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ANTIOXIDANT ACTION OF METALS AND ORGANOMETAL COMPOUNDS IN FLUOROESTERS AND POLYPHENYL ETHERS

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ABSTRACT

Aircraft gas turbine engines in the Mach 2 to 3 range, now in the development stage, will require lubricants considerably more stable to oxidation (to 500°F) than present jet engine lubricants. Fluoroesters and polyphenyl ethers are among the potential high-temperature lubricants being considered for this application. It has been discovered at NRL that a high degree of oxidation stability can be imparted to these fluids by a variety of metals and organometal compounds.

Three fluoroesters and a polyphenyl ether [bis(phenoxy-phenoxy)-benzene] were subjected to oxidizing conditions at relatively high temperatures (437° to 650°F) in the presence and absence of the metals and organometal compounds, and data were obtained to show the oxidation inhibition due to the additive. These data included viscosity change at 100°F, neutralization number increase, evaporation loss, corrosivity to metals, and sample appearance.

At 437°F copper and steel improved the stability of the fluoroalcohol (ψ'-alkyl) esters of 3-methylglutaric and camphoric acids. At 482°F, the camphorate was substantially stabilized by copper, barium, monel, and chromium; by toluates or benzoates of barium, nickel, chromium, cobalt, manganese, praseodymium, titanium, ytterbium, and strontium; by cerium disalicylalpropylene diamine and cerium (ψ'-heptyl) hydrogen-3-methylglutarate; and by the copper salts of perfluoroundecanoic acid, (ψ'-heptyl) hydrogen 3-methylglutarate, toluic acid, and phenylstearic acid.

Bis(ψ'-amyl)2,2′-diphenate possessed generally high inherent stability up to 617°F. Some HF was evolved, however, which was greatly reduced by the presence of copper. At 642°F the ester underwent extensive pyrolysis, which the inhibitors did not prevent.

The polyphenyl ether, bis(phenoxy-phenoxy)benzene, was effectively protected from oxidation at 600°F by copper, cupric toluate, and ceric toluate. At 650°F effective inhibitors were barium metal, and the toluates or benzoates of barium, manganese, cerium, nickel, lead, praseodymium, cobalt, chromium, titanium, and ytterbium.

The degree of stability given to these fluids increases interest in them as potential high-temperature lubricants for aircraft gas turbines in the Mach 2 to 3 range.

PROBLEM STATUS

This is an interim report; work on this problem is continuing.

AUTHORIZATION

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ANTIOXIDANT ACTION OF METALS AND ORGANOMETAL COMPOUNDS IN FLUOROESTERS AND POLYPHENYL ETHERS

INTRODUCTION

Power requirements for jet aircraft have increased manyfold since World War II, concomitantly imposing more stringent demands on engine lubricants. One property critical to the satisfactory performance of these lubricants is resistance to oxidation.

Experience with petroleum oils and aliphatic diester fluids has taught that if metals have any effect on lubricant stability, it is generally adverse. Certain metals, copper being a notable example, are considered to be particularly deleterious in this respect. It is customary, therefore, for laboratory tests which attempt a realistic measure of the oxidation stability of lubricants to specify the inclusion of the metals of construction pertinent to the application for which the fluid is to be used.

The present investigation is concerned with a study of the oxidative stability of fluoroesters and aromatic polyethers, both potentially useful as high-temperature jet aircraft engine lubricants, and, more particularly, with the unexpected resistance to oxidation at high temperatures imparted to them by certain metals and salts. The results are reminiscent of those obtained during a parallel investigation of the high-temperature inhibition of silicones (4).

There are few data available on the use of organometal compounds as oxidation inhibitors. Naphthenates of copper and cobalt have been reported to enhance synergistically the activity of phenolic antioxidants in lubricating oils (14). Dispersions of inorganic salts of alkali metals are reported to have antioxidant properties in lubricant compositions containing petroleum and synthetic esters (22).

To place in proper perspective the oxidation stability requirements for high-temperature jet engine lubricants, it will be useful to review briefly the development of both the engines and the lubricants. Early jet engines, such as the J-33 and J-34, developed thrusts of 3,000 to 6,000 lb. Sump temperatures were of the order 130° to 150°F and oil-out temperatures at the bearings were 210° to 260°F. These engines were lubricated adequately with petroleum oils, grades 1005 and 1010, conforming to military specifications (24). The specification corrosion-oxidation test required that the lubricant be stable at 250°F for 72 hours, which may be taken as an indication of the stability required of them under service conditions. In the early 1950's engines (e.g., J-57 and J-79) in the Mach 1 to 2 range, with thrusts of from 10,000 to 16,000 lb came into general use. These engines currently power the majority of U. S. firstline fighter aircraft. Sump temperatures range from 230° to 275°F, and oil-out temperatures from 340° to 400°F. The oxidative stresses to which the lubricants for these engines are subjected are of such magnitude that petroleum-based fluids cannot be employed because of their rapid deterioration. Aliphatic ester-based fluids (2,9,11), however, when properly inhibited with an efficient antioxidant such as phenothiazine (21), have proved to be eminently satisfactory lubricants for these engines. The specification (17) covering these fluids requires that they withstand a corrosion-oxidation test at 347°F for 72 hours.

Jet engines such as the J-58 and J-93, now in the development stage, are in the Mach 2 to 3 range and have thrusts of from 18,000 to 26,000 lb. Sump temperatures range from 300° to 450°F, and oil-out temperatures may attain 650°F. Although a lubricant specification (16) for these engines has been written, based on trimethylolpropane-type esters, no oils

presently qualify under it. In the original version of the specification, a 500°F corrosion-oxidation test was listed but proved to be of no practical value because no oils could be found to meet the stability requirements (6). No corrosion-oxidation requirement is incorporated in the latest version of this specification (16). In all of the specifications noted above, the corrosion-oxidation tests provide for various metal specimens to be present, both to simulate engine conditions and to catalyze oxidative breakdown of the lubricants.

EXPERIMENTAL PROCEDURE

Because some of the experimental fluids for this study were available only in limited quantities, it was not feasible to evaluate their corrosion-oxidation stability according to current standard methods, which require up to several hundred milliliters per run. Therefore, cells were employed which require sample volumes of only 20 ml (2,23). The cells were constructed of borosilicate glass, as are all corrosion-oxidation cells described in military specifications, and were maintained at the desired test temperatures in thermostatted aluminum block furnaces. Clean air, freed of CO_2 and moisture, was bubbled through the samples at the rate of 1 cc gas/gm sample/min. Metal specimens present generally had surface areas of 10 square centimeters.

The data obtained on oxidized oils generally included viscosity change at 100°F, neutralization number increase, evaporation loss, corrosivity to metals, and sample appearance. In a number of fluoroester runs the effluents were passed into water traps, after which the HF contents of the trap liquids were determined by the lead chlorofluoride method.

All of the compounds employed as additives in the study were prepared at this Laboratory. Synthesis of the copper and cerium salts of organofluorine-containing compounds has been reported (25). Except for cerium toluate, all of the metal benzoates and toluates were prepared by a double decomposition reaction between aqueous solutions of the sodium salts of the organic acid and the chloride of the appropriate metal. Ceric toluate was prepared by the reaction of ceric isopropoxide with toluic acid (3). Ceric disalicylidenepropylenediamine, Ce(DSPD), was prepared by treating ceric ammonium nitrate with sodium toluate; the resulting basic ceric toluate was reacted with DSPD to form ceric (DSPD) (3). Even in the low concentrations employed, none of these additives was completely soluble in the test fluids. It was therefore difficult to determine at the conclusion of the majority of runs whether the insoluble material found was undissolved additive, or sludge formed during the oxidation. In general, all such material was reported as sludge.

OXIDATION STUDIES

Fluorinated Esters

Combination of Metals Present – Previous investigations have indicated that esters from polybasic acids and fluoroalcohols (ψ'-alcohols) of the general formula $H(CF_2CF_2)_n CH_2OH$ were unusually stable to oxidation, even in the absence of conventional inhibitors (13,15,19). In those studies the fluids were in contact with a combination of some of the metals used in specification oxidation-corrosion tests (16,17), generally copper, steel, and silver-plated steel. In Table 1, oxidation experiments under these conditions are summarized for esters of 3-methylglutaric, camphoric, and 2,2'-diphenic acids. Esters of both 3-methylglutaric and camphoric acids demonstrated excellent resistance to oxidation at 437°F as evidenced by small viscosity changes and acid numbers, minimum fluoride evolution (reported for the camphorate only), and excellent sample appearance. At 482°F, oxidative changes in the fluids were evident. Fluoroesters from the more stable aromatic acids are more oxidation resistant than their analogs from aliphatic acids. Thus, after 72 hours at 527°F, bis(ψ'-amyl)2,2'-diphenate showed little degradative change.

Table 1
Oxidation Stability of Fluoroesters With and Without Metal Combinations Present

Temp (°F)	Test Period (hr)	*Metal Wt Chge (mg/cm²)			Oil Loss (wt percent)	Viscosity Increase at 100°F (percent)	Neutralization Number Increase	mg F/gm	Final Sample Appearance
		Copper	Steel	Silver-Plated Steel					
Bis(ψ'-amyl)3-Methylglutarate									
437	168	-0.3	<+0.1	<-0.1	24	6.3	7.2	†	Clear, slight lacquer
437	168	-	-	-	65	†	215	†	Very dark, sludge, lacquer
Bis(ψ'-Heptyl)3-Methylglutarate									
437	168	<-0.1	<-0.1	nil	†	0.5	0.07	†	Clear, amber, slight lacquer
437	168	-	-	-	34	72	21	†	Very dark, sludge, lacquer
482	168	-0.1	+0.6	nil	38	1.8	1.2	†	Opaque, light lacquer
482	168	-	-	-	36	46	11	†	Opaque, heavy sludge, lacquer
Mixed Fluoroalcohol Camphorate									
392	168	-	-	-	12	†	17	2.1	Opaque
437	168	nil	nil	nil	7.1	5.2	0.06	0.19	Clear, light yellow
437	168	-	-	-	27	64	7.7	4.1	Opaque, heavy sludge
482	168	-0.2	<+0.1	-0.1	23	†	5.4	3.2	Opaque, dark brown fluid
482	168	-	-	-	76	Gelled	†	2.9	Gelled
482	72	-	-	-	39	Gelled	†	†	Gelled
Bis(ψ'-amyl)2,2'-Diphenate									
527	72	-0.4	<+0.1	<-0.1	0.2	3.4	0.11	0.11	Light amber
527	72	-	-	-	†	3.9	0.58	5.3	Light amber

*A dash indicates the absence of the specified metal.
†Not determined.

No Metals Present - When, in the course of the present investigation, the experiments summarized previously were repeated, except that no metals were present, an unexpected and significant decrease in the stability of the fluids resulted (Table 1). The more outstanding of these stability changes due to the absence of metals are noted below.

1. (Bis(ψ'-amyl)3-methylglutarate at 437°F for 168 hours. The neutralization number rose from 7.2 to 215.

2. Bis(ψ'-heptyl)3-methyglutarate at 437°F for 168 hours. The 100°F viscosity increase rose from 0.5 to 72 percent and the neutralization number from 0.07 to 21. At 482°F, the viscosity increase rose from 1.8 to 46 percent and the neutralization number from 1.2 to 11. Although the viscosity increase and generation of acids were greater at 437° than at 482°F, there was much more sludge formed at the higher temperature, a possible indication that the oxidation reactions followed different courses.

3. The camphorate from mixed fluoroalcohols at 437°F for 168 hours. The viscosity increase rose from 5.2 to 64 percent, the neutralization number from 0.06 to 7.7, and the evolved fluoride from 0.19 to 4.1 mg/g sample. (At 437°F with the stated metals present, this ester was more stable with regard to viscosity, acidity, and fluoride evolution than it was at 392°F with no metals present.) Exposure to 482°F for 72 hours or longer caused the camphorate without metals to gel; it was still fluid, however, after 168 hours at this temperature with the three metals present.

4. Bis(ψ'-amyl)2,2'-diphenate at 527°F for 72 hours. The fluoride evolved increased from 0.11 to 5.3 mg/g sample although in other respects no significant differences were noted.

Individual Metals, or Organocopper Compounds Present - It was apparent from the results that the stabilities of the fluoroalcohol esters of 3-methylglutaric, camphoric, and diphenic acids are measurably improved by contact with the combination of steel, copper, and silver-plated steel. The analogy to be drawn between these results and those from previous investigations on the high-temperature stabilization of silicone fluids by both metals and organometal compounds was inescapable. In these latter studies it was demonstrated that the stable life of lightly phenylated polymethyl silicones was extended severalfold when they were in contact with a combination of chelating agents and certain metals, most notably copper (4). To separate the effects produced in the fluoroesters by each of the three metals previously employed in combination, the fluids were subjected to oxidation in the presence of the individual metals. Following out the analogy to the silicones, these fluids were also oxidized with organocopper compounds present.

In Table 2 are summarized experimental results demonstrating that both copper metal and copper compounds impart a high degree of oxidation stability to fluoroesters from both camphoric and 3-methylglutaric acids; conversely, steel, stainless steel, or organocerium compounds have little or no beneficial effects. For comparison, data on the stability of the fluids with neither metals nor salts present are included in Table 2.

Marked beneficial responses to copper were shown by bis(ψ'-amyl)3-methylglutarate at 437°F, and by the corresponding bis(ψ'-heptyl) compound at 482°F. After 168 hours, the neutralization number of the former compound in the presence of copper was only 0.03 as compared with 215 in the absence of metals. Similarly, with copper present the neutralization number of the latter compound was 0.18 as compared with 11 in its absence, and the percent viscosity increase was 4.6 instead of 46. Both copper (ψ'-heptyl)3-methylglutarate and copper phenylstearate stabilized bis(ψ'-heptyl)3-methylglutarate, but not as effectively as did copper metal.

Response of the camphorate ester to copper metal was excellent during a 437°F, 168-hour run, as evidenced by small viscosity and acidity increases, minimal evolution of

Table 2
Antioxidant Activity of Copper Metal and Copper Salts in Fluoroesters

Temp (°F)	Test Period (hr)	Additive* (wt percent)	Metal Wt Chge (mg/cm²)†			Oil Loss (wt percent)	Viscosity Increase at 100°F (percent)	Neutralization Number Increase	mg F/gm	Final Sample Appearance
			Copper	Steel	Silver-Plated Steel					
Bis(ψ'-amyl)3-Methylglutarate										
437	168	-	-	-	-	65	‡	215	‡	Very dark, sludge, lacquer
437	168	-	<-0.1	-	-	9.2	2.5	0.03	‡	Clear, light yellow
Bis(ψ'-Heptyl)3-Methylglutarate										
482	168	-	-	-	-	36	46	11	‡	Opaque, heavy sludge, lacquer
482	168	-	-0.6	-	-	34	4.6	0.18	‡	Opaque, medium lacquer
482	168	Cu(ψ'-C_7) 3-megl(0.1)	-	-	-	31	20	3.0	‡	Opaque, dark amber
482	168	Cu(PS)(0.1)	-	-	-	‡	18	7.6	‡	Opaque, black
Mixed Fluoroalcohol Camphorate										
437	168	-	-	-	-	27	64	7.7	4.1	Opaque, heavy sludge
437	168	-	0.2	-	-	9.1	3.5	0.18	0.18	Clear, amber, slight sludge
437	168	-	-	<+0.1	-	49	Gelled	‡	1.5	Gelled
437	168	-	-	-	-0.2	36	‡	16	2.7	Opaque, tarlike
437	168	Cu(PS)(0.03%)	-	-	-	16	7	0.84	0.27	Clear, dark amber
437	168	Cu(Tol)(0.03%)	-	-	-	11	2.7	0.06	0.2	Clear, light yellow, slight lacquer
437	168	Cu(ϕ-C_{11})(0.5)	-	-	-	26	31	1.5	nil	Very dark
482	168	-	-	-	-	76	Gelled	‡	2.9	Gelled
482	168	-	+2.9	-	-	57	215	8.1	1.9	Opaque
482	168	-	-	+1.5	-	94	Gelled	‡	1.5	Gelled
482	168	-	-	+0.5¶	-	94	Gelled	‡	1.7	Gelled
482	72	-	-	-	-	39	Gelled	‡	‡	Gelled
482	72	-	-0.3	-	-	26	2.7	5.2	‡	Opaque, dark amber
482	72	Cu(ϕ-C_{11})(0.5)	-	-	-	20	111	6.0	nil	Very dark
482	72	Cu(ψ'-C_7) H-3-megl(0.5)	-	-	-	12	1.6	1.7	‡	Very dark
482	72	Cu(Tol)(0.1)	-	-	-	20	20	1.4	‡	Opaque
482	72	Cu(PS)(0.1%)	-	-	-	23	13	1.6	‡	Opaque
Bis(ψ'-amyl)2,2'-Diphenate										
617	72	-	-	-	-	7.6	12	4.4	1.8	Opaque, lacquer
617	72	-	+0.1	-	-	16	19	0.6	0.4	Dark amber, clear
617	72	Cu(Tol)(0.5)	-	-	-	27	77	1.0	4.0	Opaque, sludge, lacquer
642	72	-	-	-	-	‡	-90	7.4	3.0	Opaque, lacquer
642	72	-	+0.2	-	-	13	-92	15	nil	Opaque, lacquer

* Additive abbreviations
Cu(ψ'-C_7)3-megl - Copper (II) (ψ'-heptyl)3-methylglutarate
Cu(PS) - Copper (II) phenylstearate
Cu(Tol) - Copper (II) toluate
Cu(ϕ-C_{11}) - Copper (II) perfluoroundecanoate
Cu(ψ'-C_7)H-3-megl - Copper (II) (ψ'-heptyl)hydrogen 3-methylglutarate.
† A dash indicates the absence of the specified metal.
‡ Not determined.
§ Concentration of metal.
¶ Stainless steel.

fluoride, and satisfactory sample appearance. By way of contrast, steel appeared to accelerate breakdown of the ester, causing it to gel; silver-plated steel was essentially inert, the ester reacting as though no metal or additive were present. Three copper salts - the phenylstearate, the toluate, and the perfluoroundecanoate - offered substantial improvement to the stability of the ester. The copper perfluoroundecanoate differed somewhat from that of other additives insofar as it permitted a larger viscosity increase than did the other additives but at the same time completely prevented the evolution of fluorides.

As already noted, 72 hours at 482°F caused gelation of the camphorate. With copper metal present, however, the viscosity increase was only 2.7 percent; even after a 168-hour exposure to this temperature the fluid did not gel, although the viscosity increase was 215 percent. Substantial improvement in stability with respect to viscosity and acidity increases was imparted to the camphorate ester by the following copper salts: perfluoroundecanoate, (ψ'-heptyl)hydrogen 3-methylglutarate, toluate, and phenylstearate. On balance, the copper (ψ'-heptyl)3-methylglutarate appeared to be the most effective of these additives, permitting viscosity and neutralization number increases of only 1.6 percent and 1.7 respectively. The effect of copper perfluoroundecanoate at 482°F was similar to that at 437°F; it permitted a substantial viscosity increase but prevented the generation of volatile fluorides.

The aromatic ester bis(ψ'-amyl)2,2'-diphenate is inherently so stable that improvement with additives is difficult. Even at 617°F, after 72 hours the 100°F viscosity increase was only 12 percent, the neutralization number increase 4.4, and the total fluoride evolved 1.8 mg/g sample (Table 2). When copper was introduced into the fluid, fluoride evolution and acidity decreased, but the viscosity increase was essentially unchanged. Copper toluate produced similar ambiguous results. When the test temperature was increased to 642°F, the compound underwent extensive pyrolysis, as shown by the viscosity decrease of 92 percent. Pyrolysis also occurred when copper metal was present.

Miscellaneous Metals and Organometal Compounds - In view of these encouraging results which resembled previous data obtained when silicones were stabilized with various metals, metal salts, and metal chelates (4,12), the antioxidant actions of a variety of metals and of salts in addition to copper were ascertained in the camphorate of the fluoroalcohol. The results are listed in Table 3 and, with those for ceric DSPD excepted, refer to 72-hour runs at 482°F. Of the bulk metals studied, barium and monel were the most effective, with chromium somewhat less so. Nickel apparently had no antioxidant activity, permitting the fluid to gel. Cobalt was employed in powder form and it could not be determined whether the tarlike appearance of the fluid after oxidation resulted from thickening of the fluid due to dispersion of the metal, or deterioration. The effects of the benzoates or toluates of the following metals were determined: barium, cerium, nickel, chromium, cobalt, manganese, praseodymium, titanium, ytterbium, and strontium. All displayed inhibitory activity, the toluate of barium in 0.1 percent concentration being the most effective, particularly with respect to the cleanliness of the fluid after the run. The salts of praseodymium, lead, chromium, and manganese were relatively the least effective. The ceric salts of disalicylalpropylene diamine (437°F for 168 hours) and (ψ'-heptyl) hydrogen 3-methylglutarate (482°F for 72 hours) were as effective in preventing a large viscosity increase as were the better toluates.

It is apparent from these data that a variety of metals with either single or multiple valences, and metal salts, impart significant oxidative stability to fluoroesters from aliphatic acids.

Polyphenyl Ethers

Among the more attractive candidates for use as high-temperature jet engine oils are the polyphenyl ethers, which have been reported to have good resistance to oxidation,

Table 3

Antioxidant Activity of Miscellaneous Metals and Organometal Compounds in Fluoroalcohol Camphorate (482°F for 72 hours)

Metal or Metal-Salt* (wt percent)	Metal Wt Chge† (mg/cm^2)	Oil Loss (wt percent)	Viscosity Increase at 100°F (percent)	Neutralization Number Increase	mg F/gm	Final Sample Appearance
	-	39	Gelled	§	§	Gelled
Nickel	<+0.1	31	Gelled	§	1.6	Gelled
Monel	<+0.1	§	8.3	7.8	3.0	Opaque, black, sludge, lacquer
Chromium	<+0.1	§	86	14	2.2	Opaque, black, sludge, slight lacquer
Cobalt‡	§	39	§	§	1.9	Tarlike
Barium	§	22	36	5.3	2.0	Dark amber, slight sludge and lacquer
Ba(Tol)(0.1)	-	16	7.5	5.7	1.9	Clear, dark amber
Ba(Tol)(0.5)	-	20	40	9.7	1.8	Opaque, dark amber, sludge
Ce(DSPD)(0.1)¶	-	28	8.3	9.5	0.47	Very dark
Ce(ψ'-C_7)H-3-Megl (0.5)	-	12	13	11	2.2	Opaque, sludge, lacquer
Pb(Benz)(0.1)	-	26	825	9.5	1.2	Opaque, black, sludge
Ni(Benz)(0.1)	-	16	32	7.5	2.4	Opaque, black
Cr(Benz)(0.1)	-	35	§	§	2.0	Tarlike
Cr(Tol)(0.1)	-	26	381	9.8	2.8	Opaque, black, sludge
Co(Benz)(0.1)	-	18	46	15	1.0	Opaque, black
Mn(Benz)(0.1)	-	40	560**	11	2.1	Opaque, black, sludge
Pr(Tol)(0.1)	-	37	§	§	2.6	Tarlike
Ti(Tol)(0.1)	-	26	135	14	2.8	Opaque, black, sludge, lacquer
Yb(Tol)(0.1)	-	23	141	13	1.4	Opaque, black, sludge, lacquer
Sr(Tol)(0.1)	-	23	43	14	2.4	Opaque, slight sludge
Sr(Tol)(0.05)	-	20	23	10	2.2	Opaque, slight sludge

*Additive abbreviations

Ce(DSPD) - Cerium (IV) disalicylalpropylene diamine
Ce(ψ'-C_7)H-3-Megl - Cerium (IV) (ψ'-heptyl)hydrogen 3-methylglutarate
Pb(Benz) - Lead (II) benzoate
Ni(Benz) - Nickel (II) benzoate
Cr(Benz) - Chromium (III) benzoate
Cr(Tol) - Chromium (III) toluate
Co(Benz) - Cobalt (II) benzoate
Mn(Benz) - Manganese (II) benzoate
Pr(Tol) - Praseodymium (III) toluate
Ba(Tol) - Barium (II) toluate
Ti(Tol) - Titanium (IV) toluate
Yb(Tol) - Ytterbium (III) toluate
Sr(Tol) - Strontium (II) toluate.

†A dash indicates the absence of metal.
‡In powder form.
§Not determined.
¶Test conditions 437°F for 168 hours.
**Approximate.

pyrolysis, and radiation (7,8,18,26). These compounds have reasonably good viscosity-temperature characteristics, high-flash points, and low-evaporation rates, provided their molecular weights are in the proper range. The meta isomer of bis(phenoxy-phenoxy)-benzene has received much attention because in addition to its possessing the desirable attributes listed above, it is a liquid (pour point of 40°F), in contrast to its ortho and para isomers, which are high-melting solids. There have been limited data reported on anti-oxidants to improve the stability of the polyphenyl ethers. Some promise has been shown by organotin compounds, oxides of copper, and metal acetylacetonoates (8,26).

For the present study, polyphenyl ether samples were obtained from two commercial sources. Both were mixed isomers of bis(phenoxy-phenoxy)benzene, with the meta isomer predominating. The fluids were equivalent as regards their stability and response to antioxidants. The reactivities of these fluids were not perceptibly affected by percolation through adsorbents to remove polar impurities. Results of oxidation stability studies on these ethers are shown in Table 4. As was the case with the fluoroesters, the organometal additives were essentially insoluble in the ether.

After 72 hours at 500°F, with no metals present, the ether was essentially unchanged. With a test temperature of 572°F, the fluid became too thick for a viscosity measurement. The ether was oxidized to a gel when exposed to 600°F for 48 hours.

Some improvement in stability was imparted to the ether at 600°F when strips of either steel or stainless steel were present in the oxidation cell. In 48-hour runs viscosity increases were of the order of 150 to 350 percent and the neutralization numbers approximately 0.5. More marked reduction of viscosity change was given by copper metal; the neutralization number increases, however, showed little improvement over those runs with only steel present. The very small neutralization number and viscosity increases obtained with the copper-steel combination might be indicative of synergistic action, but the reproducibility of these test results is not sufficiently reliable to justify this conclusion. When silver-plated steel was introduced into the fluid, the stability imparted was of the same order as when copper metal was present.

The effect of individual metals on the stability of the ether at 650°F was determined. In 48-hour runs, only barium, of the metals investigated, was at all effective; it permitted a viscosity increase of 256 percent and a neutralization number of 1.0. Neither copper, steel, nickel, monel, nor chromium prevented gelation of the fluid. With cobalt powder present, the fluid presented a tarlike appearance after oxidation, as was the case previously with the camphorate ester.

At 600°F the ether displayed a significant response to the stabilizing effect of copper toluate, and copper toluate together with a strip of steel; in 48-hour runs the viscosity increases and neutralization numbers were remarkedly small, averaging 12 percent and 0.17 respectively. However, when the run was extended to 168 hours, the combination of copper toluate and steel did not prevent gelation. A marked degree of oxidation stability was likewise imparted to the ether by ceric toluate in 0.05 percent concentration; after 48 hours at 600°F the neutralization number increase was of the order of 1.0 and the 100°F viscosity increase was 81 percent. Although very little additional toluate appeared to go into solution when the concentration was raised to 0.1 percent, the neutralization number was one-third and the viscosity increase one-half that of the ether with the lower concentration of additive.

At 650°F, the toluates or benzoates of barium, cerium, nickel, lead, praseodymium, manganese, cobalt, chromium, titanium, and ytterbium each displayed significant anti-oxidant activity. On balance, manganese benzoate and barium toluate (despite the relatively large neutralization numbers that resulted) offered the most substantial protection to the ether primarily because in both instances the oil was clear and substantially free of sludge, and did not incur a large viscosity increase. Of those additives which displayed

Table 4
Antioxidant Activity of Metals and Organometal Compounds in Bis(phenoxy-phenoxy)benzene

Temp (°F)	Test Period (hr)	Metal or Metal-Salt* (wt percent)	Metal Wt Chge† (percent)	Oil Loss (wt percent)	Viscosity Increase at 100°F (percent)	Neutralization Number Increase	Final Sample Appearance
500	72	-	-	1.0	5.8	0.09	Dark amber
572	72	-	-	7.1	‡	0.38	Opaque, black
600¶	48		-	2.7	Gelled	§	Gelled
600	48	-	-	2.8	Gelled	§	Gelled
600¶	48	Steel	<+0.1	1.8	132	0.47	Opaque, black
600	48	Steel	nil	2.8	239	0.49	Opaque, black
600¶	48	Copper	-0.3	<1.0	96	0.45	Opaque, black
600	48	Copper	-0.1	3.6	81	0.41	Opaque, black
600	48	Copper	+0.2	§	22	0.28	Opaque, black
		Steel	+0.1				
600	48	Silver-plated steel	<-0.1	<1.0	114	0.47	Opaque, black
600	48	Steel**	+0.1	5.1	361	0.66	Opaque, black
600	48	Cu(Tol)(0.1)	-	8.9	11	0.17	Opaque, black, sludge
600	48	Cu(Tol)(0.1)	-				
		Steel	-.1	14	14	0.15	Opaque, black, sludge
600	168	Cu(Tol)(0.1)	-				
		Steel	+0.1	15	Gelled	§	Gelled
600	48	Ce(Tol)(0.05)	-	3.4	81	0.98	Opaque, black, sludge
600	48	Ce(Tol)(0.1)	-	§	26	0.39	Opaque, black, sludge
650	48	Copper	††	10	Gelled	§	Gelled
650	48	Steel	††	3.5	Gelled	§	Gelled
650	48	Barium	§	4.0	256	1.0	Opaque, amber
650	48	Nickel	§	4.0	Gelled	§	Gelled
650	48	Cobalt‡‡	§	4.8	§	§	Tarlike
650	48	Monel	-0.1	7.2	Gelled	§	Gelled
650	48	Chromium	<-0.1	6.4	Gelled	§	Gelled
650	48	Ce(Tol)(0.1)	-	2.3	27	nil	Opaque, black, sludge
650	48	Cu(Tol)(0.1)	-	4.9	Gelled	§	Gelled
650	48	Ni(Benz)(0.1)	-	4.0	127	0.03	Opaque, amber, slight sludge
650	48	Pb(Benz)(0.1)	-	6.7	279	0.06	Opaque, amber, slight sludge
650	48	Pr(Tol)(0.1)	-	3.8	63	0.06	Opaque, amber, sludge
650	48	Mn(Benz)(0.1)	-	10	52	0.09	Clear, green-amber
650	48	Co(Benz)(0.1)	-	6.4	83	0.08	Opaque, amber, sludge
650	48	Cr(Tol)(0.1)	-	4.0	130	0.18	Opaque, amber, sludge, lacquer
650	48	Cr(Benz)(0.1)	-	3.6	103	0.2	Opaque, amber, sludge
650	48	Ba(Tol)(0.1)	-	1.2	65	0.80	Clear, amber
650	48	Ba(DNNS)(0.1)	-	3.2	Gelled	§	Gelled
650	48	Ti(Tol)(0.1)	-	4.0	353	0.32	Opaque, amber, slight lacquer, sludge
650	48	Yb(Tol)(0.1)	-	4.0	§	0.22	Opaque, amber, sludge

*Additive abbreviations
Ce(Tol) - Cerium (IV) toluate
Cu(Tol) - Copper (II) toluate
Ni(Benz) - Nickel (II) benzoate
Pb(Benz) - Lead (II) benzoate
Pr(Tol) - Praseodymium (III) toluate
Mn(Benz) - Manganese (II) benzoate
Co(Benz) - Cobalt (II) benzoate
Cr(Tol) - Chromium (III) toluate
Cr(Benz) - Chromium (III) benzoate
Ba(Tol) - Barium (II) toluate
Ba(DNNS) - Barium (II) dinonylnaphthalene sulfonate
Ti(Tol) - Titanium (IV) toluate
Yb(Tol) - Ytterbium (III) toluate.

†A dash indicated the absence of metal.
‡Too viscous to measure.
§Not determined.
¶Percolated through Florisil and alumina.
**Stainless steel.
††Metal specimen heavily encrusted.
‡‡In powder form.

antioxidant activity, lead benzoate and titanium toluate permitted the largest viscosity increases, 279 and 353 percent respectively. The only toluate which offered no protection to the ether was that of copper; likewise, barium dinonylnaphthalene sulfonate did not prevent gelation of the fluid.

DISCUSSION

Silicones, fluoroesters, and polyphenyl ethers are all so stable that comparatively elevated temperatures are required to effect their oxidation. Therefore, significant reaction products may be so short-lived as to be difficult or impossible to identify. Consideration of the well-known oxidative reactions of the aliphatic diesters may serve to illustrate this latter point (20). The overall reaction rate of these fluids is a function of peroxide concentration; at any specified temperature the peroxide content rises to a maximum and then falls off rather sharply as secondary reactions become significant. As the oxidation temperature is raised, a peak concentration is more rapidly attained and the subsequent decrease is more precipitate. Finally, a temperature is reached (ca. 450°F) above which peroxides are difficult to detect because they are so rapidly destroyed. In the case of silicones, peroxides have been postulated as high-temperature reaction products (1). Nevertheless, at the temperatures at which such peroxides are presumed to form (above 500°F) they are evidently too short-lived to be detected by conventional chemical methods. The polyphenyl ethers may be an exception to this generalization regarding short-lived high-temperature reaction products, since they are reported to generate stable free radicals above 600°F (26,27). Although these radicals have been detected by electron paramagnetic resonance spectroscopy, their precise molecular configuration has not been determined.

The difficulties associated with the identification of the initial high-temperature oxidation reaction products of fluoroesters and polyphenyl ethers apply also to the elucidation of the mechanism responsible for the inhibition imparted by metals and organometal salts. Nevertheless, certain assumptions may be reasonably made. For one thing, probably the activities of only the salts are relevant to the inhibition process since, at the elevated temperatures employed in the present investigation, bulk metals undoubtedly react with oxidation products of the base fluids. The resulting superficial layers of salts would be at least slightly soluble in the fluid. It may be further speculated that the usual catalytic role of metal salts is reversed in the subject fluids and instead of oxidation proceeding by an electron transfer to a metal ion (possibly as a complex) from a hydroperoxide (5), the ion has the general attributes of an energy sump, interrupting the autocatalytic oxidation chain. Thus, the consequent deactivation of the chain-propagating entity (hydroperoxide, free radical, or energy-rich particle) would drastically curtail the overall oxidation rate of the base fluid.

It is apparent from the present study that traditional concepts of factors affecting the oxidation stability of petroleum or aliphatic diester lubricants may not automatically be assumed valid for fluids of different chemical constitution. In particular, the presently accepted level of stability of fluoroesters and polyphenyl ethers, as determined in the specification tests, would probably not correlate well with their stabilities in an operating gas-turbine engine. In laboratory tests, copper metal is traditionally present to promote deterioration of the fluids, whereas for precisely the same reason, copper metal and its alloys are rigorously limited as materials of engine construction. The ironic fact is that copper at high temperatures is a potent antioxidant for these fluids and they would display a higher degree of stability in the laboratory where copper is present than in an engine where copper is absent.

One then may reasonably speculate whether other experimental conditions for the evaluation of lubricant stability, hitherto taken for granted, should not be re-examined to determine their precise effect on the fluid. Among the factors which might merit such

re-examination are the effect of light and the influence of glass. For example, the composition of glass containers has been shown to affect significantly the room temperature storage stability of aircraft fuels (10).

SUMMARY

The discovery has been made at this Laboratory as to the beneficial effect of certain metals and organometal salts on the oxidation stabilities of a polyphenyl ether, and three fluoroalcohol esters of polybasic acids. The fluoroalcohols (ψ'-alcohols) were of the general formula $H(CF_2\text{-}CF_2)_nCH_2OH$.

In the absence of metals, esters of 3-methylglutaric and camphoric acids were unstable at 437°F and seriously degraded at 482°F. Outstanding improvement in the stability of the esters was obtained at 437°F in the presence of copper, either alone or together with steel and silver-plated steel. At 482°F the response of both fluids to copper was good, but steel or silver-plated steel showed no inhibitory effect. Barium, monel, and chromium each prevented significant degradation of the camphorate at 482°F, the former being the most effective with respect to cleanliness of the fluid. The activity of cobalt was marginal; nickel permitted the fluid to gel. The bis(ψ'-amyl) ester of the aromatic 2,2'-diphenic acid was inherently so stable, even at 617°F, that the only improvement imparted to it by copper was a lessening of evolved fluorides. At 642°F the ester underwent extensive pyrolysis regardless of the presence of copper.

Various relatively insoluble organocupric salts markedly improved the 482°F stability of both the 3-methylglutarate and the camphorate fluoroesters. The copper compounds investigated were the (ψ'-heptyl)3-methylglutarate, (ψ'-heptyl)hydrogen 3-methylglutarate, phenylstearate, toluate, and perfluoroundecanoate. In the camphorate ester, the benzoates or toluates of the following metals all displayed antioxidant activity at 482°F to varying degrees: barium, nickel, chromium, cobalt, manganese, praseodymium, titanium, ytterbium, and strontium. Of these the most effective was barium toluate. Cerium disalicylalpropylene diamine and cerium (ψ'-heptyl) hydrogen-3-methylglutarate also displayed effective inhibition in the camphorate at this temperature.

The polyphenyl ether studied was a mixed isomer of bis(phenoxy-phenoxy)benzene, the meta isomer being predominant. With no metals present, the fluid gelled when exposed to 600°F for 48 hours. Although either steel or silver-plated steel prevented gelation of the fluid, copper, cupric toluate, and ceric toluate were more effective in preventing thickening of the fluid. At 650°F, barium prevented gelation; copper, steel, nickel, monel, chromium, and cobalt had no antioxidant activity. The toluates or benzoates of cerium, nickel, lead, praseodymium, manganese, cobalt, chromium, titanium, ytterbium, and barium all displayed significant antioxidant activity; the most effective were manganese benzoate and barium toluate. Copper toluate and barium dinonylnaphthalene sulfonate both permitted the ether to gel.

The opposite roles played by metals such as copper as antioxidants in fluoroesters, polyphenyl ethers, and silicones, or as prooxidants in aliphatic and petroleum oils, call for more careful examination of their use in the laboratory evaluation of lubricant stability. It will be necessary to know the specific effect of such metals before the inherent stability and probable service utility of new lubricant fluids can be reliably assessed.

The results reported herein demonstrate the unusual and outstanding high-temperature antioxidant properties of certain metals and organometal compounds in fluoroesters and polyphenyl ethers. A program is now in progress to synthesize more soluble compounds, not only of the metals reported here, but of others being investigated, to improve further the stabilities of fluoroesters, aromatic ethers, and other high-temperature fluids. Suitable studies of the inhibition mechanisms involved may yield information leading to the selection and synthesis of even more efficient antioxidants.

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UNCLASSIFIED

Naval Research Laboratory. Report 5794.
ANTIOXIDANT ACTION OF METALS AND ORGANOMETALLIC COMPOUNDS IN FLUOROESTERS AND POLYPHENYL ETHERS, by H. Ravner, E.R. Russ, and C.O. Timmons. 14 pp., December 5, 1962.

A [illegible] turbine engines in the Mach 2 to 3 range, now in the development stage, will require lubricants considerably more stable to oxidation than present jet engine lubricants. Fluoroesters and polyphenyl ethers are among the potential high-temperature lubricants being considered for this application. It has been discovered at NRL that the degree of oxidation stability can be improved [illegible] by a variety of metals and organometallic compounds.

Three fluoroesters and a polyphenyl ether [illegible] benzene] were subjected to oxidizing conditions at temperatures [illegible] 447° to 650°F, in the presence and absence of the metals and organometallic compounds, and data were obtained to show the [illegible] due to the additives. These data included [illegible] 100°F, neutralization number increase, evaporation loss, [illegible] metals, and sample appearance.

UNCLASSIFIED (over)

1. Oxidation inhibitors
2. Fluoroesters - Oxidation
3. Polyphenyl ethers - Oxidation
I. Ravner, H.
II. Russ, E.R.
III. Timmons, C.O.

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Naval Research Laboratory. Report 5794.
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III. Timmons, C.O.

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[illegible] Report 5794.
[illegible] ORGANOMETALLIC COMPOUNDS IN FLUOROESTERS AND POLYPHENYL ETHERS, [illegible] E.R. Russ, and C.O. Timmons.
[illegible]

[illegible]

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[illegible]

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At 497°F copper and steel improved the stability of the fluoroalcohol (ω'-alkyl) esters of 3-methylglutaric and camphoric acids. At 482°F, the camphorate was substantially stabilized by copper, barium, monel and chromium; by toluates or benzoates of barium, nickel, chromium, cobalt, manganese, praseodymium, titanium, ytterbium, and strontium; by cerium disalicylalpropylene diamine and cerium (ω'-heptyl) hydrogen-3-methylglutarate; and by the copper salts of perfluoroundecanoic acid, (ω'-heptyl) hydrogen 3-methylglutarate, toluic acid, and phenylstearic acid.

Bis[(ω'-amyl)2,2'-adipinate] possessed generally high inherent stability up to 617°F. Some HF was evolved, however, which was greatly reduced by the presence of copper. At 642°F the ester underwent extensive pyrolysis, which the inhibitors did not prevent.

The polyphenyl ether, bis(phenoxy-phenoxy)benzene, was effectively protected from oxidation at 600°F by copper, cupric toluate, and ceric toluate. At 650°F effective inhibitors were barium metal, and the toluates or benzoates of barium, manganese, cerium, nickel, lead, praseodymium, cobalt, chromium, titanium, and ytterbium.

The degree of stability given to these fluids increases interest in them as potential high-temperature lubricants for aircraft gas turbines in the Mach 2 to 3 range.

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-- 8 - TITLE CLASSIFICATION: UNCLASSIFIED
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--24 - DESCRIPTOR CLASSIFICATION: UNCLASSIFIED
--25 - IDENTIFIERS: PHENYL RADICALS, CAMPHORS
--26 - IDENTIFIER CLASSIFICATION: UNCLASSIFIED
--27 - ABSTRACT: THREE FLUOROESTERS AND A POLYPHENYL ETHER (BIS(PHENOXY-
-- PHENOXY)-BENZENE) WERE SUBJECTED TO OXIDIZING CONDITIONS AT 437 TO
-- 650 F IN THE PRESENCE AND ABSENCE OF THE METALS AND ORGANOMETAL

-
-- COMPOUNDS, AND DATA WERE OBTAINED TO SHOW THE OXIDATION INHIBITION
-- DUE TO THE ADDITIVE. AT 437 F CU AND STEEL IMPROVED THE STABILITY
-- OF THE FLUOROALCOHOL (PSI-ALKYL) ESTER F 3-METHYLGLUTARIC AND
-- CAMPHORIC ACIDS. AT 482 F, THE CAMPHORATE WAS SUBSTANTIALLY
-- TABILIZED BY CU, BA, MONEL, AND CR; BY TOLUATES OR BENZOATES OF BA,
-- NI, CR, CO, MN, PR, TI, YB, AND SR; BY CERIUM DISALICYLALPROPYLENE
-- DIAMINE AND CERIUM (PSIHEPTYL) HYDROGEN-3-METHYLGLUTARATE; AND BY
-- THE CU SALTS OF PERFLUOROUNDECANOIC ACID, (PSI-HEPTYL) HYDROGEN 3-
-- METHYLGLUTARATE, TOLUIC ACID, AND PHENYLSTEARIC ACID. BIS(PSI-AMYL)
-- 2,2-DIPHENATE POSSESSED GENERALL HIGH INHERENT STABILITY UP TO
-- 617 F. AT 642 F THE ESTER UNDERWENT EXTENSIVE PYROLYSIS, WHICH THE
-- INHIBITORS DID NOT PREVENT. THE POLYPHENYL ETHER, BIS(PHENOXY-
-- PHENOXY)BENZENE, WAS EFFECTIVEL PROTECTED FROM OXIDATION AT 600 F
-- BY COPPER, CUPRIC TOLUATE, AND CERIC TOLUATE. AT 650 F EFFECTIVE
-- INHIBITORS WERE BA METAL, AND THE TOLUATES OR BENZOATES OF BA, MN,
-- CE, NI, PB, PR, CO, CR, TI, YB. (AUTHOR)
--28 - ABSTRACT CLASSIFICATION: UNCLASSIFIED
--30 - ANNOTATION: ANTIOXIDANT ACTION OF METALS AND ORGANOMETAL
-- COMPOUNDS IN FLUOROESTERS AND POLYPHENYL ETHERS. POTENTIAL HIGH
-- TEMPERATURE LUBRICANTS FOR AIRCRAFT GAS TURBINES IN THE MACH 2 TO 3
-- RANGE.
--33 - LIMITATION CODES: 2