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DEVELOPMENT OF LUBRICATING OILS SUITABLE
FOR USE WITH LIQUID OXIDIZERS

QUARTERLY PROGRESS REPORT NO. 3
1 June 1970 - 31 August 1970

Contract NAS8-25510
Control DCN 1-X-50-20131(1F)

MRI Project No. 3380-C

For

National Aeronautics and Space Administration
George C. Marshall Space Flight Center
Marshall Space Flight Center, Alabama 35812

Attn: A&TS-PR-M

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by

L. W. Breed
R. L. Elliott

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PREFACE

This report was prepared by Midwest Research Institute, 425 Volker Boulevard, Kansas City, Missouri 64110, under Contract NAS8-25510, "Development of Lubricating Oils Suitable for Use With Liquid Oxidizers," for the George C. Marshall Space Flight Center of the National Aeronautics and Space Administration. The work was administered under the technical direction of the Science and Engineering Astronautics Laboratory of the Marshall Space Flight Center with Mr. C. F. Key acting as the Contracting Officer's technical representative.

This report covers work conducted from 1 June 1970 to 31 August 1970.

The work at Midwest Research Institute was designated 3380-C and was carried out by Mr. R. L. Elliott and Mr. L. W. Breed, who acted as Principal Investigator, under the supervision of Dr. C. C. Chappelow, Jr., Head, Organic and Polymeric Materials Section.

Approved for:

MIDWEST RESEARCH INSTITUTE

Handwritten signature of H. M. Hubbard in cursive script, with a small 'HMH' monogram at the end.

H. M. Hubbard, Director
Physical Sciences Division

14 September 1970

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ABSTRACT

The search has continued for fluorinated ester compositions, which have improved vacuum compatibility but at the same time have satisfactory pour points and LOX-compatibility. A series of neopentyl polyol esters of ψ' -alkoxyacetic acid were prepared and screened as fluids for use in grease compositions during the current report period. Although the evaporation rates of the fluids were considerably lower than those of the ψ' -alkyl 3-methylglutarates, oils with much greater viscosities at room temperature and higher pour points were obtained. Two of the experimental fluids had pour points as low as -40°F . Improved viscosity indexes in this series seemed to be related more to the higher viscosities than to the structure itself. When mixed with tricresyl phosphate, the fluids performed satisfactorily on the wear tests. Samples of two of the fluids have been forwarded to Marshall Space Flight Center for LOX-compatibility testing. Other fluid compositions based on unsymmetrical esters and on blends of symmetrical esters showed no improvement over the pure esters in their useful temperature range. In additional work, two samples of ψ' -alkyl 3-methylglutarates containing 2 wt. % of tricresyl phosphate and thickened with Vydax 1000 have been prepared and forwarded for LOX-compatibility screening. Also, corrosion tests have shown that bis(ψ' -pentyl) 3-methylglutarate has a marked effect on the reduction of rusting on 52-100 steel balls when the balls are stored with the fluorinated fluid in the presence of water.

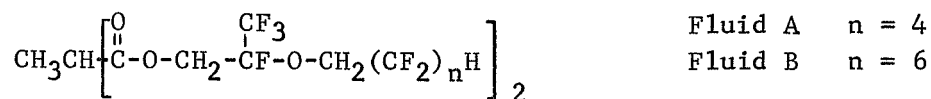
I. INTRODUCTION

The objective of this work is primarily the optimization of the lubrication properties and vacuum compatibility of selected fluoroester based greases that were prepared and studied under Contract NAS8-21269. The specific goals and the accomplishments under Contract NAS8-21269 were reviewed in Quarterly Progress Report No. 1. In that report experimental results were presented and published reports were cited to show that additive modification of the fluoroester based greases adequately improved the wear properties in lubricity tests and that oxidation-corrosion inhibitors probably were not necessary within the projected service range of up to 300°F. The chief limitation on the fluoroester compositions was their relatively high evaporation rate at 300°F and consequently their poor vacuum compatibility. Satisfactory properties of these lubricants include low pour point, LOX-compatibility, hydrolytic stability, noncorrosiveness, nonreactivity with aluminum under shear, and ease of gelation to a grease.

At a project conference at Marshall Space Flight Center, 23 June 1970, it was determined that grease requirements could be differentiated with respect to systems requirements: Since LOX systems require low pour point performance, but can accept a compromise on the evaporation test, the gelled ψ '-alkyl 3-methylglutarate greases can be considered satisfactory; lubricant requirements for GOX systems demand some additional structural modification of the esters to achieve the evaporation requirement, but the requirements are satisfied in the low temperature range by esters having pour points in the range of -45 to -50°F. On the basis of a survey of the currently manufactured lubricants and the experimental work so far completed under this contract, it is improbable that a single lubricant can meet the requirements for both systems.

The continued effort has largely been directed toward achieving structural modification of the esters in order to satisfy the requirement for the second class of lubricants. A decrease in the volatility of the oil requires modification of the chemical structure in one of the following ways: A decrease in the extent of fluorination; an increase in the formula weight; or the introduction of polar groups into the structure. The specific modifications require that the LOX-compatibility not be compromised and that the low temperature viscometric properties be maintained.

During the second quarter, a first series of structurally modified fluoroester oils were prepared and some of their properties were determined. The particular structural modification selected met one or more of the structural criteria for decreasing the volatility of the fluid without being detrimental to the low temperature viscometric properties. The following is the generalized structure for this new class of fluids.



Fluid A n = 4
 Fluid B n = 6

The structure increased the formula weight through the addition of an ether linkage and a fluorine-substituted aliphatic group, yet maintained a high degree of fluorine content.

The pour point of Fluid A was -65°F and of Fluid B -50°F, both higher than the pour points of the unmodified esters. However, the extent of the increase was minimal considering the increase in the formula weight of the fluid. Bis(ψ' -nonyl) 3-methylglutarate, the next higher homologue in the unmodified ester series reported to freeze at +77°F.¹ In selecting the modified structures, it had been anticipated that the presence of the ether linkage in the molecular structure would allow freer chain coiling and consequently better temperature-viscosity properties. A lower rate in the increase in viscosity as the temperature is lowered would result in a lower pour point. Contrary to expectations, no tendency toward viscosity index improvement was observed in Fluids A and B.

Volatilities were reduced, but not so much as might be expected from the formula weight increase. After 1 hr. at 300°F, Fluid A showed a 5% evaporation whereas bis(ψ' -amyl) 3-methylglutarate showed a 23% evaporation; Fluid B showed about a 1% evaporation as compared with 5% evaporation for bis(ψ' -heptyl) 3-methylglutarate. However, an overall comparison of pour points and evaporation rates indicates that the properties for Fluid A and bis(ψ' -heptyl) 3-methylglutarate are much the same and that no substantial improvement was effected in the structural modification.

The chief effort during this quarter has involved the synthesis and screening of a second chemically modified series of esters, the structural class favored for the LOX system lubricant.

II. PROPERTIES OF MODIFIED FLUORINE-SUBSTITUTED ESTERS

A. ψ' -Alkoxyacetic Acid Esters

A series of newly modified ester fluids incorporated an ether structure and allowed an increase in the proportion of hydrogen and the formula weight of the molecular structure. These fluids, which are structurally similar to the commercial neopentyl polyol esters, were prepared by condensing neopentyl polyols with ψ' -alkoxyacetic acids.



Structural variations included the products of the esterification of ψ' -propyloxyacetic acid, ψ' -pentyloxyacetic acid, or ψ' -heptyloxyacetic acid with 1,1,1-trimethylolethane, 1,1,1-trimethylolpropane, 2,2-dimethylolpropane, or 2,2,3,3,4,4-hexafluoropentane-1,5-diol. Specific procedures for the preparation of the esters are described in the experimental portion of this report.

<u>Compound No.</u>	<u>Structure</u>	<u>Name</u>
1	$\text{CH}_3\text{C}[\text{CH}_2\text{O}_2\text{CCH}_2\text{OCH}_2(\text{CF}_2)_2\text{H}]_3$	1,1,1-trimethylolethane bis(ψ' -propyloxyacetate)
2	$\text{CH}_3\text{CH}_2\text{C}[\text{CH}_2\text{O}_2\text{CCH}_2\text{OCH}_2(\text{CF}_2)_2\text{H}]_3$	1,1,1-trimethylolpropane bis(ψ' -propyloxyacetate)
3	$(\text{CH}_3)_2\text{C}[\text{CH}_2\text{O}_2\text{CCH}_2\text{OCH}_2(\text{CF}_2)_2\text{H}]_2$	2,2-dimethylolpropane bis(ψ' -propyloxyacetate)
4	$\text{CH}_3\text{C}[\text{CH}_2\text{O}_2\text{CCH}_2\text{OCH}_2(\text{CF}_2)_4\text{H}]_3$	1,1,1-trimethylolethane bis(ψ' -pentyloxyacetate)
5	$\text{CH}_3\text{CH}_2\text{C}[\text{CH}_2\text{O}_2\text{CCH}_2\text{OCH}_2(\text{CF}_2)_4\text{H}]_3$	1,1,1-trimethylolpropane bis(ψ' -pentyloxyacetate)
6	$(\text{CH}_3)_2\text{C}[\text{CH}_2\text{O}_2\text{CCH}_2\text{OCH}_2(\text{CF}_2)_4\text{H}]_2$	2,2-dimethylolpropane bis(ψ' -pentyloxyacetate)
7	$\text{CF}_2[\text{CF}_2\text{CH}_2\text{O}_2\text{CCH}_2\text{OCH}_2(\text{CF}_2)_4\text{H}]_2$	2,2,3,3,4,4-hexafluoro- pentane-1,5-diol bis(ψ' - pentyloxyacetate)
8	$(\text{CH}_3)_2\text{C}[\text{CH}_2\text{O}_2\text{CCH}_2\text{OCH}_2(\text{CF}_2)_6\text{H}]_2$	2,2-dimethylolpropane bis(ψ' -heptyloxyacetate)

Initially, a small quantity of each of the fluids was prepared and screened for pour point, evaporation rate, and viscosity. Subsequently, larger samples of Fluids 5 and 6 were prepared and submitted for LOX-compatibility screening.

The results of the determinations of fluid properties are summarized in Table I. In the determination of evaporation rates, some problems in repeatability required refinements in the procedure; therefore, new values for several commercial materials and previously prepared fluids are provided for comparison. Some previously determined pour points and viscosities for the same fluids are also included.

Only the pour points of the dimethylolpropane derivatives were satisfactory, values of -40 and -45° being obtained, and evaporation rates were lower than the evaporation rates for ψ' -alkyl 3-methylglutarate. In the new series, somewhat higher viscosity indexes were observed, but the improvement appeared to be related to the higher viscosities of these oils at 100 and 210°F rather than to changes in the viscometric properties inherent in the structural modification. Four-ball wear tests on two of the fluids, with and without added tricresyl phosphate are summarized in Table II. Tricresyl phosphate afforded adequate wear protection to these two fluids.

If the overall properties of the fluids in Table I are compared, the pour points, evaporation rates, and viscosities of 2,2-dimethylolpropane bis(ψ' -pentyloxyacetate) (Compound 6), tris(ψ' -amyl) tricarballylate, and Krytox 143AA are roughly equivalent. On the basis of these data, it now appears that tris(ψ' -amyl) tricarballylate and bis(hydroxymethyl)propane bis(ψ' -pentyloxyacetate) as pure substances are the best candidates as GOX system lubricants. There is considerable advantage in materials costs in the second compound, but results have not yet been obtained on its LOX-compatibility.

In the earlier work, the tricarballylate ester showed 0/20 reactions in the LOX compatibility test. The evaporation rates of neither of these compounds approach the requirement of less than 1% at 300°F and less than 5% at 400°F, yet their evaporation rates are not greater than those of the best commercially available materials.

B. Unsymmetrical Esters

It is reported that lower pour points and evaporation rates at no sacrifice in the viscosity or viscosity index can be achieved in the aliphatic diester series through the use of esters with mixed ligands. This improvement was observed by Cohen and others in comparing the properties

TABLE I

POUR POINTS, EVAPORATION RATES, VISCOSITIES, AND VISCOSITY
INDEXES FOR NEW MODIFIED FLUORINE-SUBSTITUTED ESTERS

Compound No.	Wt. % Evaporation 300 ± 2°F		Pour Point °F	Viscosity cSt.		ASTM Viscosity Index
	1 Hr.	6 Hr.		210°F	100°F	
1	--	3.0	-5	14.41	339.4	-18
2	--	1.4	-5 m.p. 33-37°C	--	--	--
3	--	13.7	-40	4.92	50.89	-31
4	--	0.7	-10	16.32	374.3	5
5	--	1.4	-10	16.12	349.6	13
6	--	5.4	-45	6.03	74.17	-49
7	--	--	-- m.p. 66-70°C	--	--	--
8	--	5.9	-35	7.02	91.03	-12
Bis(ψ '-amyl) 3-methylglutarate	10.5	--	< -90	2.78	16.27	-59
Bis(ψ '-heptyl) 3-methylglutarate	2.4	14.6	-75	3.57	26.11	-80
Tris(ψ '-amyl) tricarallylate	0.9	4.8	-45	6.78	86.23	-25
Fomblin L	13.0	37.3	< -80	--	--	--
Krytox 143AA	1.8	6.1	-50	--	--	--
Krytox 143AZ	9.4	32.0	-70	--	--	--

TABLE II

EXPERIMENTAL FOUR-BALL WEAR TEST DATA^{a/}

<u>Additive</u>	<u>Wear Scar Diameter (mm.) at 50 Kg.</u>
<u>2,2-Dimethylolpropane bis(ψ'-pentyloxyacetate)</u>	
<u>Fluid</u>	
None	0.75
2 wt. % Tricresyl phosphate	0.56
<u>1,1,1-Trimethylolethane tris(ψ'-pentyloxyacetate)</u>	
<u>Fluid</u>	
None	0.69
2 wt. % Tricresyl phosphate	0.38

a/ Two hours at 147°, 600 rpm, 52-100 steel balls.

of the unsymmetrical esters with blends of pure esters containing the same proportions of alcohol and acid ligands.^{1/}

The properties of two unsymmetrical fluorated esters are reported in Table III. A comparison of the pour points and evaporation rates of the esters in Table III with the corresponding values for similar symmetrical esters in Table I indicate the values for the unsymmetrical esters are not significantly different from the values for the symmetrical esters, provided the formula weights are about the same.

C. Ester Blends

The possibility of achieving a wider useful fluid range through the use of blends of fluorine-substituted esters was also considered. Because of the similarity in chemical composition, such blends should be compatible in all proportions. It was of particular interest to determine if the -10°F pour point of 1,1,1-trimethylolethane tris(ψ' -pentyloxyacetate) could be effectively lowered by a small proportion of a low pour point fluid without seriously increasing its low evaporation rate (0.7% in 6 hr.). In some mixtures that were investigated and are reported in Table IV, changes in pour points and evaporation rates were both roughly proportional to the percentage of each component in the blends. None of the combinations produced compositions with properties as favorable as tris(ψ' -amyl) tri-carballylate or 2,2-dimethylolpropane bis(ψ' -pentyloxyacetate).

TABLE III

PROPERTIES OF UNSYMMETRICAL ESTERS

<u>Components in Ester Preparation</u>	<u>Pour Point (°F)</u>	<u>Evaporation Rate (6 Hr. at 300 ± 2°F)</u>
Tricarballic acid (0.085 mole) ψ' -Pentyl alcohol (0.17 mole) ψ' -Heptyl alcohol (0.099 mole)	-40	3.8
2,2-Dimethylolpropane (0.10 mole) ψ' -Pentyloxyacetic acid (0.10 mole) ψ' -Heptyloxyacetic acid (0.10 mole)	-45	7.3

TABLE IV

POUR POINTS AND EVAPORATION RATES OF BLENDS OF FLUORINATED ESTER FLUIDSFluids

- A. 1,1,1-Trimethylolethane tris(ψ' -pentyloxyacetate)
 B. Bis(ψ' -amyl) 3-methylglutarate
 C. Bis(ψ' -heptyl) 3-methylglutarate
 D. 2,2-Dimethylolpropane bis(ψ' -pentyloxyacetate)

<u>Blend Composition (wt. %)</u>				<u>Wt. % Evaporation at 300°F, 6 Hr.</u>	<u>Pour Point (°F)</u>
<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>		
100	--	--	--	0.7	-10
90	10	--	--	5.5	-15
75	25	--	--	14.0	-35
50	50	--	--	26.6	-50
--	100	--	--	10.5 (1 hr.)	< -90
90	--	10	--	2.2	-15
75	--	25	--	4.8	-25
50	--	50	--	9.8	-45
--	--	100	--	14.6	-75
90	--	--	10	1.2	-15
75	--	--	25	1.9	-25
50	--	--	50	3.2	-30
--	--	--	100	5.4	-45

D. Water Corrosion

An additional property of ψ' -alkyl 3-methylglutarate fluids was examined during this report period. When small quantities of water were mixed with the commercial and many of the experimental fluids and a ball bearing was stored in the mixture at 60°F, rusting occurred as if water alone were present. A similar test with ψ' -pentyl 3-methylglutarate fluid showed no rusting, although some pitting was observed. The results of a series of tests run for 91 hr. are summarized in Table V. In a second series of experiments, the water corrosion tests were run for much longer periods. The appearances of the bearings after the tests are shown in Figure 1.

TABLE V

WATER CORROSION DATA^{a/}

<u>Fluid</u>	<u>First Sample</u>	<u>Second Sample</u>
Tris (ψ' -amyl) tricarballylate	Loose rust	Loose rust
Bis(ψ' -heptyl) 3-methylglutarate	Loose rust	Loose rust
Bis(ψ' -amyl) 3-methylglutarate	Slight staining	Slight pitting
2,2-Dimethylolpropane bis(ψ' - pentyloxyacetate	Heavy staining	Slight staining
Krytox 143AA	Loose rust	Loose rust
Fomblin L	Loose rust	Loose rust
Mineral oil	Loose rust	Slight staining and pitting

a/ 52-100 Steel balls in the presence of water and the test fluid for 91 hr.
at 60°F.

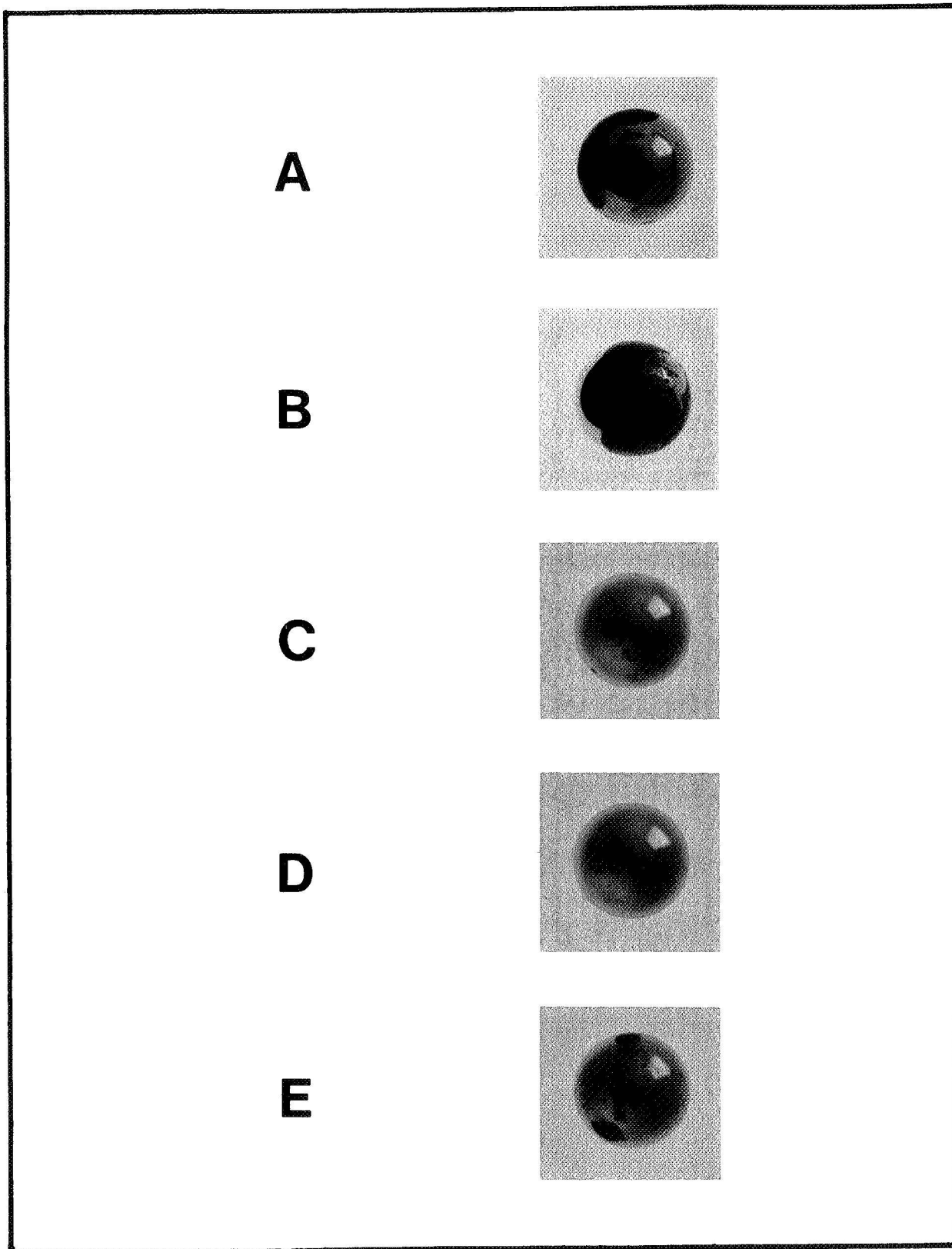


Figure 1 - Corrosion on 52-100 Steel Balls in the Presence of Fluorine-Containing Fluids and Water: A. Water only (14 days at 60°C); B. PR 143AA (4 days at room temperature); C. Fomblin L (22 days at 60°); D. Bis(ψ' -heptyl) 3-Methylglutarate (22 days at 60°); E. Bis(ψ' -pentyloxytetrafluoropropyl) 3-Methylglutarate (22 days at 60°).

E. Samples

During this report period, the following lubricant samples were forwarded to Marshall Space Flight Center for LOX-compatibility screening.

Bis(ψ' -pentyloxytetrafluoropropyl) 3-methylglutarate, 24 g.

Bis(ψ' -heptyloxytetrafluoropropyl) 3-methylglutarate, 24 g.

Bis(ψ' -pentyl) 3-methylglutarate (containing 2% tricresyl phosphate) thickened with 16% Vydax 1000, 194 g.

Bis(ψ' -heptyl) 3-methylglutarate (containing 2% tricresyl phosphate) thickened with 16% Vydax 1000, 219 g.

2,2-Dimethylolpropane bis(ψ' -pentyloxyacetate), 181 g.

1,1,1-Trimethylolethane bis(ψ' -pentyloxyacetate), 142 g.

None of the results of these tests has been received.

III. ANTICIPATED WORK

After the work on characterizing the fluids discussed in this report is complete, the final report covering the work under the entire program will be prepared. When the results of LOX-compatibility testing is complete, recommendations can be made concerning the fluid which most nearly meets the specified requirements.

IV. EXPERIMENTAL PART

A. Preparation and Characterization of ψ' -Alkoxyacetic Acids

Two procedures were employed for preparing these acids. The results of preparations in which the ψ' -alkanol was first treated with sodium hydride and subsequently with chloroacetic acid are reported in Table VI. The following summarizes the conditions for the two larger preparations. The sodium hydride dispersion in mineral oil, mixed with 800 ml. of ether, was treated with the ψ' -alkanol over a 2 hr. period, and then the chloroacetic acid was added over a 1.5 hr. period. After the mixture cooled to room temperature and was stored overnight, 400 ml. of 25% hydrochloric acid was added and the ether layer was separated and dried over sodium sulfate.

TABLE VI

PREPARATION OF ψ' -ALKYLOXYACETIC ACIDS: FIRST METHOD

<u>Compound No.</u>	<u>ψ'-Propyl Alcohol</u>	<u>ψ'-Pentyl Alcohol</u>	<u>Chloroacetic Acid</u>	<u>Sodium^{a/} Hydride</u>	<u>Yield (%)</u>
1	232.0 g. (1.76 moles)		94.5 g. (0.80 mole)	38.4 g. (1.60 moles)	89 (136 g.)
2		102.1 g. (0.44 mole)	18.9 g. (0.20 mole)	9.6 g. (0.40 mole)	83 (96 g.)
2		408.3 g. (1.76 moles)	75.6 g. (0.81 mole)	38.4 g. (1.60 moles)	84 (196 g.)

^{a/} Used as a 55% dispersion in mineral oil.

When the ether was evaporated, a first vacuum distillation gave the acid contaminated with mineral oil. After the mineral oil was extracted with petroleum ether, b.p. 35-60°, the acid was purified by fractional distillation under vacuum.

In the second method, the ψ' -alkanol, chloroacetic acid, and aqueous sodium hydroxide were heated together in one step. The results of these preparations are summarized in Table VII. The following is a representative procedure. When an aqueous solution of the sodium salt of chloroacetic acid was added to a mixture of the ψ' -alkanol and sodium hydroxide during 1.5 hr. an exothermic reaction occurred. The mixture was refluxed overnight, cooled, and neutralized with 20% aqueous hydrochloric acid. After the lower layer was separated, washed with two portions of 20% aqueous hydrochloric acid, and two portions of water, the acid was purified by fractional distillation.

The properties and the results of the characterization of these acids are summarized in Table VIII.

TABLE VII

PREPARATION OF ψ' -ALKYLOXYACETIC ACIDS: SECOND METHOD

Compound No.	Chloroacetic Acid	ψ' -Pentyl Alcohol	ψ' -Heptyl Alcohol	NaOH	Water (ml.)	Yield (%)	Alcohol Recovered (%)
2	18.9 g. (0.20 mole)	51.0 g. (0.22 mole)		88 g. (0.22 mole)	44	27 (16 g.)	42
2	378 g. (4.00 moles)	1,020 g. (4.40 moles)		176 g. (4.40 moles)	1,000	50 (585 g.)	45
3	189 g. (2.00 moles)		730 g. (2.20 moles)	88 g. (2.20 moles)	500	20 (154 g.)	64

TABLE VIII

PROPERTIES OF ψ' -ALKYLOXYACETIC ACIDS

Compound No. ^{a/}	Boiling Point [°C (mm.)]	n_D^{20}	Analyses [Found/(calcd)]			Calcd. for	Infrared Analysis
			C	H	F		
1 ^{b/}	92-93 (0.90) 134-136 (9)	1.3697	31.48 (31.59)	3.05 (3.18)	40.98 (39.98)	C ₅ H ₆ F ₄ O ₃	Figure 2
2	134-135 (10)	1.3565	29.08 (28.98)	2.03 (2.09)	52.23 (52.39)	C ₇ H ₆ F ₈ O ₃	Figure 3
3	128-130 (0.3)	1.3471	27.73 (27.71)	1.62 (1.55)	58.56 (58.44)	C ₉ H ₆ F ₁₂ O ₃	Figure 4

^{a/} For identification of Compound Nos., see Tables VI and VII.

^{b/} Reported, b.p. 109-114° (24 mm.), n_D^{26} 1.3632. (Ref. 2).

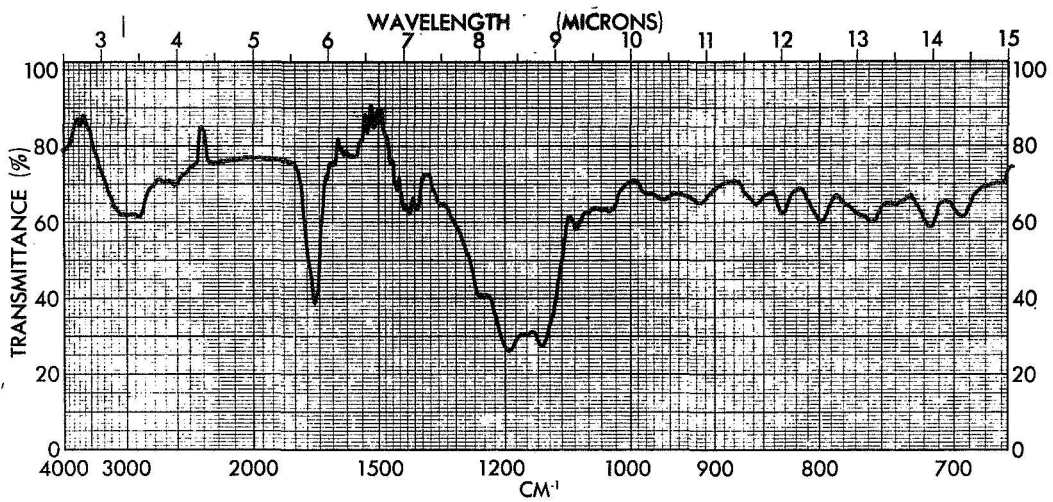


Figure 2 - Infrared Spectrum of η^1 -Propyloxyacetic Acid (Liquid)

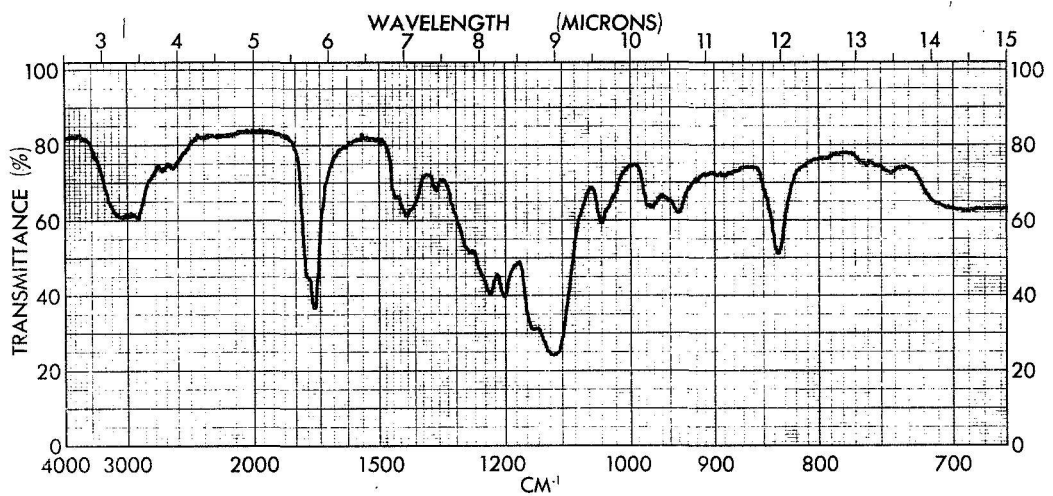


Figure 3 - Infrared Spectrum of η^1 -Pentyloxyacetic Acid (Liquid)

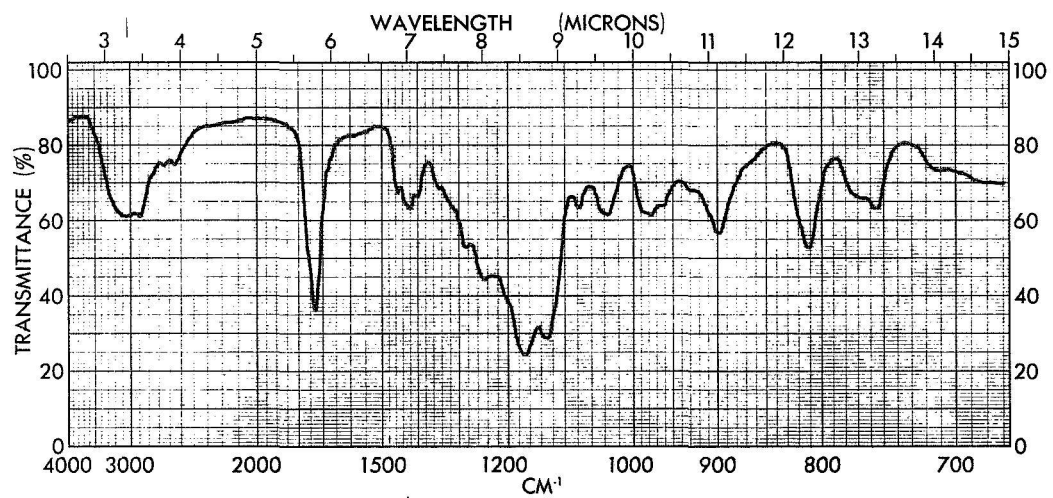


Figure 4 - Infrared Spectrum of η^1 -Heptyloxyacetic Acid (Liquid)

B. Preparation and Characterization of Modified Fluorinated Esters From ψ' -Alkyloxyacetic Acids and Various Polyols

The quantities, described in Table IX, of ψ' -propyloxyacetic acid or ψ' -pentyloxyacetic acid and 1,1,1-trimethylolethane, 1,1,1-trimethylolpropane, 2,2-dimethylolpropane, or 2,2,3,3,4,4-hexafluoropentane-1,5-diol were dissolved in toluene to which was added sulfuric acid. The mixtures were heated from 4-17 hr. until the specified quantity of water had been collected in a Dean-Stark trap. After cooled mixtures were washed sequentially with water, aqueous potassium carbonate, and water, the toluene was distilled off and the esters were purified by fractional distillation. The characterization and properties of these fluids are reported in Table X.

C. Preparation of Fluorinated Esters from ψ' -Alkanols and Various Aliphatic Acids

1. Bis(ψ' -amyl) 3-methylglutarate: A mixture of 114.0 g. (0.78 mole) of 3-methylglutaric acid, 408.0 g. (1.76 moles) of ψ' -amyl alcohol, 600 ml. of toluene and 4 g. of sulfuric acid was refluxed for 21 hr. A total of 31.6 ml. of water (calcd., 28.1 ml.) was collected in a Dear-Stark trap. When the cooled mixture was added dropwise to 200 ml. of water, the lower phase separated and was added dropwise successively to 200 ml. of 5% potassium carbonate and 200 ml. of water. After the solvent and traces of water were removed on a rotary evaporator, fractional distillation of the residue gave 411.4 g. (92%) of bis(ψ' -amyl) 3-methylglutarate, b.p. 123° (0.07 mm.), n_D^{20} 1.3605 [reported b.p. 130-132° (0.03 mm.), n_D^{20} 1.3606].^{3/}

2. Mixed ψ' -pentyl, ψ' -heptyl ester of tricarballic acid: When the procedure in the preceding paragraph was followed, 15.0 g. (0.085 mole) of tricarballic acid, 40.1 g. (0.17 mole--2% excess) of ψ' -pentyl alcohol, and 32.8 g. (0.099 mole--14% excess) of ψ' -heptyl alcohol, heated in 50 ml. of toluene with 0.2 g. of sulfuric acid for 20 hr. gave 4.6 ml. (calcd., 4.6 ml.) of water. Purification and fractional distillation of the product gave 41 g. (53%) of the mixed ester, b.p. 176-184° (0.07 mm.), pour point -40°F, n_D^{20} 1.3580.

D. Determination of Lubricant Properties

Fluid viscosities were determined by ASTM method D 445-65 and viscosity indexes were calculated by method D 2270-64. The method for pour points followed ASTM method D 97-57. Wear scar diameters were determined on the four-ball wear test at a load of 50 kg. after 2 hr. at 146° with 52-100 steel balls at 600 rpm.

TABLE IX

PREPARATION OF MODIFIED FLUORO-SUBSTITUTED ESTERS FROM ψ^1 -ALKYLOXYACETIC ACIDS AND VARIOUS POLYOLS

Compound No.	ψ^1 -Propyloxy-acetic Acid	ψ^1 -Pentyloxy-acetic Acid	ψ^1 -Heptyloxy-acetic Acid	Trimethylol-ethane	Trimethylol-propane	Dimethylol-propane	Hexafluoro-pentanediol	Sulfuric Acid (g.)	Toluene (ml.)	Water [MI. Found/ (Calcd.)]	Yield (%)
1	38.0 g. (0.20 mole)			7.2 g. (0.059 mole)				0.25	50	3.3 (3.2)	a/
2	38.0 g. (0.20 mole)				8.0 g. (0.060 mole)			0.25	50	3.5 (3.2)	82 (32 g.)
3	38.0 g. (0.20 mole)					10.4 g. (0.10 mole)		0.25	50	3.5 (3.6)	52 (23 g.)
4		46.4 g. (0.16 mole)		6.0 g. (0.049 mole)				0.25	50	3.0 (2.7)	84 (39 g.)
4		190 g. (0.66 mole)		24.0 g. (0.20 mole)				1.0	50	11.5 (10.8)	91 (171 g.)
4		95 g. (0.33 mole)		12.0 g. (0.10 mole)				0.25	50	6.0 (5.4)	88 (82 g.)
5		46.4 g. (0.16 mole)			6.7 g. (0.50 mole)			0.25	50	3.0 (2.7)	86 (41 g.)
6		46.4 g. (0.16 mole)				7.8 g. (0.075 mole)		0.25	50	3.1 (2.7)	81 (40 g.)
6		351 g. (1.21 moles)				57.2 g. (0.55 mole)		1.5	300	19.9 (19.8)	94 (337 g.)
7		46.4 g. (0.16 mole)					15.9 g. (0.075 mole)	0.25	50	3.0 (2.7)	86 (49 g.)
8			85.8 g. (0.22 mole)			10.4 g. (0.10 mole)		0.25	50	4.0 (3.6)	94 (80 g.)
9		29.0 g. (0.10 mole)	39.0 g. (0.10 mole)			10.4 g. (0.10 mole)		0.25	50	3.9 (3.6)	86 (64 g.)

a/ After a portion of the product was lost through spillage, 18.1 g. of the fluid was obtained.

TABLE X

PROPERTIES OF MODIFIED FLUORO-SUBSTITUTED ESTERS

Compound No. <u>a/</u>	Boiling Point [°C (mm.)]	Pour Point (°F)	Evaporation (% after 6 hr. at 300°F)	n _D ²⁶	n _D ²⁰	Analysis [Found/(calcd)]			Calcd for	Infrared Analysis
						C	H	F		
1	212-222 (0.08)	-5	3.00	1.463	1.4036	37.97 (37.74)	3.84 (3.80)	35.38 (35.83)	C ₂₀ H ₂₄ F ₁₂ O ₉	Figure 5
2	223-224 (0.09)	m.p. 33- 37°C	1.40	1.450	1.4048	38.73 (38.78)	3.94 (4.03)	35.47 (35.05)	C ₂₁ H ₂₆ F ₁₂ O ₉	Figure 6
3	154-156 (0.10)	-40	13.69	1.367	1.3962	40.16 (40.18)	4.54 (4.50)	33.71 (33.91)	C ₁₅ H ₂₀ F ₈ O ₆	Figure 7
4	233-236 (0.07) <u>b/</u>	-10	0.67	1.606	1.3815	32.87 (33.35)	2.62 (2.58)	48.52 (48.69)	C ₂₆ H ₂₄ F ₂₄ O ₉	Figure 8
5	230-240 (0.10)	-10	1.44	1.582	1.3822	33.64 (34.12)	2.89 (2.75)	48.44 (47.98)	C ₂₇ H ₂₆ F ₂₄ O ₉	Figure 9
6	171-174 (0.08) <u>c/</u>	-45	5.44	1.514	1.3760	35.24 (35.19)	2.91 (3.11)	46.67 (46.89)	C ₁₉ H ₂₀ F ₁₆ O ₆	Figure 10
7	168-178 (0.07)	m.p. 66- 70°C	--	--	1.3601	29.67 (30.17)	1.96 (1.87)	55.15 (55.27)	C ₁₉ H ₁₄ F ₂₂ O ₆	Figure 11
8	179-185 (0.06)	-35	5.92	1.639	1.3642	32.80 (32.56)	2.51 (2.38)	34.66 (53.75)	C ₂₃ H ₂₀ F ₂₄ O ₆	Figure 12
9	169-190 (0.1)	-45	--	--	1.3709	--	--	--	--	--

a/ For identification of Compound Nos., see Table IX.b/ Decomposition precedes boiling at 385°C.c/ B.P. 359°C (d.t.a.).

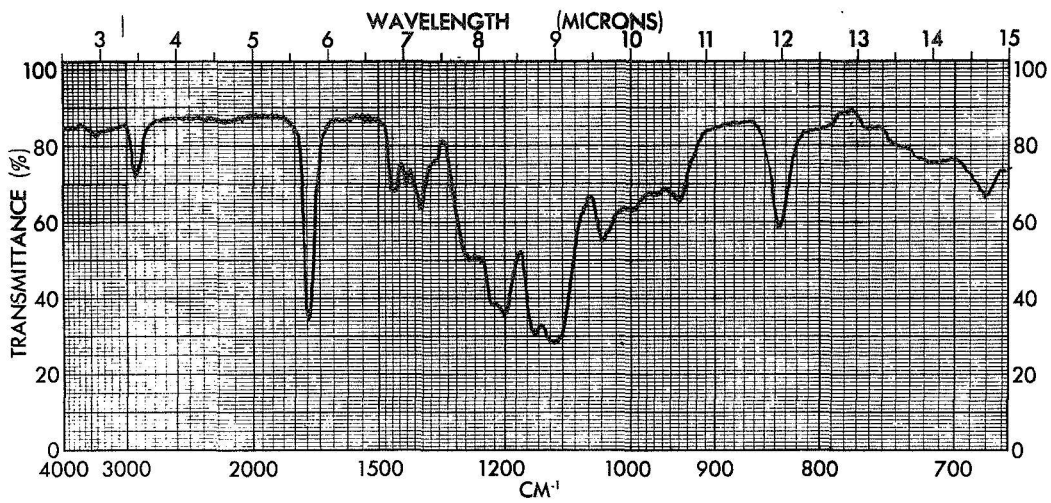


Figure 5 - Infrared Spectrum of 1,1,1-Trimethylolethane Tris-
(ψ' -propyloxyacetate) (Liquid)

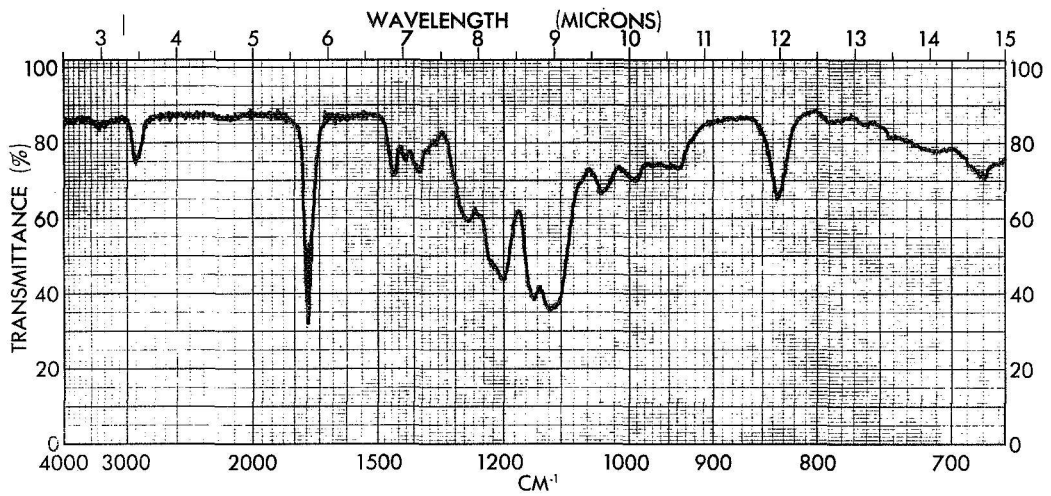


Figure 6 - Infrared Spectrum of 1,1,1-Trimethylolpropane Tris-
(ψ' -propyloxyacetate) (Liquid)

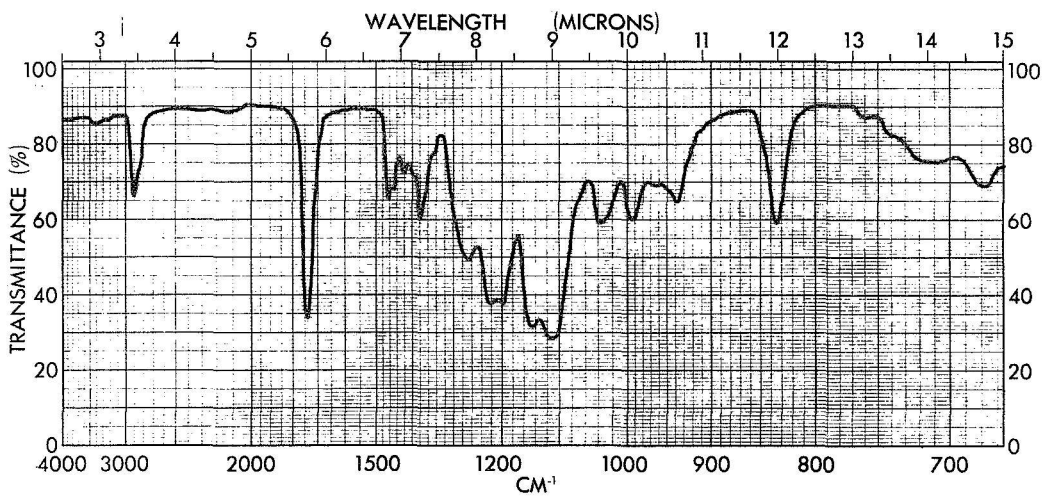


Figure 7 - Infrared Spectrum of 2,2-Dimethylolpropane Bis-
(ψ' -propyloxyacetate) (Liquid)

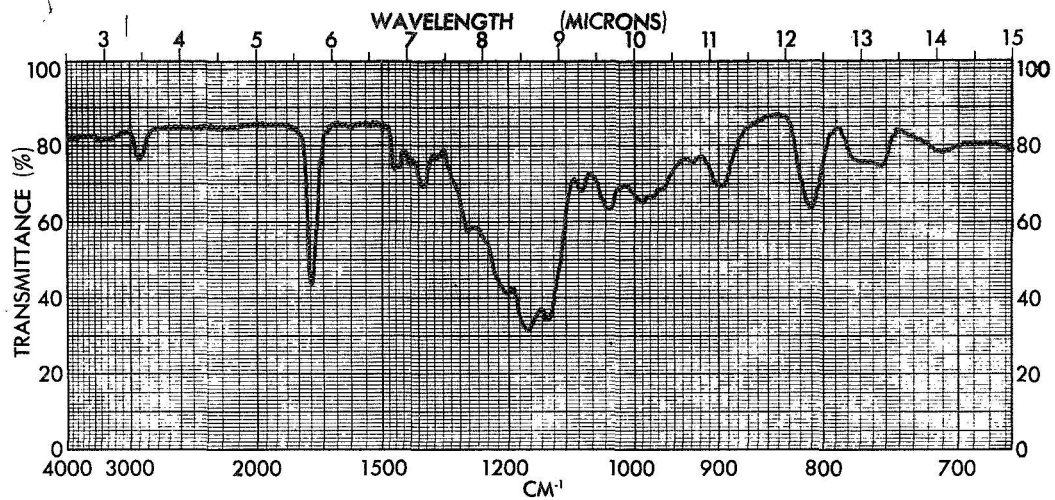


Figure 8 - Infrared Spectrum of 1,1,1-Trimethylolethane
Tris(ψ' -pentyl-oxyacetate) (Liquid)

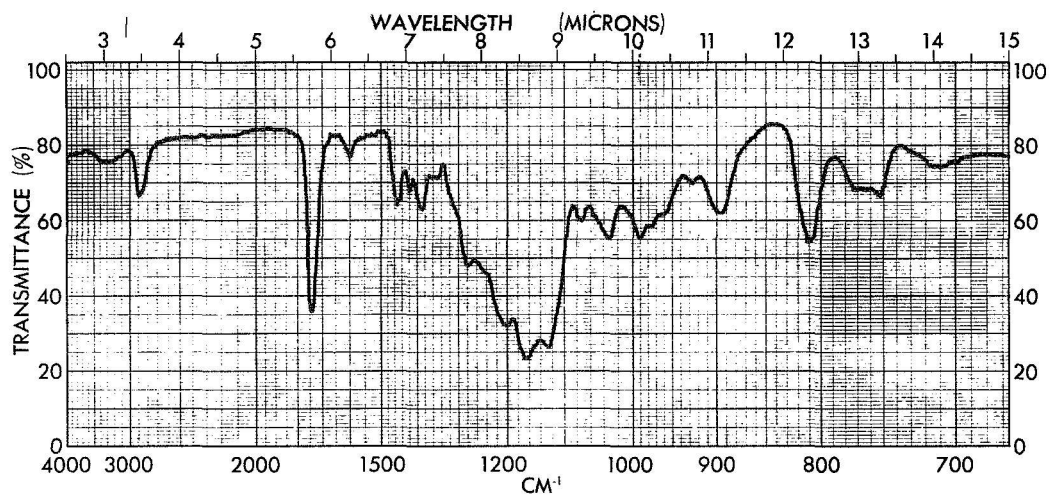


Figure 9 - Infrared Spectrum of 1,1,1-Trimethylolpropane
Tris(ψ' -pentyl-oxyacetate) (Liquid)

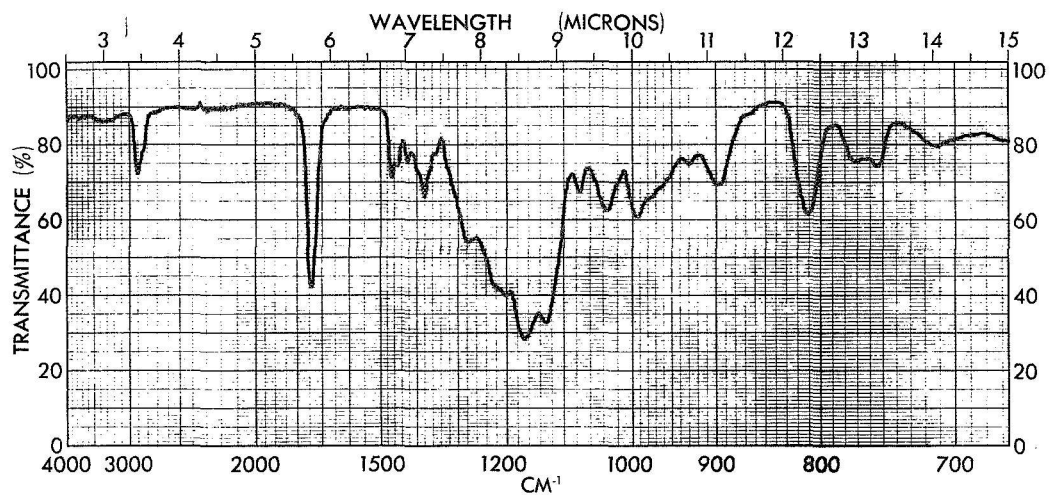


Figure 10 - Infrared Spectrum of 2,2-Dimethylolpropane
Bis(ψ' -pentyl-oxyacetate) (Liquid)

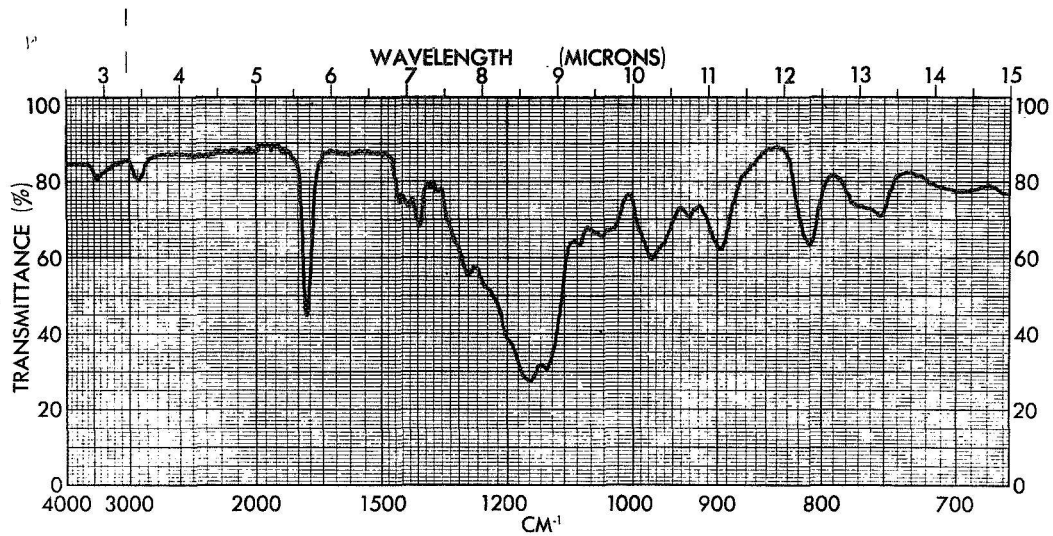


Figure 11 - Infrared Spectrum of 2,2,3,3,4,4-Hexafluoropropanediol Bis(ψ^1 -pentyloxyacetate) (Liquid)

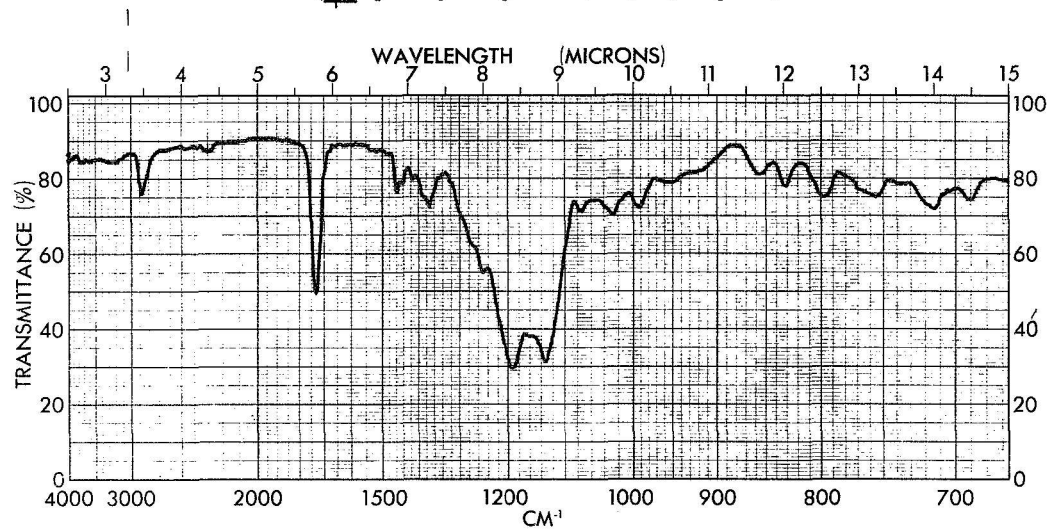


Figure 12 - Infrared Spectrum of 2,2-Dimethylolpropane Bis(ψ^1 -heptyloxyacetate) (Liquid)

Evaporation rates represent the value obtained when about 2.5 g. of a fluid weighed in a 24 mm. diameter and 7 mm. deep aluminum dish was heated on a hot plate at $300 \pm 2^\circ\text{F}$ for 1 or 6 hr. The temperature was determined with a thermocouple just touching the bottom of the pan.

E. Water Corrosion Tests

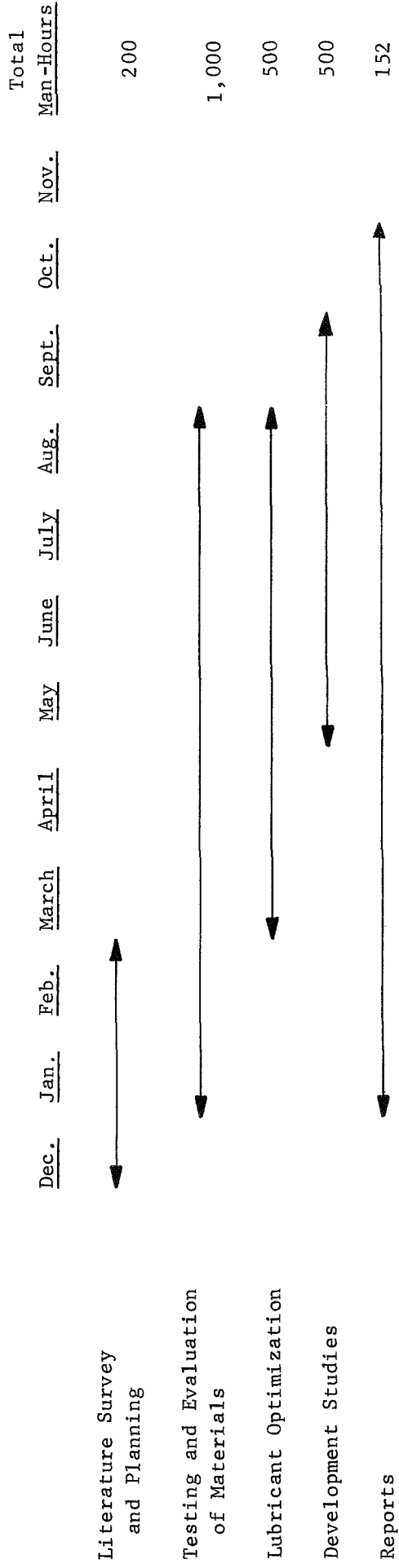
In a series of tests a mixture of 3.0 g. of a fluid and 0.15 g. of water was placed in a jar in contact with a 52-100 steel ball. The steel balls used were not new and had been previously used on various four-ball wear tests, but all were corrosion free at the beginning of the tests. The following fluids were examined: PR 143AA; Fomblin L; bis(ψ' -heptyl) 3-methylglutarate; and bis(2- ψ' -pentyloxytetrafluoropropyl) 3-methylglutarate. The samples were stored at 60°C for at least 14 days, except for the PR 143AA fluid, which was stored for 4 days. All of the balls, except the ball in the bis(ψ' -heptyl) 3-methylglutarate showed rusting during the storage period. Rusting was particularly heavy with water alone and with the PR 143AA fluid. Photographs of the steel balls are shown in Figure 1. The dark mark at the center of each ball is a reflection of the camera lens. A light reflection also shows on each ball.

A second series of tests is summarized in Table V. In duplicate experiments 52-100 steel ball bearings were contacted thoroughly with each of the following fluids and three drops of water were added. The samples were stored at 60° for a total of 91 hr. At the end of the test period, the ball bearings were examined for loose rust, staining and pitting.

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2. Bucham Research Laboratories, Ltd., Brit. Patent, 873,244 (1962) C.A. 56, 780 (1962).
3. L. W. Breed, J. C. Wiley, Jr., and C. F. Key, Ind. Eng. Chem. Prod. Res. Develop., 9, 53 (1970).

PROGRAM PLANNING CHART



Estimated Monthly Man-Hours	100	245	245	246	246	246	246	246	246	246	40		2,352
Actual Monthly Man-Hours	106	196	275	269	278	326	173	145	166				1,944
Cumulative Total Man-Hours	106	312	587	856	1,134	1,460	1,633	1,778	1,944				1,944
Expenditures to Date													\$34,067
Funds Required for Completion													\$5,898
Problem Areas:	None												

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