Critical Comparison of Several Fluids as High Temperature Lubricants

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THE APPLICATION of fluids and lubricants at extreme temperatures emphasizes the properties of fluids and lubricants at temperatures exceeding those required for incipient thermal degradation and at which oxidation inhibitors are ineffective. The effects on lubrication of high temperature physical properties as well as the chemical changes in the fluid as a result of high temperatures need to be determined. The mechanism of lubricity for several promising fluid types and the lubricity properties of mineral oils and esters are compared and contrasted with those of silicones and silicates. A recent survey (5) conducted in cooperation with the National Aeronautics and Space Administration shows a significant number of hydraulic fluid and lubricant needs in the range of 500° to 700° F. as well as other needs in the area of 1000° to 2000° F. These applications range in time of operation between oil change of from 5 minutes to 20,000 hours.

This discussion is concerned primarily with hydrocarbon, organic acid ester, silicate, and silicone fluids and lubricants. Thus far, 700° to 800° F. appears to be a practical upper limit for these liquid fluids in applications involving appreciable operating time at this temperature. Certainly one of the major problems concerning research in this area is the paucity of standard test procedures and adaptable test equipment. Another problem area is the lack of established hardware in which to demonstrate trends and theories developed from laboratory studies.

The test equipment used by this laboratory in the evaluation of chemical and physical properties of liquid fluids and lubricants at temperatures of 500° F. and above has been described (*12, 13*).

Hydrodynamic and Boundary Components of Lubricants. Many practical applications at conventional operating temperatures illustrate quasi-hydrodynamic lubrication involving a hydrodynamic (viscous) component as well as a boundary (chemical) component of lubrication. Examples of applications involving this hybrid case are gear lubrication, such as the Ryder gear tester (*11*), and hydraulic pumps, such as the Vickers vane pump (*10*). In both cases the hydrodynamic component of lubrication is demonstrated at viscosity levels of 5 to 50 centistokes at the test temperatures.

All of the measured viscosities of high temperature hydraulic fluids and lubricants at 500° F. and above are low. There are no effective and efficient thermally stable polymeric additives for improving viscosity-temperature properties available to increase significantly the viscosity at temperatures above 500° F. Subjection of fluids to high temperatures under oxidative or thermal stresses produces volatile products.

These fluid properties affect mechanical design and the lubricity problems encountered in high temperature hardware. The generally low viscosity level increases reliance on the boundary or chemical component of lubricity. The low viscosity requires closer clearances in pumps, valves, and seals, to contain the fluid and maintain efficiency against external and internal leakage. The need for closer clearances increases the component of boundary lubrication still further. There is some indication in gear lubrication and in the four-ball wear tests, that volatile components in the lubricant affect adversely quasihydrodynamic and boundary lubrication (*9*). The formation of vapor pockets in the bearing area by frictional heat may hamper the reapplication of the components of the volatile lubricant that provide improved boundary lubrication through chemical reaction with the bearing surface.

Lubricity Testers. Two test devices have been used to measure lubrication at elevated temperatures. The Vickers vane-type power steering pump Model VT4-100-40-75-10 has been used for lubricity evaluations over the range of 100° to 600° F. (*12, 13*). The over-all high temperature pump test system comprises the pump, a high pressure orifice and bypass system, a fluidized solids bed-type heat exchanger, an orifice flowmeter, a filter, and the pump reservoir in that order. A recording thermometer is placed in the line from the reservoir to the pump and a thermocouple is located on the downstream side of the heat exchanger to measure maximum fluid temperature. The pump and the rest of the hydraulic system are placed in separate transite boxes to insulate against heat loss and to protect the operator. Previous studies (*9*) with the Vickers vane pump have shown that at viscosity levels encountered at 500° and 600° F., boundary lubrication predominates. The Shell four-ball wear tester in all of the test loadings used in this study illustrates boundary lubrication (*8*) at all viscosity levels. The four-ball wear tester has been used over the range of 167° to 700° F. under atmospheres of air and nitrogen (*12, 13*).

Data obtained in a Pesco gear-type hydraulic pump at moderate temperatures and in the Shell four-ball extreme pressure tester have been used to supplement high temperature test data to demonstrate further the mechanism of the chemical reaction of silicones and silicates with the rubbing steel surfaces.

Test Fluids. The superrefined mineral oils comprise a class of hydrocarbons derived from mineral oils by special treatments to remove essentially all of the polar nonhydrocarbon impurities originally present. Two superrefining treatments used to obtain paraffinic and naphthenic mineral oils essentially free of unsaturates and polar impurities comprise complete hydrogenation over a nickel catalyst and exhaustive acid treatment (*14*). In addition, these materials may be deep-dewaxed to provide paraffinic hydrocarbons of high viscosity index (> 100 V.I.) and cloud and pour points of the order of −75° F. (*14*). Esters studied include conventional dibasic acid esters as well as esters of the neopentyl configuration for increased thermal stability. Phenothiazine is used as an oxidation inhibitor in esters, while phenyl-α-naphthylamine or 2,6-di-*tert*-butyl-*p*-cresol is used in mineral oils. These antioxidants do not exhibit significant antiwear activity in the four-ball wear tester or the Vickers vane pump. Several silicones including methyl and chlorophenylmethyl have been evaluated with and without lubricity additives. The silicates studied include tetra-2-ethylhexyl silicate as well as two commercially compounded silicates, O.S.45 and MLO 8200.

TEST RESULTS

Preliminary tests with the Vickers vane pump and the four-ball wear tester show that, at high temperatures, mineral oils and esters provide better lubricity for both the pump and the wear tester than do silicones and silicates

(Table I). Failure of lubricant in the pump at 500° F. is characterized by failure to maintain fluid flow and hydraulic pressure coupled with formation of colloidal metal and/or high wear in the pump vanes. The general area of correlation between the vane pump and the wear tester is at the 1- and 10-kg. loads in the wear tester. The silicones and silicates involved are compounded fluids with lubricity additives built into the formulation, and the silicone fluid (Versilube F-50) has a relatively high viscosity at 500° F.

There is an apparent difference in the temperature coefficient of lubrication between esters and mineral oils on the one hand and silicones and silicates on the other (Table II). Viscosity level undoubtedly has a significant effect on the behavior of test fluids at low temperatures in the vane pump, where a substantial hydrodynamic component of lubrication has been demonstrated. A similar trend can be seen, however, in the wear tester which has no appreciable hydrodynamic component. In this case, the more effective correlation appears to be in the 1- to 10-kg. load range.

Table I. Lubricity Characteristics of Several Fluids

Conditions	Silicate (O.S. 45)	Silicone (Versilube F-50)	Dibasic Acid Ester	Mineral Oil
Vickers Vane Pump Tests				
Test temperature, ° F.	500	400	500	500
Test time, hours	0.5	4	4	4
Viscosity at test temp., Cs.	0.9	3.9	0.8	0.9
Flow rate, gal./min.				
Original	1.8	<1.0	3.4	1.8
Final	1.2	<1.0	2.7	1.8
Av. wt. loss/vane, mg.	1.3[a]	1.3[a]	2.3	0.0
Shell Four-Ball Tester[b]				
	Average Wear Scar Diameter, Mm.			
1 kg.	0.98	0.44	0.29	0.38
10 kg.	1.17	0.93	0.47	0.51
40 kg.	1.43	1.56	0.78	1.04

[a] Severe cam ring and valve plate wear.
[b] M-10 balls; bulk oil temp. 600° F.

Table II. Effect of Temperature on Lubricity

Vickers Vane Pump Tests

Test Fluid	Test Temp., ° F.	Test Time, Hr.	Visc. at Test Temp., Cs.	Flow Rate Gal./Min. Orig.	Flow Rate Gal./Min. Final	Av. Wt. Loss/ Vane, Mg.
Silicate (O.S. 45)	300	4	1.9	4.9	4.9	0.7
	400	4	1.2	4.3	2.8	1.5[a]
	500	0.5	0.9	1.8	1.2	1.3[a]
Silicone (Versilube F-50)	100	4	44.6	5.4	5.4	0.0
	400	4	3.9	<1.0	<1.0	1.3[a]
Dibasic acid ester	300	4	1.8	5.4	5.4	0.4
	400	4	1.0	4.9	4.6	+0.3
	500	4	0.8	3.4	2.7	2.3
Mineral oil	500	4	0.9	1.8	1.8	0.0

Shell Four-Ball Tester[b]

Test Fluid	Test Temp., ° F.	Av. Wear Scar. Diameter, Mm. 1 kg.	10 kg.	40 kg.
Silicate (O.S. 45)	167	0.21	0.44	0.63
	500	0.72	1.04	1.62
	600	0.78	1.17	1.19
Silicone (Versilube F-50)	167	0.18	0.31	0.67
	500	0.39	0.77	1.56
	600	0.29	1.38	1.30
Dibasic acid ester	167	0.34	0.56	0.69
	500	0.22	0.68	0.96
	600	0.22	0.63	1.10
Mineral oil	167	0.28	0.42	0.60
	500	0.31	0.47	1.38
	600	0.20	0.57	1.71

[a] Severe valve plate and cam ring wear.
[b] 52-100 steel balls.

The effectiveness of lubricity additives of the phosphorus type in esters and mineral oils at 500° F. in the pump and at 500° to 700° F. in the wear tester is demonstrated in Table III. The use of tritolyl phosphate causes some decrease in pump wear. A more effective antiwear additive (dialkyl acid phosphite) decreases wear and substantially increases volumetric efficiency of the pump. Again these effects are shown with the four-ball wear tester for phosphorus type additives in mineral oil and ester base stocks. The dialkyl acid phosphite, particularly, shows continued effectiveness at 700° F.

The pump tests discussed thus far have been conducted with a relatively soft steel valve plate. A hardened steel valve plate has been used to evaluate the relatively poor lubricants as shown in Table IV. In all cases, the use of the hardened valve plate improved the wear characteristics of the pump. However, lubrication deficiencies are still apparent for silicones and silicate fluids in this unit.

These relative lubricity values have been borne out by subsequent evaluation in studies with hydraulic pumps (*15*), gears (*1*), and bearings (*18*) operated at temperatures in the range of 400° to 700° F.

MECHANISM OF LUBRICATION

The behavior of mineral oil and ester lubricants and the excellent additive susceptibility of these base stocks for high and low temperature application has been studied and discussed (*10, 12, 13*). In previous discussions, particular emphasis has been placed on the mechanism of lubrication with phosphorus type lubricity additives. Silicones and silicates, on the other hand, by their viscosity and stability properties show an excellent potential for use as high temperature lubricants. Silicon-containing fluids do, however, exhibit consistently poor lubricity characteristics for steel-on-steel systems (*4, 6, 7*). These inadequacies in lubricity for ferrous systems have been attributed to several of the unique properties of silicone fluids, such as: extreme stability of this type of molecular structure to deterioration by thermal and oxidative environments (*17*), unusual nature of the absorbed film on the metal surface—i.e., the film is not sufficiently condensed to provide significant load-carrying qualities (*16*)—and unusually high compressibility and viscosity-pressure coefficients of silicones affecting the hydrodynamic component of lubricity (*1*).

Lubrication studies (*2, 3*) with silicones have indicated the build-up on bearings of gel-like thermal and oxidative degradation products which appear to decrease wear in internal combustion engines and to increase the load-carrying ability of journal bearings. Increased load-carrying capacity of journal bearings has been obtained by pretreatment of the journal and bearing with silicones at high temperature. This pretreatment of journal bearings appears to be much less effective for steel-on-steel bearing systems than for nonferrous systems. The beneficial break-in effects of silicones and silicates in internal combustion engines is attributed to the polishing action of smaller particles of silicone dioxide formed in the combustion zone (*19*). Use of silicones in the crankcase, where extensive thermal breakdown was not encountered, resulted in poor lubrication of camshaft, push rods, rings, and cylinder. These phenomena appear to be associated with high temperature degradation products of silicones and silicates and the physical action of these products with bearing surface.

A survey of experimentally determined lubricity data obtained by this laboratory points to still another potential explanation of lubrication difficulties experienced with silicones and silicates in ferrous bearing systems. These data indicate that the fluids may preferentially react with the ferrous bearing surface to form a relatively soft, but inert, compound or alloy involving iron and silicon. The formation of a relatively low-melting, soft or ductile compound parallels the behavior of phosphorus-containing antiwear additives in providing antiwear or chemical polishing and surface mating for low bearing loads. The mechanism of antiwear action of materials such as tritolyl phosphate has been shown to comprise formation at the bearing surface of an iron-phosphorus alloy of relatively low melting point and good ductility, so that larger bearing areas are formed, resulting in lower bearing pressures and temperatures. The low threshold of seizure and welding may be an indication of extreme inertness of the surface film formed on the bearing surface which effectively prevents chemical erosion that typifies action of extreme pressure (E.P.) and mild E.P. lubricity additives. This theory of silicone and silicate lubricity action with ferrous bearing surfaces appears to be consistent with and supported by experimental data which are presented here.

Table III. Effect of Phosphorus Type Additives on Lubricity

Vickers Vane Pump Tests[a]

Test Fluid, Concn., Wt. %	Visc. at at Test Temp., Cs.	Flow Rate, Gal./Min.		Av. Wt. Loss Vane, Mg.
		Orig.	Final	
Dibasic acid ester	0.8	3.4	2.7	2.3
+ 1.0 tritolyl phosphate	0.8	2.8	2.4	0.2
+ 0.2 dialkyl acid phosphite	0.8	3.9	3.6	0.2
Mineral oil	0.9	1.8	1.8	0.0
+ 1.0 tritolyl phosphate	0.9	3.0	3.0	0.2
+ 0.5 dialkyl acid phosphite	0.9	4.3	4.0	+1.3

Shell Four-Ball Tester[b]

Test Fluid	Test Temp., ° F.	Av. Wear Scar Diameter, Mm.		
		1 kg.	10 kg.	40 kg.
Dibasic acid ester	600	0.29	0.47	0.78
+ 5.0 tritolyl phosphate	600	0.39	0.46	0.54
+ 0.5 dialkyl acid phosphite	600	0.36	0.51	0.54
Mineral oil	700	0.24	0.58	1.54
+ 0.5 dialkyl acid phosphite	700	0.27	0.30	0.57

[a] Test conditions: temp. 500° F., pressure 700 p.s.i., time 4 hrs.
[b] M-10 steel balls.

A series of lubricity tests was conducted with a Pesco gear pump under 2500-p.s.i. load for 100 hours at 200° F. reservoir temperature, and 3600 r.p.m. pump speed (Table V). These are the severe conditions used for evaluation of Spec MIL-H-5606 fluids during the early developmental stages. Gear testing has shown a substantial hydrodynamic component (viscosity) of lubricity as well as a boundary component (chemical activity) of lubricity. The data sequence with PRL 1912, which is a Spec. MIL-H-5606 fluid without tritolyl phosphate, shows the response of the Pesco gear pump to antiwear additives. The stepwise addition of tritolyl phosphate and ester plus tritolyl phosphate shows substantial improvement in antiwear properties for steel-on-steel surfaces.

The methyl silicone (PRL 1836) fluid shown in Table V was used for a total of 700 hours in seven tests of 100 hours' duration. The reservoir temperature for these tests was 100° or 200° F.; the pump speed was 1800 or 3600 r.p.m.; and the system pressure 1000 or 3000 p.s.i. The conditions given in the table are for the last 100-hour test which was conducted under the most severe conditions. The total gear wear in the 700 hours of silicone testing is as low as that obtained with the best mineral oil-base fluid in a severe 100-hour test. Several observations about this series of tests appear pertinent. The silicone fluid has a viscosity of 16 centistokes at 200° F. compared with a base stock viscosity of 1.3 and an over-all viscosity of 5.5 centistokes at 200° F. for the mineral oil-base fluid. The silicone, then, has a substantially higher viscosity and hydrodynamic component of lubricity. Observation of the used gears after tests with the silicone indicates a substantial amount of surface distortion on the gears—i.e., these gears show a surface appearance generally encountered with fluids exhibiting

Table IV. Effect of Hardened Steel Valve Plate in Vane Pump[a]

Test Fluid	Valve Plate	Test Time, Hr.	Wt. Loss of Parts, Mg.			Flow Rate, Gal./Min.	
			Valve Plate	Vanes, Av.	Cam Ring	Orig.	Final
Silicate (O.S. 45)	Hardened	3	13	0.6	130	<1.0	<1.0
	standard	0.5	[b]	1.3	207	1.8	1.2
Silicone (Versilube F-50)	Hardened	2	6.5	2.1	12,400	3.6	2.4
	standard	4[c]	[b]	1.3	[b]	<1.0	<1.0
Dibasic acid ester + 1.0 wt. % tritolyl phosphate	Hardened	4	+4.7	0.9	70	2.4	2.2
	standard	4	+7.0	0.2	100	2.8	2.4

[a] Test conditions: temp. 500° F., pressure 700 p.s.i.
[b] Weight loss was not determined but severe wear was evident.
[c] Test temperature for this run 400° F.

Table V. Lubricity Tests Conducted in a Pesco Model 349 Gear Pump[a]

Test Fluid, Concn., Wt. %	Test Pressure, P.S.I.	Rate of Flow, Gal./Min.	Viscosity at 200° F., Cs.	Loss in Weight of Pump Parts, Gram		
				Drive gear	Idler gear	Four bushings total
Mineral oil base fluid without antiwear additive (PRL 1912)	2500	3.43	5.5	0.104	0.090	0.167
+ 1.0 tritolyl phosphate	2500	3.26	5.5	0.026	0.018	0.130
+ 20 di(2-ethylhexyl) sebacate + 1.0 tritolyl phosphate	2500	2.65	5.3	0.005	0.006	0.530
Methyl silicone oil (PRL 1836)[b]	3000	3.28	16	0.010[b]	0.000[b]	0.105[b]

[a] Test conditions: reservoir temp. 200° F., time 100 hrs., speed 3600 r.p.m.
[b] Seven 100-hr. tests conducted on this fluid (one set of pump parts throughout). Pressures 1000 to 3000 p.s.i.; pump speed 1800 or 3000 r.p.m.; test temperature = 100° or 200° F.; values are total for 700 hours.

high wear. This appearance, coupled with low weight loss, suggests gross plastic deformation of the metal surface. These data suggest strongly the formation of a layer of material on the gear surface which is lower melting and/or more ductile than the original hardened steel surface.

In general, there is good agreement between 1- and 10-kg. load wear values in the four-ball wear tester and the behavior of lubricants in gear- and vane-type hydraulic pumps. The four-ball wear and E.P. data for dimethylsilicone and several mineral oil and ester formulations are shown in Tables VI and VII. Consistent improvement of antiwear properties with phosphorus type lubricity additives and improved wear and antiseize properties with the acid phosphite additive are shown for mineral oil and ester fluids. Silicone shows relatively good antiwear properties at 1 and 10 kg. but poor antiseize properties in the wear tester at 40 kg. and in the E.P. tester. Silicone also shows a lack of improvement in wear and seizure properties with addition of a polar and effective phosphorus type lubricity additive. Again close evaluation of wear surface in the four-ball tests may be helpful in establishing a mechanism for silicone action. The wear scar of silicone fluid at low loadings contains pock marks indicative of spot welding randomly located throughout the mated surface, despite a generally well-mated or worn-in surface. At high loadings, evidence of seizure and welding dominates the picture.

This basic behavior of methylsilicone suggests the positive action or reaction of this material with the steel surface to form a soft, ductile, but extremely unreactive surface film. Such a film lends itself to surface mating in much the same fashion as the film formed by mineral oils containing phosphorus type lubricity additives. The lack of antiseize or antiweld properties suggests the inertness of such a film to further chemical reaction. In general, E.P. properties are achieved by materials which react readily with the bearing surface to form a chemical compound which in turn is easily wiped from the bearing surface. This mechanism results in a continuous chemical erosion at the bearing surface. The inability of normally reactive antiwear or E.P. additives to function adequately in the silicones also suggests that the silicones have a high order of affinity for the metal surface (polarity). To become involved in the wear or lubricity process, it is estimated that the molecules involved must be within a few molecular layers of the actual metal surface. Low-melting, chemically inert alloys of silicon and iron such as those suggested by these studies are known in the field of metal alloys.

Table VI. Wear Characteristics of Several Fluids in Shell Four-Ball Wear Tester[a]

52-100 Steel Balls

	Av. Wear Scar Diameter, Mm.		
Test Fluid, Concn., Wt. %	1 kg.	10 kg.	40 kg.
Mineral oil-base fluid (PRL 1912)	0.34	0.54	1.04
+ 1.0 tritolyl phosphate	0.14	0.23	0.47
	0.14	0.25	0.46
+ 20 di(2-ethylhexyl) sebacate			
+ 1.0 tritolyl phosphate	0.16	0.22	0.51
Naphthenic white oil (3 cs. at 100° F.)	0.46	0.71	0.89
+ 1.0 tritolyl phosphate	0.15	0.23	0.44
+ 0.5 dialkyl acid phosphite	0.18	0.28	0.46
Ester-base fluid	0.34	0.56	0.69
+ 5.0 tritolyl phosphate	0.15	0.26	0.40
+ 0.2 dialkyl acid phosphite	0.16	0.22	0.39
Methyl silicone oil (PRL 1836)	0.32	0.39	1.40
Methyl silicone oil (D.C. 200)	0.35	0.48	1.75
+ 0.5 dialkyl acid phosphite	0.39	0.56	1.17

[a] Test conditions: temp. 167° F., time 1 hr., speed 620 r.p.m.

Poor lubricity at high temperature as well as a high temperature coefficient of lubricity has been demonstrated for silicones and silicates in Tables I through IV. Silicone and silicate lubricant failures by the seizure and welding mechanism accelerate with rise in bulk system temperature to a much greater extent than occurs with mineral oils and esters. The suggested formation of a lower melting, inert surface layer where sufficient heat from environment plus friction leads to seizure- and welding-type failures is consistent with experimentally determined trends exhibited by silicates and silicones. In the case of esters and mineral oils, however, higher temperature increases the reactivity of the fluid with the metal surface to form an easily sheared film which counteracts the trend of increased lubricity failures with increasing temperature.

Another series of tests has been used to confirm further the polarity of silicones and silicates and their participation in the reaction at the bearing surface (Tables VIII and IX). The effect of 1.0 weight % of tritolyl phosphate in each base stock is shown as a reference point. Silicone-containing materials show antiwear effectiveness in both solvents. Antiwear action appears to be more effective at 1- and 10-kg. loads than at 40 kg.

Silicones and silicates cause little or no improvement in the seizure and weld points of base fluids in the E.P. lubricity testers. In general, silicones and silicates behave as additives in mineral oils and esters in essentially the same fashion as when evaluated neat. That is, in both cases silicones and silicates act as chemical polishing, antiwear additives at low bearing loadings, but show little or no effectiveness in preventing seizure and welding. In this respect, they show a close analogy to the behavior of the phosphorus type antiwear additives such as tritolyl phosphate.

Table VII. Lubricity Characteristics of Several Fluids in Shell Four-Ball E.P. Tester[a]

	Approximate Load for		Av. Wear Scar. Diameter, Mm.					
Test Fluid, Concn., Wt. %	Incipient seizure, kg.	Permanent welding, kg.	40 kg.	60 kg.	80 kg.	100 kg.	120 kg.	140 kg.
Naphthenic white oil (3 Cs. at 100° F.)	<40	100	1.78	1.97	2.62	Welded	...	...
+ 1.0 tritolyl phosphate	40	100	0.45	2.18	2.40	Welded	...	...
+ 0.5 dialkyl acid phosphite	130	140	...	0.43	...	0.49	0.54	Welded
Methyl silicone oil (D.C. 200)	<40	120	1.36	...	2.34	...	Welded	...
+ 0.5 dialkyl acid phosphite	<40	120	1.56	2.25	...	2.66	Welded	...
Ester-base fluid	50	100	0.42	2.42	2.66	Welded	...	...
+ 5.0 tritolyl phosphate	70	140	0.32	0.35	2.29	...	2.98	Welded
+ 0.5 dialkyl acid phosphite	190	200[b]	...	...	...	...	...	...[b]

[a] Test conditions: temp. 70° to 80° F., time 1 min., speed 1750 r.p.m., 52-100 steel balls.
[b] 160 Kg. = 0.52; 180 kg. = 0.55; 200 kg. = welded.

The phosphorus type antiwear additive mechanism as a chemical polishing agent can be adequately demonstrated by a sequence of tests in the four-ball wear tester. In this sequence, two successive 1-hour tests in the four-ball wear tester are conducted with the same set of test balls on the same wearing surfaces. The first step is a conventional 1-hour test. Following this test, the balls and ball pot are thoroughly cleaned with a solvent without removing the balls from the ball pot or rotating chuck. The apparatus is then reassembled and a second 1-hour test is conducted with a new charge of test fluid. Using this technique, the test fluid may be the same for both tests or a different test fluid may be used in the second portion of the test.

A series of double runs illustrating the "run-in" properties of various types of additives in a mineral oil base stock is shown in Table X. In the case of the nonadditive fluid and all of the antifriction and E.P. additives, wear continues at a substantial rate for the second incremental test using the same fluid in both tests. For the same series of test fluids, the wear continues for the second incremental test if a nonadditive mineral oil is used for this second test. However, if a phosphorus type antiwear additive such as tritolyl phosphate, triphenyl thiophosphate, or diisopropyl acid phosphite is used in the first test, a second test with the same fluid or with a nonadditive fluid can be conducted with essentially no increase in the wear scar. In general, these double runs adequately illustrate the mechanical erosion of nonadditive fluids, and the chemical polishing (surface mating) of the phosphorus-containing antiwear additives.

Table VIII. Effect of Silicones and Silicates as Antiwear Additives

Shell Four-Ball Wear Tester[a]

Test Fluid, Concn., Wt. %	Av. Wear Scar Diameter, Mm.		
	1 kg.	10 kg.	40 kg.
Dibasic acid ester	0.36	0.52	0.70
+ 1.0 tritolyl phosphate	0.14	0.26	0.37
+ 5.0 methyl silicone (D.C. 200)[b]	0.15	0.25	0.62
+ 5.0 methyl silicone (D.C.500)[b]	0.18	0.25	0.50
+ 1.0 tetra-(2-ethylhexyl) silicate	0.39	0.54	0.78
+ 5.0 tetra-(2-ethylhexyl) silicate	0.15	0.25	0.60
+ 5.0 silicate fluid (MLO 8200)	0.16	0.25	0.46
+ 5.0 silicone fluid (Versilube F-50)	0.17	0.29	0.50
Mineral oil	0.49	0.62	0.99
+ 1.0 tritolyl phosphate	0.15	0.23	0.44
+ 5.0 methyl silicone (D.C. 200)	0.22	0.37	0.84
+ 5.0 methyl silicone (D.C. 500)	0.25	0.40	1.06
+ 5.0 tetra-(2-ethylhexyl) silicate	0.36	0.56	1.04
+ 5.0 silicate fluid (MLO 8200)	0.26	0.58	0.79
+ 5.0 silicone fluid (Versilube F-50)	0.41	0.41	0.64

[a] Test conditions: temp. 167° F., time 1 hr., speed 620 r.p.m.; 52-100 steel balls.

[b] Blend was slightly cloudy indicating incomplete solubility at room temperature.

A series of double runs has been made with silicones and silicates as antiwear additives in mineral oil and ester base stocks (Table X). The second run of the series was made, in each case, with nonadditive base stock. Using a 1-kg. load, all of the double runs with silicones show the same kind of chemical polishing or antiwear effect as has been demonstrated for the phosphorus type antiwear additive. At 10 and 40 kg., silicones are not completely effective in providing a well run-in surface. The tritolyl phosphate additive provides a well run-in surface for 1- and 10-kg. loads in this test sequence, but is not always effective at 40 kg. In view of the relative merits of silicone and tritolyl phosphate in preventing seizure and welding, comparison between their behavior as antiwear or chemical polishing agents seems to be of the right order of magnitude. Silicate does not appear to be as effective as silicone as a chemical polishing agent. The MLO 8200 is more effective than the tetra-2-ethylhexyl silicate. MLO 8200 is a finished formulation which probably contains, in addition to a silicate-type base stock, a silicone thickener, and lubricity additives.

Silicones, in this double-run sequence in the four-ball wear tester, illustrate antiwear behavior consistent with data obtained in hydraulic pumps and other four-ball wear tester studies.

Thus far, all data point to the similar behavior of silicones and phosphorus-containing antiwear additives. An additional series of four-ball studies has been carried out to explore further the nature of these two types of antiwear effects and the competition for the preferential position on the bearing surface between silicon-type and phosphorus type additives. Tritolyl phosphate and phosphoric acid are the two phosphorus type additives used in this comparison. These materials differ in polarity and, therefore, in minimum concentration to provide good antiwear properties.

Table IX. Effect of Silicones and Silicates as Lubricity Additives

Shell Four-Ball E.P. Tester[a]

Test Fluid, Concn., Wt. %	Approximate Load for		Av. Wear Scar. Diameter, Mm.			
	Incipient seizure, kg.	Permanent welding, kg.	40 kg.	60 kg.	80 kg.	100 kg.
Dibasic acid ester	< 60	100	...	2.38	2.51	Welded
+ 5.0 tritolyl phosphate	90	100	...	0.36	0.45	Welded
+ 5.0 methyl silicone (D.C. 200)[b]	< 60	100	...	1.88	2.47	Welded
+ 5.0 methyl silicone (D.C. 500)[b]	90	100	...	0.39	0.42	Welded
+ 1.0 tetra-(2-ethylhexyl) silicate	< 60	100	...	2.21	2.47	Welded
+ 5.0 tetra-(2-ethylhexyl) silicate	70	100	...	0.42	2.47	Welded
+ 5.0 silicate fluid (MLO 8200)	70	120	...	0.39	2.40	2.34[c]
+5.0 silicone fluid (Versilube F-50)	70	100	0.39	0.46	2.62	Welded
Mineral oil	< 40	100	1.78	1.97	2.62	Welded
+ 5.0 methyl silicone (D.C. 200)	< 40	100	1.56	...	3.31	Welded
+ 5.0 methyl silicone (D.C. 500)	< 40	100	1.15	2.97	...	Welded
+ 5.0 tetra-(2-ethylhexyl) silicate	70	100	...	0.42	2.47	Welded
+ 5.0 silicate fluid (MLO 8200)	40	100	0.93	2.03	1.95	Welded
+ 5.0 silicone fluid (Versilube F-50)	< 40	80	1.86	2.43	Welded	...

[a] Test conditions: temp. 70° to 80° F.; time 1 min., speed 1750 r.p.m., 52-100 steel balls.

[b] Blend was slightly cloudy indicating incomplete solubility at room temperature.

[c] Welds at 120 kg. load.

Table X. Effect of "Run-In" on the Shell Four-Ball Wear Tester[a]

Lubricity Additive Concn., Wt. %		Av. Wear Scar Diameter, Mm.					
		1-Kg. load		10-Kg. load		40-Kg. load	
1st Test	2nd Test	1st Test[b]	2nd Test[c]	1st Test[b]	2nd Test[c]	1st Test[b]	2nd Test[c]
	Mineral Oil-Base Hydraulic Fluid (No Lubricity Additive)						
None	None	0.40	0.48	0.56	0.68	0.66	0.76
1.0 tritolyl phosphate	1.0 tritolyl phosphate	0.18	0.18	0.23	0.24	0.54	0.63
1.0 triphenyl thiophosphate	1.0 triphenyl thiophosphate	0.19	0.20	0.22	0.23	0.42	0.46
0.5 dialkyl acid phosphite	0.5 dialkyl acid phosphite	...	...	0.44	0.45	...	...
1.0 stearic acid[d]	1.0 stearic acid[d]	...	...	0.35	0.47	0.42	0.58
1.0 chloronaphtha xanthate	1.0 chloronaphtha xanthate	...	...	0.61	0.73	0.84	0.95
1.0 tritolyl phosphate	None	0.16	0.16	0.23	0.23	0.56	0.57
1.0 triphenyl thiophosphate	None	0.19	0.20	0.22	0.22	0.38	0.40
0.5 dialkyl acid phosphite	None	0.27	0.28	0.36	0.37	0.45	0.46
1.0 dilauryl acid phosphate	None	...	...	0.35	0.54	0.45	0.68
1.0 stearic acid[d]	None	0.30	0.40	0.35	0.54	0.42	0.62
1.0 chloronaphtha xanthate	None	0.43	0.45	0.61	0.72	0.84	0.91
	Dibasic Acid Ester						
None	None	0.44	0.48	0.56	0.64	0.85	1.04
5.0 silicate fluid (MLO 8200)	None	0.16	0.17	0.28	0.44	0.69	0.86
5.0 tetra-(2-ethylhexyl) silicate	None	0.16	0.35	0.24	0.57	0.66	0.93
5.0 methyl silicone (D.C. 500)[d]	None	0.21	0.22	0.36	0.45	0.57	0.63
2.0 methyl silicone (D.C. 500)[d]	None	0.16	0.33	0.28	0.46	0.69	0.86
5.0 silicone fluid (Versilube F-50)	None	0.17	0.23	0.29	0.48	0.50	0.68
	Naphthenic White Mineral Oil						
None	None	0.46	0.58	0.71	0.86	0.89	1.06
5.0 silicate fluid (MLO 8200)	None	0.24	0.25	0.56	0.71	0.82	1.17
5.0 tetra-(2-ethylhexyl) silicate	None	0.22	0.26	0.42	0.47	1.00	1.12
5.0 methylsilicone (D.C. 500)	None	0.29	0.31	0.42	0.49	0.89	1.11
5.0 methyl silicone (D.C. 200)	None	0.30	0.32	0.50	0.56	0.96	0.99
5.0 silicone fluid (Versilube F-50)	None	0.41	0.41	0.41	0.51	0.64	0.93

[a] Test conditions: temp. 167° F., time 1 hr., speed 620 r.p.m., 52-100 steel balls.
[b] Test conducted with indicated fluid and new set of ball bearings in conventional fashion.
[c] Balls from first test were used in the same position for second test; between tests ball pot and balls were thoroughly washed and dried and second fluid charged; second test scar is total scar size resulting from 2-hour running.
[d] The blend is slightly cloudy indicating incomplete solubility at room temperature.

Data obtained with several phosphorus-containing materials having different degrees of polarity are shown in Table XI. These data illustrate the use of a triaryl phosphate, a dialkyl acid phosphate, and phosphoric acid as antiwear additives in di-(3-methylbutyl) adipate. In this diester, 3 to 5 weight % of tritolyl phosphate is required to give antiwear improvement. In contrast, a concentration of 0.05 weight % of dilauryl acid phosphate or 0.01 weight % of phosphoric acid gives optimum antiwear behavior.

Phosphoric acid may be considered a bifunctional additive in mineral oils and esters. At concentrations of less than 0.1 weight %, this material provides antiwear properties with a minimum effect on E.P. properties. This behavior is typical of tritolyl phosphate at concentrations of 1 to 5%. At concentrations of 0.5 weight % and higher, phosphoric acid provides E.P. properties as well as antiwear properties. The highest concentration (1.0 weight %) of phosphoric additive used in the four-ball tester shows indications of the chemically erosive E.P. properties characteristic of the acid group rather than the antiwear properties of the phosphorus portion of the molecule. Diisopropyl acid phosphite behaves like dilauryl acid phosphate. At high concentrations of diisopropyl acid phosphite, the chemically erosive nature of the acid grouping begins to be evident in the reaction at the bearing surface.

The E.P. effect of diisopropyl acid phosphite on mineral oil and ester base stocks is illustrated in Table XII. The same concentration of this additive has also been evaluated in silicone and silicate fluids. Acid phosphite is not effective in these silicon-containing materials.

Table XI. Effect of Concentration on Antiwear Properties of Phosphorus-Containing Additives

Shell Four-Ball Wear Tester[a]

Test Fluid (Concn., Wt. %)	Av. Wear Scar Diameter, Mm.		
	1 kg.	10 kg.	40 kg.
Di-3-methylbutyl adipate	0.39	0.71	0.91
+ 1.0 tritolyl phosphate	0.38	0.71	0.97
+ 3.0 tritolyl phosphate	0.40	0.64	0.97
+ 5.0 tritolyl phosphate	0.23	0.25	0.78
+ 0.01 dilauryl acid phosphate	0.21	0.41	0.84
+ 0.05 dilauryl acid phosphate	0.19	0.28	0.43
+ 1.0 dilauryl acid phosphate	0.17	0.28	0.42
+ 0.001 phosphoric acid	0.41	0.69	0.90
+ 0.01 phosphoric acid	0.16	0.37	0.50
+ 1.0 phosphoric acid	0.38	0.60	0.78

[a] Test conditions: temp. 167° F., time 1 hr., speed 620 r.p.m., 52-100 steel balls.

Shell four-ball wear and E.P. tester results with diisopropyl acid phosphite and silicone or silicate additives tested separately and in combination are shown in Table XII. Base stocks for these additive tests are a diester and a highly refined naphthenic white oil. The 0.5 weight % of diisopropyl acid phosphite provides good antiwear, antiseize, and antiweld properties. The two silicones and the silicate antiwear additives at 5.0 weight % concentration provide antiwear properties, but do not alter significantly the antiseize and antiweld properties of the base stock. The combination of phosphorus- and silicon-containing additives shows some or all of the E.P. effects of diisopropyl acid phosphite. In both base stocks, however, there is a general trend indicating interference between the two additive types in the reactions occurring at the bearing surface. This interference is best illustrated by the consistent trend toward higher wear with combined additives at the 10-kg. load than with either additive alone; and a general trend for a reduction in seizure and weld point with combination of additives as compared to that obtainable by the acid phosphite alone.

CONCLUSIONS

High temperature fluid properties place increased emphasis on the boundary (chemical) component of lubricity primarily because of the consistently low viscosity levels encountered at elevated temperatures. Mineral oils and esters show excellent retention of lubricity properties at 500° F. and above with continuing sensitivity to the beneficial effects of phosphorus-containing lubricity additives in this temperature region. Silicones and silicates exhibit relatively poor lubricity properties at elevated temperatures. Because of the relatively poor lubricity level of silicones and silicates, these materials show higher sensitivity than do mineral oils and esters to the increased hardness (mechanical improvements) of the wearing pump parts. A closer evaluation of silicones and silicates shows that these materials do in fact provide antiwear characteristics when used neat or as additives in esters and mineral oils. The antiwear characteristics of these materials parallel closely the behavior of tritolyl phosphate and the phosphorus type antiwear additives. Despite antiwear activity, silicones and silicates display poor antiseize and antiweld properties. This over-all behavior of silicones and silicates can be demonstrated consistently to be a function of chemical reactivity with the bearing surface. The reactivity of silicones and silicates is nullified sufficiently and effectively.

Table XII. Effect of Phosphorus- and/or Silicon-Containing Additives on Lubricant Behavior

	Wear Tester,[a] Av. Wear Scar Diam., Mm.			Extreme-Pressure Lubricity Tester[b]					
				Approximate load, kg., for		Av. Wear Scar Diameter, Mm.			
Additive Concn., Wt. %	1 kg.	10 kg.	40 kg.	Incipient seizure	Permanent welding	40 kg.	60 kg.	80 kg.	100 kg.
Tetra-(2-ethylhexyl) Sebacate									
None	0.27	0.41	0.74	40	100	0.74	...	3.90	Welded
0.5 dialkyl acid phosphite	0.26	0.54	0.51	60	100	0.38	...	2.34	Welded
Methyl Silicone (D.C. 200)									
None	0.35	0.48	1.75	...	...	...	...	...	...
0.5 dialkyl acid phosphite	0.39	0.56	1.17	<40	120	1.56	2.25	...	2.66[c]
Silicone Fluid (Versilube F-50)									
None	0.18	0.31	0.67	40	100	...	0.93	1.86	Welded
0.5 dialkyl acid phosphite	0.21	0.41	0.80	40	100	0.74	...	2.19	Welded
Dibasic Acid Ester									
None	0.43	0.56	0.80	50	100	0.42	2.38	2.51	Welded
0.5 dialkyl acid phosphite	0.15	0.24	0.40	190	200	...	...	...	...[d]
5.0 tetra-(2-ethylhexyl) silicate	0.16	0.24	0.66	70	100	...	0.42	2.47	Welded
5.0 tetra-(2-ethylhexyl) silicate and 0.5 dialkyl acid phosphite	0.47	0.54	0.63	190	200	...	...	...	0.47[e]
5.0 methyl silicone (D.C. 500)[f]	0.21	0.36	0.57	90	100	...	0.39	0.42	Welded
5.0 methyl silicone (D.C. 500)[f] and 0.5 dialkyl acid phosphite	0.19	0.47	0.53	150	160	...	...	...	...[g]
5.0 silicone fluid (Versilube F-50)	0.17	0.29	0.50	70	100	...	0.46	2.62	Welded
5.0 Versilube F-50 and 0.5 dialkyl acid phosphite	0.19	0.44	0.53	190	200	...	...	...	0.44[h]
Mineral Oil									
None	0.46	0.71	0.89	<40	100	1.78	1.97	2.62	Welded
0.5 dialkyl acid phosphite	0.27	0.36	...	130	140	...	0.43	...	0.49[i]
5.0 tetra-(2-ethylhexyl) silicate	0.22	0.42	1.00	<40	80	2.01	...	Welded	...
5.0 tetra-(2-ethylhexyl) silicate and 0.5 dialkyl acid phosphite	0.36	0.56	1.04	90	100	...	...	0.48	Welded
5.0 methyl silicone (D.C. 500)	0.29	0.42	0.89	<40	100	1.15	2.97	...	Welded
5.0 methyl silicone (D.C. 500) and 0.5 dialkyl acid phosphite	0.30	0.38	0.61	60	100	0.36	...	2.79	Welded
5.0 silicone fluid (Versilube F-50)	0.41	0.41	0.64	<40	80	1.86	2.43	Welded	...
5.0 Versilube F-50 and 0.5 dialkyl acid phosphite	0.32	0.50	0.57	50	100	0.36	2.73	2.73	Welded
1.0 tritolyl phosphate	0.15	0.23	0.44	...	...	...	...	...	...
5.0 methyl silicone (D.C. 200)	0.22	0.37	0.84	...	...	...	...	...	...
5.0 methyl silicone (D.C. 200) and 1.0 tritolyl phosphate	0.21	0.36	0.56	...	...	...	...	...	...

[a] Test conditions: temp. 167° F., time 1 hr., speed 620 r.p.m., 52–100 steel balls. [b] Test conditions: temp. 70° to 80° F., time 1 min., speed 1750 r.p.m., 52–100 steel balls. [c] Welded at 120 kg. [d] 0.52 at 160 kg., 0.55 at 180 kg., and welded at 200 kg. [e] 0.49 at 120 kg., 0.51 at 160 kg., 0.57 at 180 kg., and welded at 200 kg. [f] Blend was slightly cloudy indicating incomplete solubility at room temperature. [g] 0.49 at 140 kg. and welded at 160 kg. [h] 0.50 at 140 kg., 0.56 at 180 kg., and welded at 200 kg. 0.54 at 120 kg. and welded at 140 kg.

These data strongly suggest the reaction of iron and silicon to form a low-melting, ductile film on the bearing surface that is much more inert to further chemical reaction than the original steel surface.

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Diarylalkanes as High Temperature, Nuclear Radiation–Resistant Hydraulic Fluids

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THE DESIRABLE characteristics of conventional hydraulic fluids include adequate lubricating properties, low volatility, low corrosivity, low flammability, a small change of viscosity over a wide temperature range (high viscosity index), and stability to oxidation, shear, and hydrolysis. A number of structurally different materials are satisfactory lubricants over a relatively narrow temperature range of application. Representative classes of these base stocks are petroleum fractions, polyglycol ethers, phosphates, silicates, and dibasic acid esters. Such materials are inadequate for future military aircraft which require fluids capable of withstanding high temperature and nuclear radiation environments.

Organic compounds vary widely in their ability to resist thermal and radiolytic change. Unsubstituted polyphenyls are known to have good radiation resistance and outstanding thermal stability (*2*). The chief deficiencies of the polyphenyls in hydraulic fluid applications are liquid range and viscosity index. A program was undertaken to improve these latter properties and retain the desirable radiation and thermal resistance of the aromatic ring by suitable "tailoring" of alkylaromatic materials. Such a combination of qualities is found in the α,ω-diarylalkanes.

A variety of diarylalkane derivatives was synthesized and screened as potentially stable hydraulic fluids. A correlation was made of molecular structure, pertinent physical properties, and thermal and radiation stability.

EXPERIMENTAL

Syntheses. Attachment of the paraffin bridge to the phenyl rings in α,ω-diphenylalkanes was in all cases at primary carbon atoms. Diphenylmethane and bibenzyl (1,2-diphenylethane) were commercial products (Distillation Products); other unsubstituted α,ω-diphenylalkanes were prepared by acylation of benzene with the appropriate aliphatic dibasic acid chlorides, followed by Wolff-Kishner reduction of the respective diketones (*3*). Over-all yields from the dibasic acids were 50 to 60%. Symmetrically substituted α,ω-diarylalkanes were obtained by the same procedure using selected aromatics (diphenyl ether, biphenyl, Tetralin, butylbenzenes). Difficulty was encountered in the synthesis of the three 1,9-bis(butylphenyl)-nonanes. Products were contaminated with about 5% of unreduced ketone. Attempts to effect complete purification were unsuccessful.

In general, the synthesis of unsymmetrically substituted α,ω-diarylalkanes was carried out by the alkylation of specific diarylalkane intermediates with 1-olefins using either chloroform-modified aluminum chloride or hydrogen fluoride (HF) as catalysts. Under the conditions employed, the point of attachment may be any carbon other than the terminal one. No attempt was made to determine the degree of concurrent meta and para substitution of the alkyl groups. The degree of disproportionation and isomerization occurring during alkylation was not well established. Boiling ranges, viscosities, refractive indices, and infrared spectral analyses were used in the characterization of products.

Phenyl(*n*-nonylphenyl)isodecane was prepared by acylation of diphenylisodecane (derived from isosebacic acid, U.S.I. Chemicals) with pelargonyl chloride and subsequent Wolff-Kishner reduction of the ketone.

Diphenylmethane derivatives were synthesized by an HF alkylation procedure using 1-olefins. Attempted alkylations of diphenylmethane by aluminum chloride catalysis yielded primarily low boiling, disproportionated materials.

Dicyclohexylisodecane was obtained by the catalytic hydrogenation of diphenylisodecane at 390° F. and 2200 p.s.i. over Raney nickel.

1,6-Bis(phenoxy)hexane was prepared by refluxing an