Antioxidant Action of Metals and Metal-Organic Salts in Fluoroesters and Polyphenyl Ethers

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Three fluoroesters and a polyphenyl ether, potential lubricants for aircraft gas turbine engines in the Mach 2 to 3 range, were subjected to oxidizing conditions at 437° to 650° F. in the presence and absence of metals and metal-organic salts. Viscosity change, neutralization number increase, evaporation loss, corrosivity to metals, and sample appearance were employed to evaluate oxidation inhibition due to the additives. At 437° F. copper and steel improved the stability of the fluoroalcohol 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)3-methylglutarate; and by the copper salts of perfluoroundecanoic acid, (ψ′-heptyl)3-methylglutaric, toluic, and phenylstearic acids. Bis(ψ′-amyl)2,2′-diphenate possessed generally high inherent stability up to 617° F. Some HF evolved, however, which was greatly reduced by the presence of copper. The polyphenyl ether, bis(phenoxyphenoxy)benzene, was effectively protected from oxidation at 600° F. by copper, and cupric and ceric toluates. 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.

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 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 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*).

To place in proper perspective the oxidation stability requirements for high-temperature jet engine lubricants, a review of the development of both the engines and the lubricants is useful. Early jet engines, such as the J-33 and J-34, had sump temperatures 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 (*20*). In the early 1950's, engines (e.g., J-57 and J-79) in the Mach 1 and 2 range came into general use and currently power the majority of U. S. first-line fighter aircraft. Sump temperatures range from 230° to 275° F., and oil-out temperatures from 340° to 400° F. The oxidative stresses to which lubricants for these engines are subjected are of such magnitude that petroleum-based fluids, apart from their excessive volatility, 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 (*23*), have proved to be eminently satisfactory lubricants for these engines. The specification (*18*) 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. Sump temperatures range from 300° to 450° F., and oil-out temperatures may attain 650° F. although a lubricant specification (*19*) 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 no oils could be found to meet the stability requirements (*6*). No corrosion-oxidation requirement is incorporated in the lastest version of this specification. The inhibitors described in this report show promise in the +500° F. range where improved oxidation stability is needed.

EXPERIMENTAL PROCEDURE

Because of the small amounts of the experimental oils available, their oxidation stability was studied in a scaled down test which had been found reliable in previous work (*2, 17*). The 30 ml. cells were constructed of borosilicate glass, and were maintained at test temperatures in thermostatted aluminum block furnaces. Clean, dry, CO_2-free air was bubbled through the samples at the rate of 1 cc. gas/gram sample/min. When metal specimens were present, they were of such dimensions as to present a surface area of approximately 10 sq. cm.

The data obtained 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 compounds employed as additives were prepared at this laboratory. Synthesis of the copper and cerium salts of organo fluorine-containing compounds has been reported (*25*). Except for ceric toluate, all 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 disalicylalpropylene diamine, 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 materials found were undissolved additives or sludge formed during the oxidation. In general, all such material was reported as sludge.

OXIDATION STUDIES

Fluorinated Esters. Effect of Metal Combinations. Esters from polybasic acids and fluoroalcohols of the general formula $H(CF_2CF_2)_nCH_2OH$ (ψ'-alcohols) have been reported to be unusually stable to oxidation, even in the absence of conventional inhibitors (*13, 15, 21*). In those studies the fluids were in contact with a combination of some of the metals used in specification oxidation-corrosion tests (*18, 19*), generally copper, steel, and silver-plated steel. Table I summarizes the results of oxidation experiments for esters of 3-methylglutaric, camphoric, and 2,2′-diphenic acids. Esters of both aliphatic 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 relatively unchanged sample appearance. At 482° F., minor oxidative changes in the fluids were evident. Fluoroesters of 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 relatively little degradative change.

Table I. Oxidation Stability of Fluoroesters With and Without Metal Combinations Present

Temp., ° F.	Test Period, Hrs.	Metal Wt. Change (Mg./Sq. Cm.) Cu	Fe	Ag-Plated Fe	Wt. %, Oil Loss	% Visc. Incr. at 100° F.	Neutral. No. Incr.	Mg. F/ Gram Sample	Final Sample Appearance
				Bis(ψ'-Amyl)3-Methylglutarate					
437	168	−0.3	+0.1	<−0.1	24	6.3	7.2	...[b]	Clear, slight lacquer
437	168	...[a]	...[a]	...[a]	65	...[b]	215	...[b]	Very dark, sludge, lacquer
				Bis(ψ'-Heptyl)3-Methylglutarate					
437	168	<−0.1	<−0.1	nil	...[b]	0.5	0.07	...[b]	Clear, amber, slight lacquer
437	168	...[a]	...[a]	...[a]	34	72	21	...[b]	Very dark, sludge, lacquer
482	168	−0.1	+0.6	nil	38	1.8	1.2	...[b]	Opaque, light lacquer
482	168	...[a]	...[a]	...[a]	36	46	11	...[b]	Opaque, heavy sludge, lacquer
				Mixed Fluoroalcohol Camphorate					
392	168	...[a]	...[a]	...[a]	12	...[b]	17	2.1	Opaque
437	168	nil	nil	nil	7.1	5.2	0.06	0.19	Clear, light yellow
437	168	...[a]	...[a]	...[a]	27	64	7.7	4.1	Opaque, heavy sludge
482	168	−0.2	<+0.1	<−0.1	23	...[b]	5.4	3.2	Opaque, dark brown fluid
482	168	...[a]	...[a]	...[a]	76	Gelled	...[b]	2.9	Gelled
482	72	...[a]	...[a]	...[a]	39	Gelled	...[b]	...[b]	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	...[a]	...[a]	...[a]	...[b]	3.9	0.58	5.3	Light amber

[a] Specified metal absent. [b] Not determined.

Sensitivity in the Absence of Metals. When the experiments summarized above were repeated, but in the absence of metals, an unexpected decrease in stability was observed, Table I. The more significant differences 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-methylglutarate at 437° F. for 168 hours. The 100° F. viscosity increase rose from 0.5 to 72% and the neutralization number from 0.07 to 21. At 482° F., the viscosity increase rose from 1.8 to 46% and the acid number from 1.2 to 11. Although the viscosity and acidity increases were more pronounced at 437° F. 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. Mixed fluoroalcohol camphorate at 437° F. for 168 hours. The viscosity increase rose from 5.2 to 64%, the acid number from 0.06 to 7.7, and the evolved fluoride from 0.19 to 4.1 mg./gram 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 at 482° F. for 72 hours or longer caused the camphorate in the absence of metals to gel; with the three metals present it was still fluid after 168 hours.
4. Bis(ψ′-amyl)2,2′-diphenate at 527° F. for 72 hours. The fluoride evolved increased from 0.11 to 5.3 mg./gram sample; no other significant differences were noted.

Effects of Individual Metals. To separate the stabilizing effects of the metals, the fluids were oxidized in the presence of the single metals. Table II compares the results obtained in the presence and absence of the individual metals. Copper imparted substantial oxidative stability to both the bis(ψ′-amyl)3-methylglutarate and the camphorate esters at 437° F.; with either steel or silver-plated steel present, the camphorate was oxidized to a gel or a tar-like mass. At 482° F. the camphorate gelled after 168 hours with stainless steel present, but remained fluid in the presence of copper. A comparable degree of stability was imparted by copper to bis(ψ′-heptyl)3-methylglutarate at 482° F. At 617° F. the main effect of this metal on the relatively stable bis(ψ′-amyl)2,2′-diphenate was to decrease substantially the quantity of evolved fluoride.

Because of the significant antioxidant activity of copper in fluoroesters, the activities of other metals were evaluated. The results for 72-hour camphorate runs at 482° F. are listed in Table II. Barium, chromium, and Monel each imparted substantial stability to the fluid, barium being particularly effective in preventing the formation of sludge and lacquer. Neither nickel nor stainless steel (168-hour run) prevented gelation of the ester. With cobalt present in powder form, the fluid was tar-like.

Metal-Organic Salts Present. Few data are available on the use of metal-organic salts as oxidation-inhibitors. Naphthenates of copper and cobalt have been reported to enhance synergistically the activity of phenolic antioxidants in lubricating oils (*14*), and dispersions of inorganic salts of alkali metals to have antioxidant properties in lubricant compositions containing petroleum and synthetic esters (*24*). Other studies have demonstrated the stable life of silicones to be extended severalfold when they are in contact with certain metals, metal salts, or metal chelates (*4, 12*). The latter were particularly effective in lightly phenylated polymethyl silicones. Following these analogies, the stabilizing effect on the fluoroesters of various metal-organic salts was ascertained. The results are given in Table III.

Copper salts of (ψ′-heptyl)hydrogen 3-methylglutaric, phenylstearic, toluic, and perfluoroundecanoic acids all displayed antioxidant activity in either the 3-methyl-

Table II. Antioxidant Activity of Individual Metals in Fluoroesters

Temp., °F.	Test Period, Hrs.	Metal	Metal Wt. Change Mg./Sq. Cm.	Wt., % Oil Loss	%, Visc. Incr. at 100° F.	Neutral. No. Incr.	Mg. F/ Gram Sample	Final Sample Appearance
			Bis(ψ′-Amyl)3-Methylglutarate					
437	168	...[a]	...[a]	65	...[b]	212	...[b]	Very dark, sludge, lacquer
437	168	copper	<−0.1	9.2	2.5	0.03	...[b]	Clear, light yellow
			Bis(ψ′-Heptyl)3-Methylglutarate					
482	168	...[a]	...[a]	36	46	11	...[b]	Opaque, heavy sludge, lacquer
482	168	copper	−0.6	34	4.6	0.18	...[b]	Opaque, medium lacquer
			Mixed Fluoroalcohol Camphorate					
437	168	...[a]	...[a]	27	64	7.7	4.1	Opaque, heavy sludge
437	168	copper	−0.2	9.1	3.5	0.18	0.18	Clear, amber, slight sludge
437	168	steel	+0.1	49	Gelled	...[b]	1.5	Gelled
437	168	silver-plated steel	−0.2	36	...[b]	16	2.7	Opaque, tar-like
482	168	...[a]	...[a]	76	Gelled	...[b]	2.9	Gelled
482	168	copper	+2.9	57	215	8.1	1.9	Opaque
482	168	stainless steel	+0.5	94	Gelled	...[b]	1.7	Gelled
482	72	...[a]	...[a]	39	Gelled	...[b]	...[b]	Gelled
482	72	copper	+0.3	20	111	6.0	nil	Very dark
482	72	nickel	<+0.1	31	Gelled	...[b]	1.6	Gelled
482	72	Monel	<+0.1	...[b]	8.3	7.8	3.0	Opaque, black, sludge, lacquer
482	72	chromium	<+0.1	...[b]	86	14	2.2	Opaque, black, sludge, slight lacquer
482	72	cobalt[c]	...[b]	39	...[b]	...[b]	1.9	Tar-like
482	72	barium	...[b]	22	36	5.3	2.0	Dark amber, slight sludge and lacquer
			Bis(ψ′-Amyl)2,2′-Diphenate					
617	72	...[a]	...[a]	7.6	12	4.4	1.8	Opaque, lacquer
617	72	copper	+0.1	16	19	0.6	0.4	Dark amber, clear

[a] Metal absent. [b] Not determined. [c] In powder form.

glutarate or camphorate esters, up to 482° F. The perfluoroundecanoate differed from that of other copper salts as it allowed a larger viscosity increase, but a decreased evolution of fluorides. Only copper toluate was evaluated in bis(ψ'-amyl)2,2′-diphenate at 617° F.; it had little effect, but the fluid is so stable that it is difficult to obtain measurable improvement.

The toluates or benzoates of the following metals were examined in the camphorate ester at 482° F.: barium, cerium, nickel, chromium, cobalt, manganese, praseodymium, titanium, ytterbium and strontium. All displayed inhibitory activity, barium toluate in 0.1% concentration being the most effective, particularly with respect to the cleanliness of the fluid. The ceric salts of disalicylclpropylene diamine (437° F. for 168 hours) and (ψ'-heptyl) hydrogen 3-methylglutaric acid (482° F. for 72 hours) were effective in preventing large viscosity increases.

These data show that a variety of metals with either single or multiple valences, as well as corresponding metal salts, impart significant oxidative stability to fluoroesters from aliphatic acids.

POLYPHENYL ETHERS. The meta isomer of bis(phenoxyphenoxy)benzene is an attractive candidate as a high-temperature jet engine oil. It is reported to have good resistance to oxidation, pyrolysis, and radiation (*7, 8, 16, 26*). It has a high flash point, a low evaporation rate and 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 antioxidants to improve the stability of the polyphenyl ethers. Some promise has been shown by organotin compounds, oxides of copper, and metal acetylacetonoates (*8, 26*).

Polyphenyl ether samples were obtained from two commercial sources. Both were mixed isomers of bis(phenoxyphenoxy) benzene, with the meta isomer predominating. The fluids were equivalent as regards initial viscosity, stability, and response to antioxidants; their reactivities were not perceptibly affected by percolation through adsorbents to remove polar impurities. Results of oxidation stability studies on these ethers are shown in Table IV. The metal-organic additives were apparently as insoluble in the ethers, as they were in the fluoroesters.

SENSITIVITY IN THE ABSENCE OF METALS. After 72 hours at 500° F., with no metals present, the ether was essentially unchanged, but at 572° F. it was too thick for a viscosity measurement. The ether was oxidized to a gel after 48 hours at 600° F.

EFFECTS OF INDIVIDUAL METALS. Some improvement in stability was imparted to the ether at 600° F. by both steel and stainless steel. In 48-hour runs viscosity increases were

Table III. Antioxidant Activity of Metal-Organic Salts in Fluoroesters

Temp., ° F.	Test Period, Hrs.	Wt., % Metal Salt[a]	Wt., % Oil Loss	%, Viscosity Incr. at 100° F.	Neutral. No. Incr.	Mg. F/ Gram Sample	Final Sample Appearance
Bis(ψ'-Heptyl)3-Methylglutarate							
482	168	...[b]	36	46	11	...[c]	Opaque, heavy sludge, lacquer
482	168	Cu(ψ'-C_7)3-Megl(0.1)	31	20	300	...[c]	Opaque, dark amber
482	168	Cu(PS)(0.1)	...[c]	18	7.6	...[c]	Opaque, black
Mixed Fluoroalcohol Camphorate							
437	168	...[b]	27	64	7.7	4.1	Opaque, heavy sludge
437	168	Cu(PS)(0.03)[d]	16	7	0.84	0.27	Clear, dark amber
437	168	Cu(Tol)(0.03)[d]	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
437	168	Ce(DSPD)(0.1)	28	8.3	9.5	0.47	Opaque, sludge, lacquer
482	72	...[b]	39	Gelled	...[c]	...[c]	Gelled
482	72	Cu(ϕ-C_{11})(0.5)	20	111	6.0	nil	Very dark
482	72	Cu(ψ'-C_7)3-Megl(0.5)	12	1.6	1.7	...[c]	Very dark
482	72	Cu(Tol)(0.1)	20	20	1.4	...[c]	Opaque
482	72	Cu(PS)(0.1)[d]	23	13	1.6	...[c]	Opaque
482	72	Ba(Tol)(0.1)	16	7.5	5.7	1.9	Clear, dark amber
482	72	Ba(Tol)(0.05)	20	40	9.7	1.8	Opaque, sludge
482	72	Ce(ψ'-C_7)3-Megl(0.5)	12	13	11	2.2	Opaque, sludge, lacquer
482	72	Pb(Benz)(0.1)	26	825	9.5	1.2	Opaque, black, sludge
482	72	Ni(Benz)(0.1)	16	32	7.5	2.4	Opaque, black
482	72	Cr(Benz)(0.1)	35	...[c]	...[c]	2.0	Tar-like
482	72	Cr(Tol)(0.1)	26	381	9.8	2.8	Opaque, sludge
482	72	Co(Benz)(0.1)	18	46	15	1.0	Opaque, black
482	72	Mn(Benz)(0.1)	40	560[e]	11	2.1	Opaque, black, sludge
482	72	Pr(Tol)(0.1)	37	...[c]	...[c]	2.6	Tar-like
482	72	Ti(Tol)(0.1)	26	135	14	2.8	Opaque, black, sludge, lacquer
482	72	Yb(Tol)(0.1)	23	141	13	1.4	Opaque, black, sludge, lacquer
482	72	Sr(Tol)(0.1)	23	43	14	2.4	Opaque, slight sludge
482	72	Sr(Tol)(0.05)	20	23	16	2.2	Opaque, slight sludge
Bis(ψ'-Amyl)2,2′-Diphenate							
617	72	...[b]	7.6	12	4.4	1.8	Opaque, lacquer
617	72	Cu(Tol)(0.5)	27	77	1.0	4.0	Opaque, sludge, lacquer

[a] Additive Abbreviations: Cu(ψ'-C-)3-Megl–Copper (II) (ψ'-Heptyl) 3-Methylglutarate; Cu(PS)–Copper (II) phenylsterate; Cu(Tol)–Copper (II) toluate; Cu(ϕ-C_{11})–Copper (II) perfluoroundecanoate; Ce(DSPD)–Cerium (IV) disalicylalpropylene diamine; Ce(ψ'-C_7)3-Megl-Cerium (IV) (ψ'-heptyl)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. [b] Metal salt absent. [c] Not determined. [d] Concentration of metal. [e] Approximate.

of the order of 150 to 350% and the neutralization numbers approximately 0.5. More marked reduction of viscosity change was given by copper metal, but there was little improvement as regards the neutralization number increases, which were small. The small viscosity increase obtained with the copper-steel combination is possibly indicative of synergistic action. Stability with silver-plated steel was of the same order as that with copper.

In 48-hour runs at 650° F., only barium proved effective; it permitted a viscosity increase of 256% 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 tar-like appearance after oxidation.

METAL-ORGANIC SALTS PRESENT. In 48-hour runs at 600° F. the ether responded to the stabilizing effect of copper toluate, and a combination of copper toluate and a strip of steel. When the run was extended to 168 hours, however, the latter combination did not prevent gelation. A marked degree of oxidation stability was imparted by ceric toluate in 0.05% concentration; after 48 hours at 600° F. the neutralization number increase was of the order of 1.0 and the viscosity increase was 81%. Although very little additional toluate appeared to go into solution when the concentration was raised from 0.05 to 0.1%, the neutralization number was one-third, and the viscosity increase one-half that at 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 antioxidant activity. On balance, manganese benzoate and barium toluate offered the most substantial protection to the ether primarily because in both instances the oil was clear and relatively free of sludge, and viscosity increases were small. The only toluate which was ineffective in the ether was that of copper; barium dinonylnaphthalene sulfonate was also ineffective.

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. The decreasing stability and consequent shortened residence time of hydroperoxides in

Table IV. Antioxidant Activity of Metals and Metal-Organic Salts in Bis(Phenoxy-Phenoxy)Benzene

Temp., ° F.	Test Period Hrs.	Wt. %, Metal or Metal-Salt[a]	%, Metal Wt. Change	Wt. %, Oil Lost	%, Visc. Incr. at 100° F.	Neutral. No. Incr.	Final Sample Appearance
500	72	...[b]	...[b]	1.0	5.8	0.09	Dark amber
572	72	...[b]	...[b]	7.1	...[c]	0.36	Opaque, black
600[d]	48	...[b]	...[b]	3.7	Gelled	...[e]	Gelled
600	48	...[b]	...[b]	2.8	Gelled	...[e]	Gelled
600[d]	48	Steel	+0.1	1.8	132	0.47	Opaque, black
600	48	Steel	nil	2.8	239	0.49	Opaque, black
600[d]	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 Steel	+0.2 +0.1	...[e] ...[e]	22	0.28	Opaque, black
600	48	Silver-plated steel	−0.1	1.0	114	0.47	Opaque, black
600	48	Steel[f]	+0.1	5.1	361	0.66	Opaque, black
600	48	Cu(Tol) (0.1)	...[g]	8.9	11	0.17	Opaque, black, sludge
600	48	Cu(Tol) (0.1), Steel	+0.1	14	14	0.15	Opaque, black, sludge
600	168	Cu(Tol) (0.1), Steel	+0.1	15	Gelled	...[e]	Gelled
600	48	Ce(Tol) (0.05)	...[g]	8.4	81	0.98	Opaque, black, sludge
600	48	Ce(Tol) (0.1)	...[g]	...[e]	26	0.39	Opaque, black, sludge
650	48	Copper	...[h]	10	Gelled	...[e]	Gelled
650	48	Steel	...[h]	3.5	Gelled	...[e]	Gelled
650	48	Barium	...[e]	4.0	256	1.0	Opaque, amber
650	48	Nickel	...[e]	4.0	Gelled	...[e]	Gelled
650	48	Cobalt[i]	...[e]	4.8	...[c]	...[e]	Tar-like
650	48	Monel	−0.1	7.2	Gelled	...[e]	Gelled
650	48	Chromium	−0.1	6.4	Gelled	...[e]	Gelled
650	48	Ce(Tol) (0.1)	...[g]	2.3	27	nil	Opaque, black, sludge
650	48	Cu(Tol) (0.1)	...[g]	4.9	Gelled	...[e]	Gelled
650	48	Ni(Benz) (0.1)	...[g]	4.0	127	0.03	Opaque, amber, slight sludge
650	48	Pb(Benz) (0.1)	...[g]	6.7	279	0.06	Opaque, amber, slight sludge
650	48	Pr(Tol) (0.1)	...[g]	8.8	63	0.06	Opaque, amber, sludge
650	48	Mn(Benz) (0.1)	...[g]	10	52	0.09	Clear, green-amber
650	48	Co(Benz) (0.1)	...[g]	6.4	83	0.08	Opaque, amber, sludge
650	48	Cr(Tol) (0.1)	...[g]	4.0	130	0.18	Opaque, amber, sludge, lacquer
650	48	Cr(Benz) (0.1)	...[g]	3.6	103	0.2	Opaque, amber, sludge
650	48	Ba(Tol) (0.1)	...[g]	1.2	65	0.80	Clear, amber
650	48	Ba(DNNS) (0.1)	...[g]	3.2	Gelled	...[e]	Gelled
650	48	Ti(Tol) (0.1)	...[g]	4.0	353	0.32	Opaque, amber, slight lacquer, sludge
650	48	Yb(Tol) (0.1)	...[g]	4.0	...[c]	0.22	Opaque, amber, sludge

[a] 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. [b] Metal and metal salt absent. [c] Too viscous to measure. [d] Percolated through Florisil and alumina. [e] Not determined. [f] Stainless steel. [g] Metal absent. [h] Metal specimen heavily encrusted. [i] In powder form.

aliphatic diesters, as temperatures are raised, is a case in point (*22*). Peroxides have also been postulated as high-temperature reaction products of silicones (*1*), but they are evidently too short-lived above 500° F. to be detected by conventional chemical methods. 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.

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 mechanisms responsible for the inhibition imparted by metals and metal salts. Nevertheless, certain speculations are in order: first, that only the activities of the salts are relevant to the inhibition process since, at the elevated temperatures employed in the present investigation, bulk metals (or metal oxides) undoubtedly react with oxidation products of the base fluids. The resulting superficial layers of salts are at least slightly soluble in the fluid; second, that in the subject fluids, the usual catalytic role of metal salts is reversed and instead of oxidation proceeding by an electron transfer to a metal ion (possibly as a complex) from a hydroperoxide (*5*), the ion has some 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 effectively curtail the overall oxidation rate of the base fluid.

The present study shows that traditional concepts of factors affecting the oxidation stability of petroleum or aliphatic diester lubricants may not be valid for fluids of different chemical constitution. In particular, the presently accepted level of stability of fluoroesters and polyphenyl ethers, as determined in specification tests, would probably not correlate well with their stabilities in an operating gas-turbine engine. In laboratory tests, for example, 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 has potent antioxidant activity in these fluids, and they would display a higher degree of stability in the laboratory with copper present than in an engine where copper is absent.

Other traditional experimental conditions for the evaluation of lubricant stability should also be re-examined to determine their precise effect on the fluid. Examples of factors which might merit such re-examination are the effect of light and the influence of glass. Variation in the composition of glass containers, for example, affects significantly the room temperature storage stability of aircraft fuels (*10*).

CONCLUSIONS

The opposite roles played by copper and other active metals as antioxidants in fluoroesters, polyphenyl ethers, and silicones, and as prooxidants in aliphatic and petroleum oils, call for more careful examination of their use in the laboratory evaluation of lubricant stability. The specific effect of these metals should be known in order to determine the inherent stability and probable service utility of new lubricant fluids.

The comprehensive study of the stabilizing effect of metals and metal salts in fluoroesters, aromatic ethers and other high-temperature fluids is continuing.

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