High Temperature Lubricants from Aromatic Acids and Fluorinated Alcohols

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Diester base oils conforming to specification MIL-L-7808C (*10*) are satisfactory lubricants for current jet engines which operate with a bulk oil temperature of approximately 300° F. New engines for supersonic aircraft will have bulk oil temperatures of 400° F. and bearing temperatures about 150° F. higher. A target specification, MIL-L-9236A (USAF) (*11*), has been issued to encourage the development of oils for these new engines.

Esters derived from fluorinated alcohols of the general formulas $F(CF_2)_nCH_2OH$ and $H(CF_2\text{-}CF_2)_mCH_2OH$, and di- or polycarboxylic acids have better oxidation stabilities than their unfluorinated analogs (*6*). Bench tests (*2*), and a full scale jet engine test (100 hours in a J-57 engine with bulk oil at 300° F.) (*9*), indicate that the $H(CF_2\text{-}CF_2)_mCH_2OH$ esters of dicarboxylic acids containing no additives are equal or superior in lubricating ability to MIL-L-7808 oils containing antiwear agents. At the conclusion of the test, properties of the used oil were almost identical with those of the new oil, and the engine was exceptionally clean, showing little evidence of sludge or lacquer. However, at bulk oil temperatures of 400° F., the aliphatic acid esters of fluorinated alcohols may be marginal or deficient as regards volatility, high-temperature viscosity, and oxidation stability at peak bearing temperatures.

The oxidation-sensitive portion of fluorinated alcohol esters of aliphatic dibasic acids is the hydrocarbon portion of the acid rather than the alcohol moiety as in analogous unfluorinated diesters. This suggests that the oxidation stability could be further improved by finding more stable acids for esterification with fluorinated alcohols. Aromatic acids, because of their resonating structure, should have better stability. The phthalate fluorinated ester, as expected, was superior in oxidation stability to the aliphatic fluorinated esters although too volatile for practical applications (*6*).

The desired decrease in volatility (increase in molecular weight) can be achieved by (A) increasing the molecular weight or chain length of the fluorinated alcohol, (B) increasing the number of fluorinated ester groups, and (C) increasing the molecular weight of the acid.

Available fluorinated alcohols are straight-chain compounds, so esters made by Method A would also show a progressive rise in freezing point with increasing chain length. Polycarboxylic acids are available for the preparation of esters containing three or more fluorinated alkyl groups, Method B, but the higher proportion of CF_2 in the ester would increase costs. Therefore, Method C, increasing the molecular weight of the acid, was considered the most promising approach.

Preference was given in this investigation to organic acids whose volume production would be feasible—e.g., 2-phenylsuccinic; 2-phenylglutaric; 2,2′-biphenyl-dicarboxylic (diphenic); and 4,4′-oxydibenzoic (diphenyl ether dicarboxylic) acids.

The fluorinated alcohols used in this program are telomers of tetrafluoroethylene and methanol, having the general formula $H(CF_2CF_2)_mCH_2OH$ (*1, 3, 8*). The abbreviated nomenclature used previously (*6*) is followed here. For example, $H(CF_2CF_2)_2CH_2OH$ or 1*H*,1*H*,5*H*-octafluoropentanol is abbreviated as ψ'-amyl alcohol. This nomenclature is extended to the ester derivatives.

EXPERIMENTAL

Esters shown in Table I were prepared by conventional procedures in yields of 90% or better using sulfuric acid as the catalyst and carbon tetrachloride for water entrainment (*7*). Esters of diphenyl ether dicarboxylic acid could not be prepared by this procedure because of the insolubility of the acid in the solvents. ψ'-Amyl alcohol was esterified using diphenyl ether as the solvent and copper sulfate to absorb water of esterification.

Some pertinent properties of the experimental oils are compared in Table I with the requirements of specifications MIL-L-7808 and MIL-L-9236. Densities of all the diesters are above 1.5 and are attributable primarily to their fluorine contents. Boiling points of these diesters at 0.5 mm. of mercury vary from 334° F. for bis(ψ'-heptyl)2-phenylsuccinate to 392° F. for bis(ψ'-amyl) diphenyl ether dicarboxylate. Evaporation losses by ASTM Method D 972-51T vary according to their boiling points. Bis (ψ'-amyl) diphenyl ether dicarboxylate has the lowest evaporation loss in the 400° F. test. To obtain liquids with evaporation weight losses of less than 5% as required by specification MIL-L-9236, compounds boiling above 400° F. at

Table I. Properties of Fluorinated Esters

Compound	d_4^{20}	B. P., °F. at 0.5 Mm. Hg	Evap. Loss, Wt. %, 400° F.	Pour Point, °F.	Flash Point, °F.	S.I.T. °F.
Bis(ψ'-heptyl) 2-phenylsuccinate	1.640	334	95	–25	465	977
Bis(ψ'-heptyl) 2-phenylglutarate	1.616	363	57	–30	465	989
Bis(ψ'-amyl) diphenate	1.562	350	71	–5	450	1108
Bis(ψ'-heptyl) diphenate	1.642^a	372	34	95^b	500	1080
Bis(ψ'-amyl) diphenyl ether 4,4′-dicarboxylate	1.573^a	392	7.1	100^b	520	1138
MIL-L-7808 requirement	0.92^c	400^c	25	–75	400	750^c
MIL-L-9236 requirement	. . .	. . .	5	R^d	500	R^d

[a] Supercooled liquid.
[b] Freezing point.
[c] Not a requirement, typical property.
[d] Report, no specification requirement.

Table II. Viscometric Properties of Fluorinated Esters

Compound	Viscosity, Cs. at 400° F.	Viscosity, Cs. at 210° F.	Viscosity, Cs. at 100° F.	Temp., °F. for 13 000 Cs.	ASTM Slope 32° to 400° F.
Bis(ψ'-heptyl) 2-phenylsuccinate	0.96	6.07	83.0	2	0.99
Bis(ψ'-heptyl) 2-phenylglutarate	1.00	5.91	66.1	–10	0.95
Bis(ψ'-amyl) diphenate	1.23	10.3	236	30	0.96
Bis(ψ'-heptyl) diphenate	1.34	12.4	323	40^a	0.96
Bis(ψ'-amyl) diphenyl ether 4,4′-dicarboxylate	1.99	16.8	375	40^a	0.84
MIL-L-7808 requirement	0.8^b	3.0 (min.)	11.0 (min.)	–65	0.71^b
MIL-L-9236 requirement	3.0	R^c	R^c	R^c	. . .

[a] Below freezing point.
[b] Not a requirement, typical property.
[c] Report, no specification requirement.

0.5 mm. Hg will be required. Excepting bis(ψ'-heptyl) diphenate and bis(ψ'-amyl) diphenyl ether dicarboxylate, all the esters failed to crystallize and had viscous pour points. Pour points of the phenyl-substituted straight-chain acid esters are lower than those derived from the aromatic acids which contain two aromatic rings.

Flammability characteristics were evaluated by semimicro flash and fire points (*16*) and spontaneous ignition temperatures (S.I.T.) (*17*). Results with the semimicromethod agree with those obtained with the Cleveland open cut method within 10° F. Flash points of these partially fluorinated esters are all above 450° F., and the two higher boiling esters have flash points of 500° F. or above. Fire points are about 30° F. above the flash points. S.I.T.'s range from 977° to 1138° F.; esters of the aromatic acids have S.I.T.'s above 1000° F.

Viscometric properties are shown in Table II. Bis(ψ'-heptyl) 2-phenylsuccinate differs from the corresponding 2-phenylglutarate by only one methylene group, yet the longer chain glutarate ester has a considerably smaller temperature coefficient of viscosity as indicated by its smaller ASTM slope. Additional evidence of the marked effect of molecular structure on viscometric properties is shown by comparing the viscosities of bis(ψ'-heptyl) 2-phenylglutarate with the corresponding ester of diphenic acid. The latter compound is more than twice as viscous as the former at 210° F., although their molecular weights, 836 and 870, are comparable.

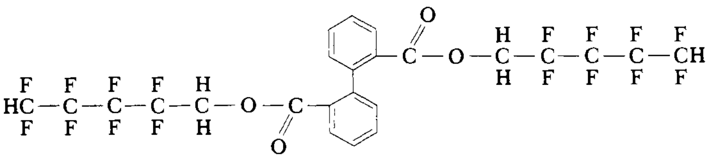
Another interesting comparison is between bis(ψ'-amyl) diphenate and bis(ψ'-amyl) diphenyl ether dicarboxylate. The former compound is the less viscous but has the larger temperature coefficient of viscosity. The average configurations of these two compounds are intermediate between their most extended configurations, shown below, and more tightly folded ones.

The diphenate is the shorter-chain compound and has a much smaller length–cross section ratio. Also, the ether linkage in the diphenyl ether dicarboxylate gives it greater flexibility. These structural differences are primarily responsible for the divergent viscometric properties of the two esters. Increasing the chain length of the fluorinated alkyl component in diphenate esters causes only a small increase in the length–cross-section ratio. Therefore, the diphenate ester of ψ'-heptyl alcohol would be expected to be more viscous than the ψ'-amyl ester but would not have appreciably better viscosity-temperature properties.

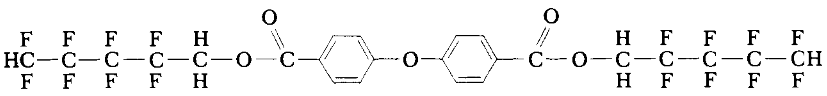
All of these partially fluorinated esters have kinematic viscosities below the minimum of 3 centistokes at 400° F. required by specification MIL-L-9236. Their absolute viscosities, a more fundamental unit in lubrication, will be larger than their kinematic viscosities, whereas liquids with densities less than 1.0 will have smaller absolute viscosities.

Oxidation stabilities of these partially fluorinated esters were studied by aerating 25-gram samples in the presence of copper, steel, and silver specimens. Tests were made at 437°, 482°, and 527° F.; results are summarized in Table III. Both the 2-phenylsuccinate and 2-phenylglutarate esters were badly oxidized after 168 hours at 437° F. as shown by their viscosity and neutralization number increases, and corrosivity to copper.

The corresponding esters of glutaric and 3-methylglutaric acids were stable at this temperature (*6*), so the introduction of a phenyl substituent in the 2-position of a straight-chain dibasic acid, apparently has an adverse effect on the oxidation stability of its esters. Although bis(ψ'-amyl) diphenyl ether dicarboxylate showed smaller oxidative changes, it was not considered sufficiently stable for use at higher temperatures. Only bis(ψ'-amyl) diphenate was resistant to oxidation at this temperature.



Bis(ψ'-amyl)diphenyl ether 4,4'-dicarboxylate or bis(1*H*, 1*H*, 5*H*-octafluoropentyl)4,4'-oxydibenzoate



Bis(ψ'-amyl)2,2'-diphenate or bis(1*H*,1*H*,5*H*-octafluoropentyl)-2,2'-biphenyldicarboxylate

Table III. Dynamic Oxidation Studies on Fluorinated Esters

Compound	Test Period, Hr.	% Visc. Increase, 100° F.	Neut. No. Increase		Metal Wt. Change, Mg./Sq. Cm.			Sample Appearance
			Volatile	Nonvolatile	Cu	Steel	Ag	
			At 437° F					
Bis(ψ'-heptyl) 2-phenylsuccinate	168	. . .[a]	17.8	7.2	- 4.6	+ 0.2	- 0.4	Opaque; black
Bis(ψ'-heptyl) 2-phenylglutarate	168	. . .[a]	16.0	13.2	- 6.9	- < 0.1	- 0.5	Opaque; dark brown
Bis(ψ'-amyl) diphenate	168	6.0	1.3	0.01	- 0.15	+ < 0.1	+ < 0.1	Clear; light amber
Bis(ψ'-amyl) diphenyl ether 4,4'-dicarboxylate	168	87	3.3	4.0	- 0.62	+ < 0.1	- 0.1	Opaque; dark brown
			At 482° F.					
Bis(ψ'-heptyl) 2-phenylglutarate	72	. . .[a]	3.2	4.6	- 1.1	+ 0.2	- < 0.1	Opaque; dark amber
Bis(ψ'-amyl) diphenate	168	10	1.7	0.32	- 0.32	+ < 0.1	+ < 0.1	Clear; amber
			At 527° F.					
Bis(ψ'-amyl) diphenate	72	15	4.5	0.17	- 0.40	+ < 0.1	+ < 0.1	Clear; amber
Bis(ψ'-heptyl) diphenate	72	15	4.2	0.23	- 0.38	+ < 0.1	+ < 0.1	Clear; amber
MIL-L-9236A requirements for 500° F. test	48	-5 to +25	. . .	R[b]	± 0.4[c]	± 0.2[c]	± 0.2[c]	. . .

[a] Fluid was very viscous but too darkly colored to measure.
[b] Report, no specification requirement.
[c] Maximum.

At 437° F., a MIL-L-7808 oil will be oxidized to a gel in less than 72 hours.

At 482° F. bis(ψ'-amyl) diphenate showed no more evidence of oxidative attack than at 437° F. The diphenate esters of both ψ'-amyl and ψ'-heptyl alcohols were studied at the next higher temperature, 527° F. Their properties after oxidation for 72 hours are compared in Table III with the requirements of specification MIL-L-9236 for a 48-hour test at 500° F. Viscosity changes were well within the specification limits. Although there is no requirement as to neutralization number increases, the increases of only 0.17 and 0.23 indicate that oxidative changes were minor. Copper weight losses were just within the specification requirements; those for the steel and silver specimens were negligible. Because of the small test cell used, titanium, aluminum alloy, and magnesium alloy specimens were not included in the test system. After the 72-hour test, the esters were amber colored but still clear, and no insolubles had precipitated. Diphenate esters of ψ'-amyl and ψ'-heptyl alcohols are much more stable to oxidation than required by specification MIL-L-9236 and are promising candidates for lubricating applications at 500° F.

A variety of conventional antioxidant types, including phenols, amines, sulfur, and selenium compounds, have been investigated for antioxidant activity in these esters. The addition of such compounds to the partially fluorinated esters stable to temperatures above 400° F. had an adverse effect upon the oxidation stability of the fluorinated esters. Since the antioxidant activity of these compounds is due to their ability to react with peroxy radicals, it appears that either the fluorinated esters are not oxidized through a peroxide mechanism, or the antioxidants themselves are oxidized to unreactive compounds at the test temperature.

Resistance to pyrolysis is an important requisite of high temperature lubricants. Thermal stability of bis(ψ'-amyl) diphenate was studied by sealing a 25-gram sample under nitrogen in a borosilicate glass vial in the presence of a steel specimen. After 24 hours at 600° F., the vial was cooled and the ester examined for changes in properties. Its color had changed from water-white to light brown, and its viscosity at 100° F. was 4% lower than initially. Assuming that the neutralization number increase of 0.5 was due entirely to the generation of the parent acid, only 0.3% of the bis(ψ'-amyl) diphenate was decomposed during the test. There was no change in weight of the steel test specimen and no evidence of pitting or corrosion. This ester has a stable temperature almost 100° F. above that of its unfluorinated analog. The absence of hydrogen from the beta carbon atom of the fluorinated alcohol is responsible for its improved stability because this absence blocks the low energy pyrolysis route via the cyclic intermediate (*13*).

As it is almost impossible to exclude water from lubricating systems, hydrolytic stability is required of lubricants. This property was evaluated by a modification of the method of military specification MIL-H-8446 (USAF) (*12*), in which the water to oil ratio was increased from 25:75 to 75:25. The water and oil were sealed in a 6-ounce beverage bottle in the presence of a copper specimen and the bottle rotated end-over-end at 5 r.p.m. for 48 hours at 200° F. The results (Table IV) reveal that the diphenate esters of fluorinated alcohols are stable to hydrolysis under these conditions, because there was only a negligible increase in acidity, and no insolubles were formed. Viscosity changes were less than 1% and changes in copper specimen weights were less than the specification maximum, 0.5 mg. per sq. cm.

Table IV. Hydrolytic Stabilities at 200° F.

Compound	Metal Wt. Change, Mg./Sq. Cm.	Neut. No.		Visc. Change 210°F., %	Insol., Wt. %
		Oil	Water		
Bis(ψ'-amyl) diphenate	– < 0.1	Nil	0.02	– 0.1	< 0.1
Bis(ψ'-heptyl) diphenate	– 0.2	Nil	0.02	+ 0.4	< 0.1
MIL-H-8446 requirements	± 0.5	0.5	0.5	± 20	0.5

CONCLUSIONS

Aromatic acid esters of fluorinated alcohols have oxidation stabilities one order of magnitude better than those of aliphatic dibasic acids. The diphenates are stable to oxidation at 527° F., to pyrolysis at 600° F. and are not hydrolyzed after 48 hours at 200° F. Although they are more volatile than desired and are too viscous for low temperature applications, their exceptional stabilities and good lubricities recommend them for use as high-temperature lubricants. Other promising high temperature applications are as hydraulic fluids, heat exchange fluids, and as base stocks for greases. Diphenic acid is not commercially available at present, but it can be prepared by oxidizing phenanthrene (*5*, *14*, *15*), a large volume by-product of the coal-tar industry (*4*). Further research on aromatic acid esters of fluorinated alcohols will probably result in products of lower volatilities and better viscosity-temperature properties but comparable oxidation and thermal stabilities.

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