility of providing base materials having stability to thermal breakdown and nuclear radiation degradation. The physical properties of such fluids do not compare with those of the silicate fluids, but changes after irradiation do not appear to be as large. A type of hydraulic fluid formulation appearing most promising based on contract work to date is composed of a C_{14}-C_{16} diphenyl ether containing a polybutene thickener, a selenide inhibitor, and a silicone defoamer (7).

Summary

Test data obtained for conventional petroleum base hydraulic fluids of the MIL-0-5606 "red oil" variety indicate radiation induced changes in viscosity (over a 50% decrease in the 130° and -40°F values) and an increase in metals corrosion during the oxidation-corrosion testing. This type of fluid is not satisfactory for hydraulic applications at even a relatively low gamma dosage.

Experimental silicate hydraulic fluids of the MLO 8200 type appear to have promise of use at gamma dosages up to 1×10^8 roentgens. Further testing will be necessary to verify this assumption. Actual rig testing will be particularly necessary for such hydraulic fluids, since properties such as gassing with irradiation have not been correlated to date with possible changes in system performance. Figure 1 shows MLO 8200 gassing in comparison with that of other irradiated organic fluids.

Polymer thickened alkyl diphenyl ethers are being considered as advanced hydraulic fluids, for combined qualities of radiation resistance and thermal stability. The capabilities of such blends are now being determined.

Work is in progress on the use of liquid metals as power transmission fluids (11).

V. RADIATION RESISTANT ENGINE OILS

The greatest emphasis in radiation resistant lubricant development has been placed in studies pertaining to engine oil development. This is quite reasonable in light of the fact that the engine oils

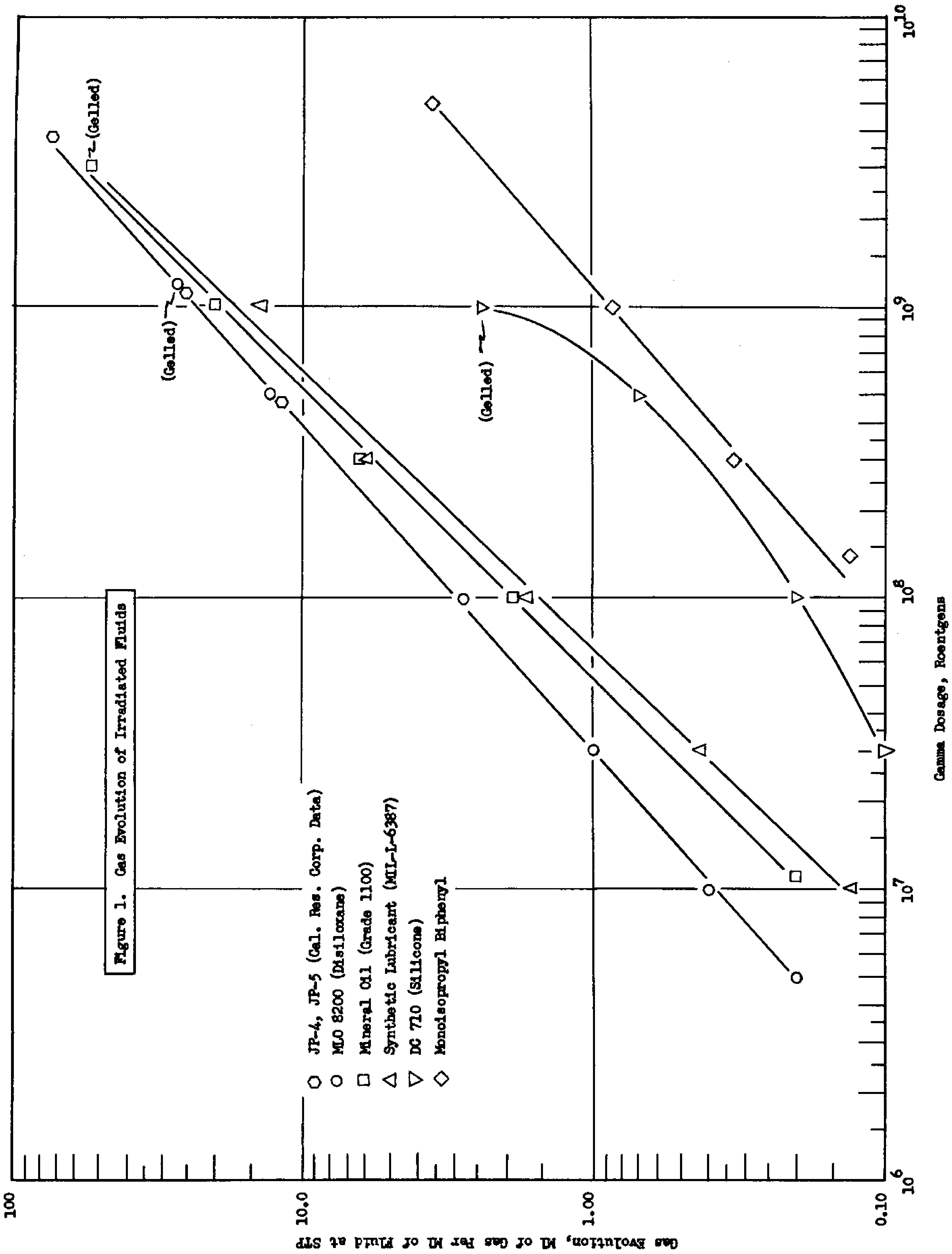


Figure 1. Gas Evolution of Irradiated Fluids

encounter the most exacting environmental conditions. For a nuclear engine, the oils must withstand the combined effects of nuclear radiation, thermal degradation, and oxidative deterioration. This requires an oil which must not only withstand radiation but must actually be superior, under non-nuclear conditions, to the best oils available today. Consequently, there are now in existence three contracts devoted wholly or in part to engine oil development. Part of the California Research Corporation effort is devoted to an engine oil study and the entirety of the contracts with the Shell Development Company and Esso Research and Engineering Company are for engine oil development.

Before discussing the contract efforts, some information will be presented showing why presently available materials do not appear overly attractive for nuclear applications. Table X shows the effects of gamma radiation on a Specification MIL-L-6387 synthetic base lubricating oil. Such an oil has additives to impart oxidation stability, improve viscosity-temperature characteristics, and improve anti-wear properties. It is intended for use in constant speed alternator drives, aircraft air compressors, expansion turbines, and similar equipment. As can be seen from the test data, a comparatively low dosage of 1×10^7 roentgens caused considerable change in physical and chemical properties. The viscosities showed a decrease, flash point was approximately 30°F lower, and rubber swell increased. The oxidation-corrosion test at 347°F for 72 hours showed a catastrophic change in metal corrosion. Aluminum was the only metal not affected during the test. All of the other metals showed very large losses in weight as a result of the test conditions. The hydrolytic stability test also indicated extreme changes, with the copper corrosion increasing prohibitively, the viscosity increase in the test oil being of a very large order, and the neutralization number of the oil increasing greatly. The overall quality of the oil after the low dosage of gamma radiation is such as to make it totally unacceptable. Exposures to the higher levels serve to verify this conclusion. It is most interesting to note however that at 1×10^9 roentgens, the corrosion on metals for the oxidation-corrosion and hydrolytic stability tests is lowest for any of the exposures. Although one would condemn the oil at this radiation exposure on the basis of the major changes in flash point, neutralization number, and viscosity, had it only been tested at the highest exposure it would not have been evident that metal corrosion is a major problem. This is again in line with previous comments on the silicate hydraulic fluids, where the lowest dosage caused the oil to be the most corrosive to metals.

TABLE X - EFFECT OF GAMMA RADIATION ON A SPECIFICATION MIL-L-6387 LUBRICATING OIL

Dosage (Roentgens) (1)	0	1.0×10^7		3.0×10^7		1.0×10^8		3.0×10^8		1.0×10^9	
Viscosity (centistokes)											
210°F	5.30	3.90	3.90	3.60	3.60	3.30	3.20	3.26	3.43	3.68	5.97
130°F	11.8	8.9	8.9	8.2	8.2	7.5	7.5	7.8	8.3	10.0	16.6
-40°F	1271	1167	1141	1124	1096	1106	1075	1466	1707	5242	7445
-65°F	8081	6911	6442	6396	6260	6547	6912	9557	11350	44540	62820
Pour Point (°F)	Below -80	Below -80	Below -80	Below -80	Below -80	Below -80	Below -80	Below -80	Below -80	-70	-70
Flash Point (°F)	390	365	352	325	310	285	250	210	150	160	115
Fire Point (°F)	410	385	405	383	385	340	355	290	270	210	145
Rubber Swell, "H" Stock (%)	47.9	58.4	57.7	58.5	60.5	57.4	57.1	56.1	53.9	49.1	50.0
Color, ASTM	3	3	3	3½	3	4½	4½	5	5	5	5½
Gas Evolution, ml/ml fluid (STP)	0	0.12	0.14	0.44	1.06	1.97	1.72	4.43	6.17	14.1	13.2
Oxidation-Corrosion (2)											
Metal Wt. Loss (mg/cm²)											
Aluminum	-0.02	0.00	0.02	-0.01	0.00	0.05	Sample turned solid	0.05	0.00	-0.03	-0.04
Steel	-0.02	4.31	2.14	16.35	11.35	3.64		13.38	0.97	0.01	-0.02
Copper	0.10	15.15	1.26	13.87	5.87	2.76		4.58	1.82	1.69	1.76
Magnesium	-0.02	17.25	16.11	41.42	43.18	18.98		52.96	17.86	1.48	0.03
Neutralization Number											
Before	0.0	3.31	3.31	5.20	5.20	8.99	8.04	13.71	13.24	18.92	18.92
After	0.5	6.61	3.31	Solid	Solid	3.19	Solid	35.71	20.44	26.02	31.12
Change	0.5	3.30	0.0	—	—	-5.80	—	22.0	7.20	7.10	12.20
Viscosity at 130°F (cs)											
Before	11.8	8.9	8.9			7.5	Solid	7.8	8.3	10.0	16.6
After	10.6	37.8	67.3	Semi-solid	Semi-solid	8.0		46.5	14.2	25.1	31.1
Increase (%)	-10.1	324	655			6.7		497	71.1	151	87.4
Hydrolytic Stability											
Copper Wt. Loss (mg/cm²)	0.36	3.70	4.40	3.50	4.20	2.20	0.70	0.40	0.30	0.12	0.10
130°F Viscosity Change (%)	-13.5	6.7	4.5	4.8	3.6	4.0	1.3	1.3	1.3	28.0	-9.2
Neutralization Number											
Water Layer		0.12	8.8	11.1	15.0	23.9	23.4	26.4	19.4	19.5	18.2
Oil Layer (Change)	4.1	27.8	50.3	Over 45.8	Over 45.8	Over 42.0	52.5	51.6	42.6	30.3	27.9
Insols. in Oil Layer (%)	0.043	0.059	0.101	0.308	0.926	0.896	0.000	0.030	0.020	0.002	0.010

(1) Irradiated in MTR Gamma Canal
(2) 72 hours at 347°F
Note: Oil was a qualified product

Table XI gives further test data on radiation effects on a synthetic lubricant, the lubricant in this case being one that meets the general requirements of Specification MIL-L-7808. This specification covers synthetic (diester) type lubricants for use in turboprop engines and in some models of turbojet engines. The test fluid was a blend of 0.5% phenothiazine with di-2-ethylhexyl sebacate (Plexol 201). At 1 x 10^8 roentgens the evaporation increased somewhat, the viscosity increased only slightly, and the flash point was essentially the same. The coking tendencies of the fluid worsened considerably at this level, as did the rubber swell. The corrosion on metals in the oxidation-corrosion test was worse only for the attack on magnesium. It would appear safe to conclude that below 1 x 10^8 roentgens the oil would show promise of usability.

The MIL-L-6387 and MIL-L-7808 type synthetics both display breakdown as a result of exposure to gamma radiation, the MIL-L-6387 type fluid appearing to be more sensitive to the radiation degradation. The MIL-L-6387 specification requires that from one-half to one per cent of tricresyl phosphate be added as an anti-wear agent. The developmental work of the Esso Research and Engineering Company has shown that in general, a limited amount of tricresyl phosphate in synthetic oils appears to be beneficial in inhibiting copper corrosion, but that it tends to increase acidity and to decrease flash points (9). That tricresyl phosphate might be a contributing cause of the greater difficulties experienced with the synthetics is further borne out by previous studies on MIL-L-7808 type fluids containing TCP as an additive. Breakdown by gamma radiation followed the usual patterns, with large drops in flash point, increases in neutralization number, and radical increase in panel coke values. This indicates that careful choice of additives in a system to be irradiated is necessary.

Information on gamma radiation stability of uninhibited diester fluids is to be found in reference (10). It is interesting to note that di-2-ethylhexyl sebacate irradiated to 3 x 10^8 roentgens showed a large increase in neutralization number and a drop in flash point from 410°F to 275°F, yet the panel coke value at 600°F was unchanged. The same base fluid inhibited with 0.5% phenothiazine (see Table XI) did not experience a drop in flash point at the same dosage level and had a relatively minor increase in neutralization number, yet the panel coke value showed a very large increase. This shows that a gain in properties by addition of inhibitor can be accompanied by just as great a loss in other properties, again emphasizing the need for complete testing of all fluid properties before conclusions are drawn.

TABLE XI - EFFECT OF GAMMA RADIATION ON A MIL-L-7808 TYPE LUBRICANT

Dosage (Roentgens)	0	3 x 10^7	1 x 10^8	3 x 10^8
Viscosity (centistokes)				
210°F	3.27	3.43	3.60	4.30
100°F	12.69	13.08	13.98	17.68
-65°F	10,118	9,762	13,931	17,978
Flash Point (°F)	460	460	455	460
Evaporation, % (6½ hrs., 400°F)	7.7	10.8	11.2	15.0
Coking at 600°F (mg) (1)	5	13	74	91
Neutralization Number (mg KOH/gm oil)	0.06	0.12	0.24	0.74
Rubber Swell, "H" Stock (%)	16.7	17.5	20.4	29.2
Gear Test (lb./inch)	2180	2210	2090	2250
Foaming (2)	Pass	Pass	Pass	Pass
Corrosion at 450°F (mg/in²)				
Silver	-0.18	-0.23	-0.22	-0.46
Copper	-0.80	-0.83	-0.98	-3.08
Oxidation-Corrosion at 347°F				
Wt. Change (mg/cm²)				
Copper	-0.02	0.02	-0.04	0.07
Silver	-0.02	0.01	0.00	0.04
Steel	0.00	0.05	-0.04	-0.11
Aluminum	0.00	0.04	0.00	0.07
Magnesium	-0.16	-0.01	-5.26	-10.21
100°F Viscosity Change (%)	2.60	1.26	13.23	22.06
Neutralization Number Change	0.23	1.86	3.58	3.77

(1) False bottom, 4 hour test.
(2) MIL-L-7808 control.
Note: Test oil was di(2-ethylhexyl)sebacate (Plexol 201) plus 0.5% phenothiazine.

Inasmuch as a great deal of experience has been obtained in use of refined petroleum oils in aircraft, it was of interest to observe the effects of gamma radiation on such materials. Table XII contains information on the radiation stability of a Specification MIL-L-6082 petroleum oil, grade 1100. Up to the radiation dosage of 3×10^8 roentgens the oil appears to have very favorable radiation resistance. Apart from a 45 degree drop in flash point and a moderate thickening, it does not seem to have changed seriously in any respect. Data on a similar product also indicate that at 1×10^8 roentgens the panel coke value was lower than for the control (10). The oxidation-corrosion data (400°F, 72 hours) are of considerable interest. The control fluid showed attack primarily on the copper, with the other metals relatively unaffected. Irradiation did not appreciably change corrosivity of the fluid until somewhere above 1×10^8 roentgens. As far as property changes are concerned, if such a fluid as this is usable before irradiation, it would probably still be effective in a similar application at least to 1×10^8 roentgens. The same conclusion can be made for the lighter grade (1065) oil that is used under this specification (10).

Contract efforts on nuclear radiation resistant engine oils have been most rewarding, amassing a valuable fund of information on available fluids and indicating the most promising avenues of approach toward obtaining superior products.

The first year of research by the Esso Research and Engineering Company has been devoted to an exhaustive study of diester fluids and mineral oils (9). It has been concluded on the basis of the work to date that virtually all synthetic and mineral based oils are reasonably stable at gamma dosages up to 1×10^7 roentgens. Exposure at 1×10^8 roentgens, however, produces appreciable lubricant degradation. While almost all properties change, the greatest changes are noted in acidity, corrosivity toward metals (especially lead, copper, and magnesium), panel coking tendencies, and flash point, all such changes being in the unfavorable direction. Mineral oils, such as inhibited Esso Aviation Oil 65, had the best resistance to irradiation to 1×10^8 roentgens. Addition of phenyl-alpha-naphthylamine gave good oxidation and corrosion resistance, the deficiency noted in the above discussions of the uninhibited MIL-L-6082 petroleum oils. Foaming tendencies of the mineral oils increase markedly after irradiation to 1×10^8 roentgens, whereas the synthetic oils retained their initially low foaming properties after irradiation. The general conclusion was that ester type synthetic lubricants are generally less stable to irradiation than the mineral oils and that there are no marked differences in gamma

TABLE XII - EFFECT OF GAMMA RADIATION ON A SPECIFICATION MIL-L-6082 (GRADE 1100) REFINED PETROLEUM OIL

Dosage (Roentgens) (1)	0	1.1×10^7	3.1×10^7	1.0×10^8	3.0×10^8	1.0×10^9
Viscosity (centistokes)						
400°F	2.98	2.96	(3)	3.17	3.60	5.95
210°F	20.26	19.46	20.25	22.22	26.80	58.73
100°F	256.8	236.3	252.9	289.6	373.7	1044
Pour Point (°F)	0	-5	-5	-5	-5	0
Flash Point (°F)	525	495	500	495	480	325
Fire Point (°F)	545	570	565	560	540	525
Autogenous Ignition (°F)	715	720	695	745	750	740
Evaporation (%) (2)	2.30	3.83	3.77	2.84	3.60	5.08
Gas Evolution (ml/ml)	0	0.2	0.0	1.9	6.5	20.0
Oxidation-Corrosion (3)						
Metal Wt. Loss (mg/cm^2)						
Aluminum	0.016	0.016	-0.076	0.033	0.084	0.016
Copper	0.287	0.084	0.237	0.321	0.847	0.711
Silver	0.101	0.050	-0.016	-0.084	0.101	0.067
Steel	0.033	0.169	0.186	0.254	0.220	0.304
Neutralization Number						
Before	0.05	0.01	0.01	0.02	0.04	0.02
After	0.56	0.28	0.22	0.56	0.22	0.20
Change	0.51	0.27	0.21	0.54	0.18	0.18
Viscosity at 210°F (cs)						
Before	20.26	19.46	20.25	22.22	26.80	58.73
After	31.05	(4)	(4)	39.34	(4)	(4)
Increase (%)	53.3			77.1		
Evaporation Loss (%)	0.50	0.52	0.51	1.16	0.52	0.48

(1) Irradiated in MTR Gamma Canal (2) 6½ hours at 400°F (3) 72 hours at 400°F (as in MIL-H-8446)

(4) Determination could not be made.

Note: Oil was a qualified product from Air Force stock.
Sample at 3×10^9R was solid, its gas evolution being 53.4 ml/ml.

radiation resistance among oils based on simple esters, polyesters, or complex esters. The materials showing promise at 1 x 10^8 roentgens were a paraffinic base stock (Barosa 56) with phenyl-alpha-naphthylamine and an antifoamant; ditridecyl carbonate; ditridecyl terephthalate; and a tridecyl terephthalate complex ester. Future studies will be devoted to extensive investigation of the most promising base stocks at higher radiation levels and formulation of an improved radiation resistant engine oil based on the best product obtained.

The California Research Corporation has placed major emphasis on alkyl aromatic compounds of the alkylated biphenyl and alkylated aromatic ether types to obtain a nuclear radiation resistant engine oil (7). Selenide additives are being extensively evaluated for their ability to impart radiative and oxidative stability. The alkyl chains added to the basic molecules have thus far been fairly long (C_8 or longer), requiring the use of additives for oxidative stability. Favored lubricants for engine oil use are the C_{16}-C_{18} alkylbiphenyl or the C_{14} diphenyl ether, with selenide or phenolic-type inhibitor added.

The initial effort of the Shell Development Company on its engine oil development program was devoted to a study of the effects of selected additives in various aliphatic and ester fluids (8). Studies were made of the oxidative stability of such blends, since this was felt to be one of the more critical fluid properties. On the basis of Dornte oxidation tests, both during and after exposures to gamma radiation, Shell has concluded that the limitation on conventional diester jet engine lubricants is about 1 x 10^7 roentgens. Up to this level they do not suffer excessive loss in oxidative stability, but for higher levels they have no resistance to the effects of oxygen, degrading readily. The safe working level of 1 x 10^7 roentgens is in agreement with the conclusions reached by the Esso Research and Engineering Company in its work on diesters and mineral oils. Shell feels further that diesters will probably be marginal in the range 1 x 10^7 to 1 x 10^8 roentgens. No inhibitor has been found to date that will impart oxidative stability at temperatures in excess of about 400°F or above gamma radiation exposures of 1 x 10^7 roentgens. As a consequence of these observations, Shell is now working extensively on the development of a basic molecule that does not require additives to impart radiation or oxidation stability. Since substitution affects thermal and oxidative stability, Shell is restricting its studies to aromatic ethers with very short alkyl chains to impart lubricity improvement and increase liquid range. The alkyl substituents being considered have the alpha hydrogens blocked to minimize oxidative attack. This program is extremely promising and has already produced compounds of excellent thermal and oxidative stability.

Table XIII gives a brief comparison of the overall approaches taken by the three engine oil development programs and typical materials under study.

Summary

At the present time, it appears that present limitations on conventional diester type lubricants exclude their use at dosages much above 1 x 10^7 roentgens or at temperatures outside the range -65° to 350°F. Improved ester types, such as are under study by the Esso Research and Engineering Company, might possibly be usable at gamma dosages up to about 1 x 10^8 roentgens, with temperatures limited to the range -40° to 400°F. Selected mineral oils appear to have potential use slightly above 1 x 10^8 roentgens, with temperatures probably limited to from 0° to 400°F. The advanced aromatic compounds of the alkylated biphenyl or alkylated aromatic ether type could be expected, on the basis of previous irradiations of similar compounds, to be stable at dosages in the neighborhood of 1 x 10^9 roentgens. Thermal stabilities of such compounds are above 400°F. It should be carefully noted, however, that the materials of most promise, such as the aromatics, have had the least amount of engineering and rig evaluation and further work is necessary to fully establish their capabilities.

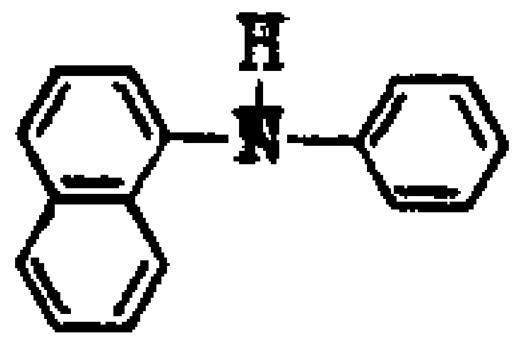
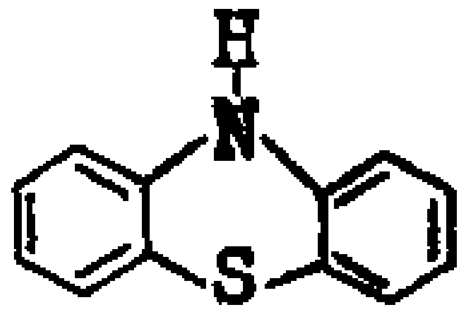
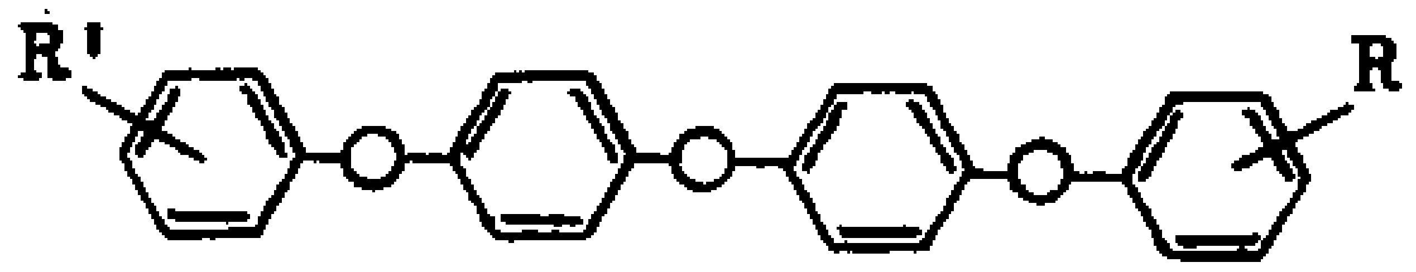
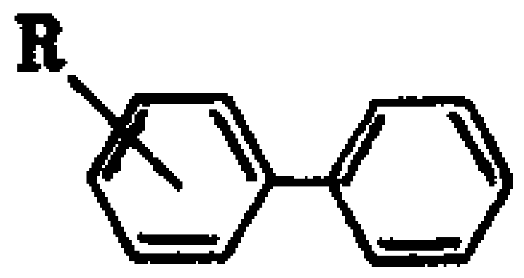
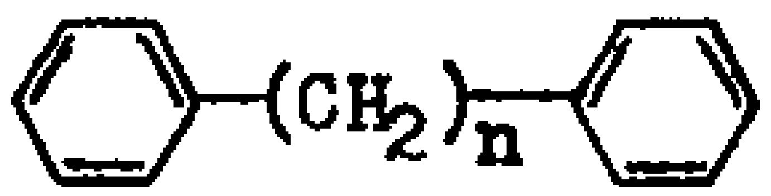
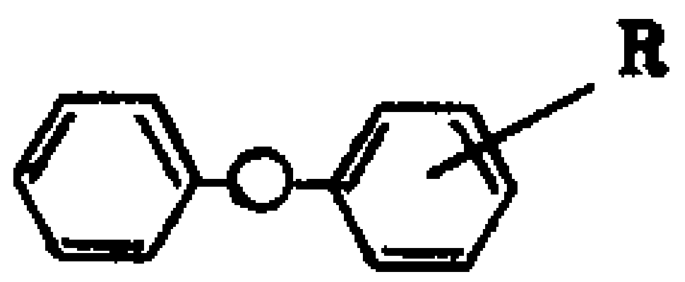
It appears that fluorocarbon elastomers such as Viton A will be the most attractive for use in conjunction with the advanced type aromatic fluids. Preliminary information has shown that this type of elastomer has the best resistance to thermal and radiative degradation and has good resistant to the solvent action of such fluids.

VI. EFFECTS OF RADIATION ON JET FUELS

Two fundamental approaches are being taken to determine the effects of nuclear radiation on jet engine fuels. Under the radiation effects studies conducted by the California Research Corporation, a portion of the work is being devoted to determining the effects of radiation on representative jet fuels. Special hydrocarbons or

TABLE XIII

NUCLEAR RADIATION RESISTANT FLUID AND LUBRICANT DEVELOPMENT PROGRAM

Contractor	Basic Fluid Type	Additive Type
Esso Research and Engineering Company (Engine Oil)	Mineral Oils Esters Aliphatic Aromatic Complex	PANA  Phenothiazine  Tricresyl Phosphate
Shell Development Company (Engine Oil)	Aromatic Ethers with Short Alkyl Group Substitution, i.e., 	None
California Research Corporation (Hydraulic Fluid, Engine Oil, Gear Oil)	Alkyl Aromatics with Long Chain Alkyl Substitution, i.e.,   Aromatic Ethers with Long Chain Alkyl Substitution, i.e., 	Generally Selenide Type Inhibitors, i.e., Dilauryl Selenide: $(CH_3(CH_2)_{11}-)_2Se$

hydrocarbon fuel fractions which appear promising from a standpoint of thermal stability are also being investigated for radiation stability. Investigations of the fuels are being made by means of engineering property changes such as CFR Fuel Coker characteristics and the various tests outlined in Air Force jet fuel specifications. These tests are designed to give sufficient information to allow predictions of fuel usability at different radiation levels and to show expected problem areas.

The second approach, being taken by the Shell Development Company under its Air Force sponsored fuel stability program, is of a more fundamental nature. Shell is investigating the effects of nuclear radiation on jet fuels, jet fuel components, and model compounds. This work is intended to determine the relationship existing between composition, nuclear radiation stability, and high temperature deposit formation. High temperature instability resulting from nuclear radiation effects is also under study. The effect of the presence of oxygen and the nature of the substrate is being considered. Fuels which show high or low stability to radiation are being characterized into their respective components, with the effect of radiation on said fuels and fuel components being studied in detail. The concentration of various trace metals is being measured and the effect of these metals on the thermal and nuclear stability of jet fuels is being determined. The overall goal of this particular study is to obtain sufficient information to develop a thorough analysis of fuel stability to nuclear radiation and to pinpoint the reasons for instability of typical jet fuels and experimental hydrocarbon fuels. By developing such a sound basis of understanding, formulation of improved organic fluids of greater nuclear radiation stability will be made possible.

The California Research Corporation concludes that on the basis of tests conducted to date, including runs on the CFR Fuel Coker, JP-4 and JP-5 fuels should be good at 1×10^8 roentgens of gamma radiation. They feel that if a JP-4 is good on control tests and is not marginal in its capabilities, it should be good up to about 5×10^8 roentgens (gamma), with JP-5 types being marginal at this level. All fuels would be questioned before use at 1×10^9 roentgens or higher. Based on the results of tests of two JP-4 types (RAF-105-55, from Middle East crude and RAF-106-55, from Mid-Continent crude), which are not complete, it appears that gamma radiation in the range of 10^8 to 10^9 roentgens improved thermal stability slightly. It was found that filter plugging tendency was reduced in all except one case and that little or no effect on preheater coating was found.

Shell Development Company has observed that the thermal instability (450°F) of three typical jet fuels, as measured by filter plugging tendency, is affected by irradiation to 1×10^8 roentgens in widely different degrees. A highly refined, high-boiling kerosene and a JP-5 type fuel improved after irradiation but a JP-4 fuel was affected adversely (5). Shell has also concluded that properties such as heat of combustion and N_H are not seriously changed by gamma dosages up to 1×10^8 roentgens, the screening level used in all their work to date.

A very serious problem concerning jet fuel stability has recently been revealed. Shell Development had three jet fuels irradiated in the Convair System Panels Test Number 2 at Fort Worth. The three fuels were the following: RAF-99-55 (a special kerosene), RAF-104-55 (a Los Angeles Basin JP-5), and RAF-107-55 (a San Joaquin JP-4). The general level of the changes in the reactor irradiated fuels suggested that they received considerably lower than the equivalent of 1×10^8 roentgens of gamma radiation. However, on testing the fuels in the CFR Fuel Coker they showed a drastic reduction in coker performance. The marked decrease in thermal stability cannot as yet be related to specific changes in composition. However, the more deleterious results observed in this test compared to gamma irradiation have indicated that greater emphasis must be placed in the future on studying the effects of pile irradiation.

Summary

Jet fuels as purchased by the Air Force must meet performance specifications but are not limited as to composition except in very general terms. There is thus no assurance that a fuel used in an aircraft one day will necessarily be the same as another used the following week. The same applies to any JP fuel in use by the Air Force. Thus, when it is found, as has been the case, that some fuels meeting specifications are susceptible to radiation, it is obvious that fuel composition is a critical factor. The basic research of the Shell Development Company will enable the Air Force to specify, in terms of actual chemical composition, the types of materials that can be used in jet fuels. Until such work is sufficiently advanced, no sound conclusions can be made on jet fuel stability to nuclear radiation.

The implications of the lack of correlation between gamma and mixed reactor radiations are vast and far reaching. Irradiations are now in progress in the MTR gamma canal at nominal gamma dosages

of 10^6 and 10^7 roentgens to see if similar loss of thermal stability of fuels occurs with low levels of gamma radiation. If this is found to be true, it will add further emphasis to the increasing importance of investigation of property changes at low dosage levels, as was pointed out for the data on the various lubricating fluids. If the fuels show resistance to the gamma radiation at these levels, it will give further indication of the necessity of careful testing in well calibrated reactor facilities. It is certainly obvious that whatever the case, end item testing of fuels and lubricants under dynamic conditions is a prime consideration. Only under conditions approaching those of the final application will reliable estimates be possible of the resistance of the fluids and lubricants to nuclear radiation.

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