Selenonophosphates as Lubricant Additives

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The purpose of this investigation was to extend the study of selenium compounds as lubricant addition agents to another class of compounds, the selenonophosphates.

By means of an extensive series of bench and engine tests, selenonophosphates have been shown to act as antioxidants for lubricating oils. L-4 Chevrolet engine tests show that the selenonophosphates reduce bearing corrosion but not to the extent desired for a bearing corrosion inhibitor. The use of 0.25% Ortholeum 202 in conjunction with tributyl selenonophosphate reduces bearing corrosion to a satisfactory level. There is an indication

N A previous paper (3), data were presented which show that small amounts (0.05 to 0.30%) of selenium dioxide in lubricating oils, act as powerful antioxidant and bearing-corrosion inhibitors, thus imparting desirable properties to the oils. Denison and Condit (2) have shown that the dialkyl selenides are incomparably more effective oxidation inhibitors than the corresponding sulfur compounds.

The purpose of this paper is to present data which extend the study of selenium compounds as lubricant addition agents to another class of selenium compounds, the selenonophosphates.

PREPARATION OF SELENONOPHOSPHATES

The nomenclature relating to compounds of the type herein referred to as selenonophosphates is both confusing and inconsistent in the literature. For the purpose of this paper, the selenonophosphates are defined as salts or esters of selenonophosphoric acid which has the formula:

which is analogous to the corresponding thionophosphoric acid having the formula:

Selenonophosphoric acid is distinguished from selenophosphoric acid

which is analogous to the corresponding thiophosphoric acid

This system of nomenclature parallels that used by Mastin, Norman, and Weilmuenster (4).

In general, the esters of selenonophosphoric acid were prepared by the reaction of elemental selenium with the corresponding phosphite according to the general equation:

$$(RO)_{3}P + Se \longrightarrow (RO)_{3}PSe$$

that the method of preparation of the selenonophosphates affects their performance as antioxidants and bearingcorrosion inhibitors. It is shown in bench tests that the selenonophosphates are significantly better antioxidants for lubricating oils than their sulfur analogs or the corresponding phosphites.

This investigation widens the scope of selenium compounds which are known to function as lubricating oil antioxidants. It adds another class of compounds to the list of those which greatly reduce oil deterioration by oxidation when small amounts are incorporated therein.

The analogous esters of thionophosphoric acid were prepared in the same manner, using sulfur in place of selenium.

The phosphites used to prepare the selenonophosphates or thionophosphates were obtained from commercial sources when available; otherwise, they were prepared in the laboratory according to the following general equation:

$$3ROH + PCl_3 \rightleftharpoons (RO)_3P + 3HCl$$

The reactions were carried out in the presence of pyridine which functions to remove the hydrochloric acid from the reaction. Hexane, or ether, was used as the reaction medium.

TRIISOPROPYL PHOSPHITE

Phosphorus trichloride (132 ml., 1.5 moles) was added dropwise to a mixture of 337 ml. (4.4 moles) of isopropyl alcohol, 366 ml. (4.5 moles) of pyridine, and 600 ml. of ether, contained in a 2-liter, 3-necked flask, equipped with a mechanical stirrer, reflux condenser, and a tube to admit nitrogen into the flask during the entire course of the preparation. Two hours after the last addition of phosphorus trichloride, the nixture was filtered to remove the pyridine hydrochloride, and the ether was removed by evaporation over a steam bath. Nitrogen was passed into the flask during the evaporation of the ether. Excess alcohol, pyridine, and ether were finally removed by evacuating the flask with a water aspirator and simultaneously raising the temperature to 130° C. The residue was finally fractionated under vacuum in a Vigreux laboratory column having 10.7 theoretical plates. The fraction boiling in the temperature range 36.0° to 37.5° C. at 0.9-mm. pressure was taken as the desired product. This has a specific gravity of 0.9054 at 25° C. and a refractive index, n⁴₂°, of 1.4108. The only specific gravity figure found in the literature was a value of 0.9361 at 0° C. (1). Analysis showed the product to contain 15.0% phosphorus. Theoretical for triisopropyl phosphite $[(C_3H_7O)_3P]$ is 14.9%

TRIISOPROPYL SELENONOPHOSPHATE

Fifty milliliters, 45.27 grams (0.22 mole), of triisopropyl phosphite were placed in a 125-ml. round-bottomed flask. The flask and contents were immersed in an ice water bath, and 17.18 grams (0.22 mole) of powdered elemental selenium were slowly added while the mixture was stirred mechanically. After the final addition of the selenium, the ice water bath was removed and the temperature was allowed to increase to room temperature. A reflux condenser was fixed to the flask and, while the mixture was stirred, the temperature increased slowly to 168° C. The mixture was then allowed to cool to room temperature, after which it was filtered to remove the unreacted selenium.



Figure 1. 10-Hour Underwood Oxidation Test

The filtrate had a strong, unpleasant odor characteristic of the —SeH group. Analyses showed that this filtrate contained 26.2% selenium and 10.9% phosphorus. Theoretical for triisopropyl selenonophosphate $[(C_8H_7O)_8PSe]$ is 27.5% selenium and 10.8% phosphorus. This crude product was distilled under high vacuum, and the fraction boiling in the temperature range of 32° to 42° C. was taken. It contained 26.9% selenium, was water-white, and had a weak and not unpleasant odor, whereas the material collected in the dry ice trap had a very strong, vile odor, indicating that the odor in the original product was caused by impurities, probably containing an —SeH group. The final product had a specific gravity of 1.1682 at 25° C.

TRIBUTYL SELENONOPHOSPHATE

SAMPLE 1. Elemental selenium was reacted with commercial tributyl phosphite. Selenium (236.9 grams, 3 moles) was added slowly to 750 grams (3 moles) of tributyl phosphite. After the final addition of the selenium, the temperature of the mixture was slowly raised to 155° C. After cooling to room temperature, the mixture was filtered, and the filtrate was then distilled under vacuum to yield a product containing 23.7%



Figure 2. 10-Hour Underwood Oxidation Test

selenium. Theoretical for tributyl selenonophosphate $[(C_1H_2O)_3-PSe]$ is 24.0% selenium.

SAMPLE 2. For purposes of conducting full scale Chevrolet engine tests, a large sample of this material was prepared by reacting 340 grams (4.3 moles) of elemental selenium with 1000 grams (4.0 moles) of commercial tributyl phosphite. After addition of the selenium, the temperature was raised to 190° C. for 10 minutes. The mixture was cooled rapidly and filtered, to remove the unreacted selenium.

The filtrate (product) was amber in color and had a very vile, disagreeable odor characteristic of selenol. It analyzed 24.1%selenium and 10.3% phosphorus. Theoretical for tributyl selenonophosphate is 24.0% selenium and 9.4% phosphorus. A sample of this material was treated with 1 N sodium hydroxide after which its odor was decidedly improved. Acidification of the sodium hydroxide layer with hydrochloric acid resulted in the separation of a very light straw-colored, oily liquid with an extremely disagreeable odor. It is concluded that the vile odor of the original product is caused by the presence of butyl selenol

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TABLE I.	10-HOUR UND	erwood O	XIDATION	Tests	OF TRIBUTYL
Selence	ONOPHOSPHATE	IN PENNS	SYLVANIA	10W B	ASE OIL ^a

Se, %	Naphtha- Insoluble, %	Sludge, Ml./10 Ml. Oil	Viscosity Increase at 100° F., %	Neutral- ization No., Mg. KOH/G.	Con- radson Carbon,	Bearing Corrosion, Mg. Loss
$\begin{array}{c} 0.00 \\ 0.05 \\ 0.10 \\ 0.15 \\ 0.25 \\ 0.15 \\ 0.15 \\ 0.15 \\ 0.15 \\ 0.15 \\ \end{array}$	7.58 • 0.25 0.29 0.19 0.01	$\begin{array}{c} 3.35\\ 0.10\\ 0.20\\ 0.05\\ 0.01\\ 0.03\\ 0.10\\ \end{array}$	$1000 \\ 171 \\ 68 \\ 54.7 \\ 31 \\ 14.5 \\ 59.6$	20.87 9.83 5.54 3.75 3.39 0.49 2.90	$\begin{array}{c} 4.75\\ 2.75\\ 1.51\\ 1.31\\ 0.88\\ \end{array}$	$131.1 \\ 61.8 \\ 26.3 \\ 34.0 \\ 23.7 \\ 69.8 \\ 24.3$
^a Eroi	m refinery A					

• Tributyl selenonophosphate (sample 1 was used). • Tributyl selenonophosphate (sample 2 was used). • Tributyl selenonophosphate (sample 2 treated with 1 N NaOH was used).



Figure 3. Indiana Stirring Oxidation Test

Stirring rods after 72 hours in tester A. Pennsylvania base uninhibited B. Pennsylvania base plus tributyl selenonophosphate C. Mid-continent base uninhibited

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Mid-continent base plus tributyl selenonophosphate

as an impurity, which forms during the high-temperature reaction between selenium and tributyl phosphite. The reason for the high phosphorus content is not clear.

TRIBUTYL THIONOPHOSPHATE

Flowers of sulfur (32 grams, 1 mole), was added in small

portions to 250 grams (1 mole) of commercial tributyl phosof sulfur, the temperature of the mixture was slowly in-creased to 125° to 130° C. and maintained for 3 hours, after which time the mixture was filtered. Analysis showed that the filtrate (product) contained 11.1% sulfur and 12.3% phos-phorus. Theoretical for tri-butyl thionophosphate $[(C_4H_9O)_3PS]$ is 11.4% sulfur and 11.0% phosphorus. It was used without further puri-fication fication.

TRIBUTYL THIOPHOSPHITE

Twenty grams of phosphorus trichloride were added slowly to a refluxing mixture of $5
{2}$ (butanethio) and 115 grams of ethylene dichloride. After the final addition of the phosphorus trichloride, the mixture was refluxed until no further liberation of hydrochloric acid could be detected. The ethyl-ene dichloride was removed by

evaporation at a pressure of 7 to 10 mm. of mercury. The final product analyzed 30.4% sulfur and 10.4% phosphorus. Theoretical for tributyl thiophosphite [(C₄H₉S)₃P] is 32.2% sulfur and 10.4% phosphorus. This product was used without further purification.

DI-n-BUTYL SELENONOPHOSPHATE

Selenium (20.5 grams, 0.26 mole) was added to 50 grams (0.26 mole) of commercial di-*n*-butyl phosphite. The temperature of the mixture was slowly increased to 130° C. (boiling point). This temperature was maintained for approximately 2 hours, This temperature was maintained for approximately 2 hours, after which time the mixture was cooled and filtered. The filtrate analyzed 13.3% selenium and 13.5% phosphorus. Theoretical for di-*n*-butyl selenonophosphate $[(C_4H_9O)_2HOPSe]$ is 28.9% selenium and 11.3% phosphorus. These results indicate that a portion of the phosphite had oxidized to phosphate previous to the reaction with selenium.

TRIAMYL SELENONOPHOSPHATE

Selenium (13.5 grams, 0.17 mole) was added to 50 grams (0.17 solution (13.5 grains, 0.17 hole) was added to 50 grains (0.17 mole) of commercial triamyl phosphite. The temperature was slowly increased to 155° C, after which the mixture was cooled and filtered. Analysis of the filtrate gave 19.7% selenium and 9.0% phosphorus. Theoretical for triamyl selenonophosphate [(C₅H₁₁O)₅PSe] is 21.3% selenium and 8.34% phosphorus. This product was used without further purification.

TRIAMYL THIOPHOSPHITE

Phosphorus trichloride (13.8 grams, 0.1 mole), was added dropwise to a refluxing mixture of 36 grams (0.35 mole) of *n*-amyl mercaptan and 91 ml. of benzene. Refluxing was continued until no further evidence of hydrochloric acid could be detected at the mouth of the reflux condenser. The benzene and unreacted mercaptan were removed by evaporation in vacuo. Analysis of the product gave 24.1% sulfur and 8.4% phosphorus. Theoretical for triamyl thiophosphite [(C₅H₁₁S)₂P] is 28.2\% sulfur and 9.1\% phosphorus.

TRIISOAMYL PHOSPHITE

This phosphite was prepared by adding, dropwise, 137.4 ml. This prospinte was prepared by adding, dropwise, 137.4 nil. (1.5 moles) of phosphorus trichloride to a mixture of 488 ml. (4.5 moles) of triisoamyl alcohol, 237 ml. of pyridine (4.5 moles), and 2000 ml. of hexane. The reaction was carried out in an at-mosphere of nitrogen. After the final addition of phosphorus trichloride, stirring was continued for 2.5 hours, after which the mixture was filtered under suction and the precipitate of pyridine hydrochloride was washed with hexane. Most of the excess

TABLE II, INDIANA STIRRING OXIDATION TESTS

			(Base	oil, Pe	nnsylva	inia 10W	a)				
	% S	% Se	MI.	Sludge /10 Ml	. Oil	Acid Mg.	io. Incre KOH/G	ease, ^c . Oil	Visco	sity Inc 100° F.,	rease %
Additive	Őil	Öil	24 hr.b	48 hr.	72 hr.	24 hr.	48 hr.	72 hr.	24 hr.	48 hr.	72 hr.
None Di-n-butyl		0.15	$1.95 \\ 0.10$	$\begin{smallmatrix}4&.40\\0&31\end{smallmatrix}$	${\substack{5.10\1.02}}$	$11.69 \\ -0.63$	$\substack{17.12\\2.00}$	$\begin{array}{c} 26.26 \\ 10.30 \end{array}$	$\begin{array}{c} 197 \\ 8.91 \end{array}$	$\begin{array}{c} 953\\ 40.5 \end{array}$	$\substack{1324\\176}$
selenonophosphate Tributyl selenonophosphate	•••	0.15	0.17	0.70	1.09	2.35	5.58	8.73	32.9	88.5	150
Tributyl	0.15		0.65	1.38	1.93	3.28	6.91	7.97	89.4	172	271
thionophosphate Tributyl thionhosphite	0.15	· • •	0.35	2.00	3.16	4.10	15.2	20.8	44.0	263	675
Triamyl		0.15	0.27	0.91	1.15	3.04	6.32	8.53	34.6	90.6	136
selenonophosphate Triamyl thiophosphite	0.15		0.22	1.63	3.00	2.61	13.19	15.30	31.2	205	445
Triisoamyl		0.15	0.11	0.11	0.20	-0.39	0.21	1.40	7.10	14.1	31.9
selenonophosphate Triisoamyl phosphite Tri-3-ethylhexyl	(0.058	3% P) 0.15	d 0.18 0.45	$\begin{array}{c} 0.40 \\ 1.05 \end{array}$	$\begin{array}{c} 4.40\\ 1.19 \end{array}$	$\substack{0.49\\2.18}$	$\begin{array}{c} 6.22 \\ 6.42 \end{array}$	$\begin{array}{r}19.93\\8.69\end{array}$	$\begin{array}{c} 12.4\\ 36.8 \end{array}$	83.3 110	$\begin{array}{c} 557\\ 154 \end{array}$
Tricresvl		0.15	0.20	0.58	1.01	1.69	4.94	9.32	19.1	70.5	129
selenonophosphate Diphenylbutyl selenonophosphate		0.13	0.11	0.25	0.92	0.42	2.38	10.07	6.57	32.0	163

^a From refinery A. ^b Testing time. ^c Acid No. increase represents the difference, in milligrams of KOH/gram oil, between the acid number after the test and the acid number before the test. ^a This oil blend contains an amount of phosphorus equivalent to that in the oil blend containing triisoamyl selenonophosphate.

hexane was evaporated from the solution on a steam bath with suction applied from a water aspirator. The resulting product was further evaporated by applying a vacuum from a Hyvac pump connected to the flask through a dry ice trap.

The final product gave a negative test for pyridine as indicated by a lack of turbidity upon the addition of hydrochloric acid to a small sample. It also gave a negative test for hydrochloric acid as indicated by the lack of turbidity upon the addition of pyridine to a small sample. The product has a specific gravity at



Figure 4. Chevrolet Engine Test

25° C. of 0.8978 and a refractive index, n_{25}^{25} , of 1.4357. Analysis gave 10.1% phosphorus. Theoretical for triisoamyl phosphite $[(C_5H_{11}O)_3P]$ is 10.6% phosphorus.

TRIISOAMYL SELENONOPHOSPHATE

Selenium (24.3 grams, 0.31 mole) was added slowly to 89.8 grams (0.31 mole) of triisoamyl phosphite. After the final addition of the selenium the temperature of the mixture was slowly increased to 175° C., after which it was allowed to cool to room temperature. The unreacted selenium was removed by filtration, and the filtrate was simply distilled under high vacuum. The liquid distilling over in the temperature range of 89° to 95° C. was taken as the desired product. This material had a specific gravity at 25° C. of 1.0869. It analyzed 21.5% selenium. Theoretical for triisoamyl selenonophosphate [(C₅H₁₁-O)₃PSe] is 21.3% selenium and 8.4% phosphorus.

TRI-3-ETHYLHEXYL SELENONOPHOSPHATE

Selenium (9.47 grams, 0.12 mole) was added slowly to 50 grams (0.12 mole) of commercial tri-3-ethylhexyl phosphite. After the final addition of selenium, the temperature was slowly increased to 155° C. The mixture was allowed to cool and the unreacted selenium removed by filtration. The filtrate was analyzed as 7.5% selenium and 7.3% phosphorus. Theoretical for tri-3-ethylhexyl selenonophosphate [($C_3H_{17}O)_3PSe$] is 15.9% selenium and 6.2% phosphorus. These figures indicate that a portion of the phosphite had been oxidized to phosphate prior to the reaction with selenium.

TRICRESYL SELENONOPHOSPHATE

Selenium (11.05 grams, 0.14 mole), was slowly added to 50 grams (0.14 mole) of commercial tricresyl phosphite. The temperature of the mixture was slowly increased to 155° C. after the final addition of selenium. The mixture was allowed to cool and the unreacted selenium removed by filtration. The product analyzed 16.2% selenium and 6.9% phosphorus. Theoretical for tricresyl selenonophosphate [(C₇H₇O)₈PSe] is 18.3% selenium and 7.2% phosphorus.

TRIPHENYL SELENONOPHOSPHATE

Elemental selenium was reacted with a sample of commercial triphenyl phosphite by adding 26.0 grams (0.33 mole) of it slowly to 100 grams (0.32 mole) of commercial triphenyl phosphite. The temperature was increased to 170° to 180° C. for 40 minutes, after which time the mixture was allowed to cool and 700 ml, of acetone were added. The resulting solution was filtered and evaporated on a steam bath to give yellowish crystals with melting points of 67° to 69° C. These crystals analyzed 20.2% selenium. Theoretical for triphenyl selenonophosphate [(C_4H_4O)₄PSe] is 20.3% selenium.

DIPHENYLBUTYL SELENONOPHOSPHATE

Selenium (13.4 grams, 0.17 mole) was added slowly to 50 grams (0.17 mole) of commercial diphenylbutyl phosphite. After the final addition of selenium, the temperature was increased to 155° C., the mixture allowed to cool, and the unreacted selenium was removed by filtration. The filtrate analyzed 20.2% selenium and 8.4% phosphorus. Theoretical for diphenylbutyl selenonophosphate [(C₁₅H₁₉O)₃PSe] is 21.4% selenium and 8.4% phosphorus.

TESTING PROCEDURE

In general, the usual testing procedures for the evaluation of antioxidants in lubricating oils were used. For the purposes of this investigation, the Underwood oxidation test, Indiana stirring oxidation test, Lauson engine test, and the L-4 Chevrolet 36-hour engine oil stability test were used. Each of these procedures is described in detail in the preceding paper (2).



Figure 5. Chevrolet Engine Test

In addition to these tests, the oxygen-absorption rates of two different types of oil to which tributyl selenonophosphate had been added were determined. A Dornte-type apparatus was used which automatically recorded the volume of oxygen absorbed by the oil sample as a function of time. The oil sample. 100 grams, contained in an appropriate reaction flask, was heated to 325° F. Oxygen was continuously bubbled through the sample, under constant pressure at a predetermined rate, and the time for the absorption of a predetermined volume was automatically recorded. Metallic copper, in the form of No. 14 wire, sufficient to provide a surface of 0.1 sq. cm. per gram of oil sample, was used as an oxidation catalyst. The volume of oxygen (cubic centimeters) absorbed per minute per 100 grams of oil was calculated and recorded as the oxidation rate. The neutralization number and per cent viscosity increase of the oxidized sample were determined.

TABLE III.	Indiana	STIRRING	Oxidation 7	Cests
	(Effect	in various of	ls)	
Base Oil	Test Hours	Sludge, Ml./10 Ml. of Oil	Acid No. Increase, Mg. KOH/- G. Oil	Viscosity Increase at 100° F., %
	Addi	tive: None		
Pennsylvania 10W ^a	$\frac{24}{48}$	$1.95 \\ 4.40 \\ 5.10$	$11.69 \\ 17.12 \\ 26.26$	$197 \\ 953 \\ 1324$
Pennsylvania $10 W^b$	24 48 72	$1.06 \\ 1.66 \\ 1.60$	7.90 11.62	1324 138 326 600
Mid-continent 10W ^b	$ \begin{array}{c} 24 \\ 48 \\ 72 \end{array} $	$1.30 \\ 1.40 \\ 1.52 \\ 1.66$	$ \begin{array}{r} 13.04 \\ 6.89 \\ 9.67 \\ 12.23 \\ \end{array} $	$ 165 \\ 359 \\ 802 $
Additive: Triisop	oropyl Se	lenonophospl	hate (0.15% Se	e in Oil)
Pennsylvania 10W ^a	24	• • • •	•••	
	$\frac{48}{72}$			· · · ·
Pennsylvania 10W	$\frac{24}{48}$	0.34 0.80	$2.02 \\ 4.91$	$\begin{array}{c} 64.7 \\ 140 \end{array}$
Mid-continent 10W ^b	$\frac{72}{24}$	$1.02 \\ 0.43$	$6.52 \\ 1.60$	$296 \\ 66.4$
	$\substack{48\\72}$	0.88 0.98	$\begin{array}{c} 3.45 \\ 4.95 \end{array}$	$\begin{array}{c} 162 \\ 396 \end{array}$
Additive: Tr	iisopropy	l Phosphite ((0.39% in Oil)	c
Pennsylvania 10W ^a	24			•••
	$\frac{48}{72}$			
Pennsylvania 10W ^o	$ \frac{24}{48} $	1.05 1.49	$\begin{array}{c} 6.71\\ 10.54\\ \end{array}$	$\begin{smallmatrix}124\\262\\$
Mid-continent $10W^{b}$	24	1,44	$ \begin{array}{r} 13.85 \\ 6.51 \\ 0.02 \end{array} $	375 155
	$\substack{48\\72}$	$1.34 \\ 1.41$	$8.96 \\ 12.33$	311 590
Additive: Tributyl Se	elenonopl	nosphate (Sa	mple 1) (0.125	% Se in Oil)
Pennsylvania 10W ^a	24	0.40	2.82	64.5
	72	1.48	6.91	206
Pennsylvania 10 w *	24 48	0.44	3.38	148 148
Mid-continent 10W ^b	$^{72}_{24}$	1.53 0.29	$\frac{4}{0.77}$	$269 \\ 36.3$
	$\frac{48}{72}$	$\begin{array}{c} 0.55 \\ 0.72 \end{array}$	$\begin{array}{c}1.96\\2.83\end{array}$	$ \begin{array}{r} 104 \\ 248 \end{array} $
Additive: Triiso	amyl Sele	enonophosph	ate (0.15% Se	in Oil)
Pennsylvania 10W ^a	$^{-}24$	0.11	-0.39	7.10
	$^{48}_{72}$	$0.11 \\ 0.20$	$\begin{array}{c} 0.21\\ 1.40 \end{array}$	14.1 31.9
Pennsylvania 10W ^b	$\frac{24}{48}$	$0.34 \\ 0.92$	$2.63 \\ 5.51$	62.9 167
Mid-continent 10Wb		1.33	7.79	440
Mid-continent 10 W	$\frac{48}{72}$	1.01 1.00	$4.15 \\ 5.18$	190 362
^a From refinery A. ^b From refinery B. ^c This provides the sa	me amou	int of phospl	norus as in the	case of the c

^c This provides the same amount of phosphorus as in the case of the oil containing triisopropyl selenonophosphate.

UNDERWOOD OXIDATION TESTS

Tributyl selenonophosphate (sample 1), in various amounts, was blended with Pennsylvania 10W base oil and tested according to the Underwood procedure. In addition, a blend containing 0.15% selenium as tributyl selenonophosphate (sample 2), and a blend containing 0.15% selenium as tributyl selenonophosphate (sample 2) treated with 1 N sodium hydroxide were tested according to this procedure. A comparison of the results of these tests, recorded in Table I and Figures 1 and 2, with similar results for the base oil without additive, shows that the selenonophosphase.

phate inhibits the oxidation of the base oil to a marked extent, as measured by sludge formation, per cent viscosity increase, neutralization number, and per cent Conradson carbon residue. The presence of tributyl selenonophosphate in the oil also greatly reduces the bearing corrosion, as shown in the last column of Table I. These data indicate that concentrations between 0.10% and 0.15% based on selenium are the optimum amounts to use in lubricating oils of this type.

The results obtained using sample 1 do not agree well with those obtained with sample 2 prior to treatment with 1 N sodium hydroxide. There is fair agreement, however, between the treated

sample 2 and sample 1. The untreated sample, No. 2, allows unusually high bearing corrosion, but imparts very much greater oxidation resistance to the oil than does the treated sample 2. However, in the case of treated sample 2, the bearing corrosion is less than half as great as with the untreated sample 2. The difference between the two samples is essentially one of temperature of the reaction between tributyl phosphite and elemental selenium. For sample 1, the temperature was held to 155° C., while for sample 2, it was allowed to rise to 190° C. Furthermore, sample 1 was distilled to remove the majority of the impurities, while sample 2 was used in the "impure" state. The data thus indicate that the impurities (probably butyl selenol) are beneficial in inhibiting oxidation of the oil but detrimental in allowing high bearing corrosion. Purification of sample 2, using a caustic wash, results in data quite comparable as regards both inhibition of oxidation and bearing corrosion, with sample 1, which was purified by distillation. One of the impurities removed by the caustic wash was identified tentatively as butyl selenol.

INDIANA STIRRING OXIDATION TESTS

Further screening tests were made, on a variety of selenonophosphates, using the Indiana stirring oxidation test. For pur-



TABLE IV. OXYGEN ABSORPTION RATES (Tributyl selenonophosphate^a as additive)

Base Oil	% Se in Oil	Time, Min.	Cc. O2 Absorbed/ 100 G.	Oxidation Rate, Cc./ Min./100 G.	Viscosity Increase 130° F., %	Neutral- ization No., Mg. KOH/G. Oil
Pennsylvania ^b SAE 30 Pennsylvania ^b SAE 30 Mid-continent ^b SAE	$\begin{smallmatrix} 0\\0.015\\0\end{smallmatrix}$	$460 \\ 920 \\ 170$	$1480 \\ 405 \\ 1480$	$\substack{3.2\\0.44\\8.7}$		$2.23 \\ 0.60 \\ 1.31$
30, solvent refined Mid-continent ^b SAE 30, solvent refined	0.015	770	415	0.53	2.4	0.30
^a Sample 1. ^b From refinery C.						

CONTAINING 0.1% SE.	LENIU	MAS	IRIBUT	AP OFT	ENONC	PHOSPH.	ATE ^a
Procedure Varnis Bearing material CuPb Oil temp. 280° J	h 250 l F.	lours	Spe Wa	ed ter tem;	p.	1600 r.p.: 170° F.	m.
Demerits at indicated hours	30	60	100	Hou 130	160	200	250
Skirt lacquer $(0-15)$ Ring belt $(0-10)$ Rings $(0-15)$ Piston underside $(0-10)$ Valves $(0-10)$ Sludging $(0-10)$ Total $(0-70)$	$0 \\ 1.3 \\ 0 \\ 0 \\ \cdots \\ \cdots \\ \cdots \\ \cdots$	0 3.0 0.5 	0 3.0 0.5 3.0 0 6.5	0.5 3.5 0 1.0 	0.5 3.5 0 1.0	$0.5 \\ 5.0 \\ 0 \\ 1.5 \\ 5.0 \\ 0 \\ 12.0$	$0.5 \\ 5.0 \\ 0 \\ 1.5 \\ 6.0 \\ 0 \\ 13.0$
Observed and measured deposits Skirt lacquer area, % Skirt lacquer thickness, inch Cylinder head deposits, g. Connecting rod deposits, g. Governor housing deposits, g.	•••	••••	Nil Nil Nil Nil	· · · · · · · · · · ·	· · · · · · · · · · · ·	5.0 Nil Nil Nil	5.0 Nil Nil Nil
Oil consumption, lb./hr. Av. for 250 hr.				•••	••••	•••	0.0028
				**			
Oil analysis at indicated hours	30	60	100	Hou 130	rs	200	250
Oil analysis at indicated hours Bearing wt. loss, mg. Original vis. at 210° F. Vis. at 210° F. Neutralization No. Ppt. No. % Original Conradson carbon residue, %	30 10.3 	60 20.5 	$100 \\ 42.8 \\ 55.9 \\ 60.4 \\ 1.39 \\ 0.5 \\ 0.39 \\ 0.5 \\ 0.39 \\ 0.5 \\ 0.39 \\ 0.5 \\ 0.39 \\ 0.5 \\ 0.39 \\ 0.5 \\ 0.39 \\ 0.5 \\ 0.39 \\ 0.5 \\$	Hou 130 69.9 	160 170.9	$200 \\ 393.1 \\ 55.9 \\ 72.0 \\ 3.57 \\ 1.0 \\ 0.39$	$\begin{array}{c} 250 \\ 667.9 \\ 55.9 \\ 81.1 \\ 4.27 \\ 0.75 \\ 0.39 \end{array}$
Oil analysis at indicated hours Bearing wt. loss, mg. Original vis. at 210° F. Vis. at 210° F. Neutralization No. Ppt. No., % Original Conradson carbon residue, % Conradson carbon residue, %	30 10.3 	60 20.5 	$100 \\ 42.8 \\ 55.9 \\ 60.4 \\ 1.39 \\ 0.5 \\ 0.39 \\ 1.07$	Hou 130 69.9 	rs 160 170.9 	$\begin{array}{c} 200\\ 393.1\\ 55.9\\ 72.0\\ 3.57\\ 1.0\\ 0.39\\ 2.53\end{array}$	$\begin{array}{c} 250\\ 667.9\\ 55.9\\ 81.1\\ 4.27\\ 0.75\\ 0.39\\ 3.88 \end{array}$
Oil analysis at indicated hours Bearing wt. loss, mg. Original vis. at 210° F. Vis. at 210° F. Neutralization No. Ppt. No., % Original Conradson carbon residue, % Conradson carbon residue, % Naphtha insoluble, %	30 10.3 	60 20.5 	$100 \\ 42.8 \\ 55.9 \\ 60.4 \\ 1.39 \\ 0.5 \\ 0.39 \\ 1.07 \\ 0.43 \\ 0.11 \\$	Hou 130 69.9 	rs 160 170.9 	$\begin{array}{c} 200\\ 393.1\\ 55.9\\ 72.0\\ 3.57\\ 1.0\\ 0.39\\ 2.53\\ 0.47\\ 0.20\\ \end{array}$	$\begin{array}{c} 250\\ 667.9\\ 55.9\\ 81.1\\ 4.27\\ 0.75\\ 0.39\\ 3.88\\ 0.40\\ 0.16\end{array}$
 Oil analysis at indicated hours Bearing wt. loss, mg. Original vis. at 210° F. Vis. at 210° F. Neutralization No. Ppt. No., % Original Conradson carbon residue, % Conradson carbon residue, % Maphtha insoluble, % Chloroform soluble, % Piston rating 1 (cleanest) to 5 A (cleanest) to E 	30 10.3 	60 20.5 	100 42.8 55.9 60.4 1.39 0.5 0.39 1.07 0.43 0.11	Hou 130 69.9 	rs 160 170.9 	200 393.1 55.9 72.0 3.57 1.0 0.39 2.53 0.47 0.20	250 667.9 55.9 81.1 4.27 0.75 0.39 3.88 0.40 0.16

TABLE V. LAUSON ENGINE DATA ON SAE 20 PENNSYLVANIA BASE OIL

their ability to inhibit the oxidation of lubricating
oils, and the results obtained in these tests show
that the phosphite increased the oxidation re-
sistance of the base oil markedly. However, con-
version of the phosphite to a selenonophosphate
resulted in a far superior material.

The effectiveness of the selenonophosphates in different types of base oils was investigated. The results obtained are summarized in Table III. This table shows the striking difference in the oxidation susceptibility of the base oils without inhibitor. Two Pennsylvania base oils obtained from different refineries showed a greater difference in oxidation characteristics than a Pennsylvania base oil and a mid-continent base oil obtained from the same refinery. The results recorded in Table III show that the selenonophosphates effectively increase the oxidation resistance of each of the base oils in which they were tested, but the degree of effectiveness differs for the different base oils. In general, the greatest effect is shown with the base oil having the least resistance to oxidation without inhibitor. The greatest difference is shown in the case of triisoamyl selenonophosphate blended in the two Pennsylvania base oils obtained from different refineries.

A direct comparison between triisopropyl phosphite and triisopropyl selenonophosphate in two additional base oils further confirms the observa-

1600 r.p.m. 170° F.

F

1,0

2

 $\begin{smallmatrix}4\\0\\1\\4\\0\\11\end{smallmatrix}$

30 0.0001

Nil Nil

0.006

58.072.22.32

5.0 0.38

3.88

 $1.82 \\ 0.64$

1 +

0000

. . .

382

11.5

 \mathbf{E}

1.25

2 5 2

ī

30 0.0002

11.25

Nil Nil

0.005

 $225 \\ 57.6 \\ 66.7 \\ 2.8 \\ 2.0 \\ 2.0 \\ 10$

0.56

2.0

 $0.72 \\ 0.38$

2

0000

0 0 0

000

TABLE VI. LAUSON ENGINE DATA. COMPARISON OF TRIBUTYL SELENONO-PHOSPHATE WITH FIVE COMMERCIAL ADDITIVES (Base oil: Pennsylvania SAE 20)

0 0 0

000

^a On second bearing installed during run.
^b Tributyl selenonophosphate (sample 1).
^c Corresponds to 0.10% Se.

Procedure Varnish 250 hours Speed Water temp. poses of comparison, several phosphites and thio-CuPb 280° F. Bearing material Oil temp. phosphites were also evaluated. The results of $\mathbf{A}^{\dot{b}}$ Additive в С D these tests, shown in Table II, confirm those of % additive 0.54 1.25 0.5 0.5the Underwood oxidation tests in that each of Demerits at 250 hours the selenonophosphates inhibits the oxidation of Skirt lacquer (0-15) Ring belt (0-10) Rings (0-15) 0.5 2 5 1 2 2 4 0 1 1 3 0 1 the base oil to a marked extent. A direct comŏ 1.5 parison between triamyl selenonophosphate and Piston underside (0-10) Valves (0-10) Sludging (0-10) Total (0-70) 5 2 17 4 2 13 triisoamyl selenonophosphate indicates that the $\frac{4}{9}$ branched-chain compound is more effective than Observed and measured deposits Skirt lacquer area, % 5 Skirt lacquer thick- Nil ness, inch Cylinder head de- ... posits, g. Connecting rod deposits, g. Nil Governor housing deposits, Nil g. the corresponding straight-chain compound. The triisoamyl selenonophosphate was the most 50 0.0005 30 Nil 20 Nil effective compound tested in this series. Comparisons between triamyl selenonophos-8.0 6.25 9.0 phate and tributyl selenonophosphate, and be-0.10 Nil Nil Nil Nil Nil tween tri-3-ethylhexyl selenonophosphate and g. triisoamyl selenonophosphate, after 48 hours in Oil consumption, lb./hr. Av. for 250 hr. the tester, indicate that the lower molecular 0.0028 0.0165 0.003 0.003 weight compounds may have slightly greater Oil analysis at 250 hours ability to inhibit oxidation of mineral oils. Dearing wt. loss, mg. Original vis. at 210° F. Vis. at 210° F. Neutralization No. Ppt. No., % Original Conradson 667 $\begin{array}{r}
 188 \\
 57.4 \\
 63.5 \\
 1.71
 \end{array}$ 810^a 550 58.0 58.0 112.4 4.5 4.0 0.4658.1 115.0 4.8 3.0The results obtained with tributyl selenonophosphate and tributyl thionophosphate indicate $1.71 \\ 3.0 \\ 0.23$ that the selenium compounds are more effective 0.51 Conradson residue, % Conradson carbon residue, % Naphtha insoluble, % Chloroform soluble, % than the analogous sulfur compounds. Further-3.88 1.39 4.84.96 more, the thionophosphates appear to be more $0.40 \\ 0.16$ 0.93 $2.6 \\ 1.3$ 2.36 effective than the corresponding thiophosphites, **0**.89 as indicated by comparing tributyl thionophos-Piston rating 1 (cleanest) to 5 A (cleanest) to E 1+ ... phate with tributyl thiophosphite. Triamvl-2 1 2 selenonophosphate is likewise superior to triamyl . . . Ring sticking demerits (0-10) No. 1 compression ring No. 2 compression ring Oil ring

The ability of selenium to impart increased oxidation resistance to lubricating oils is very well illustrated by comparing the results obtained with triisoamyl selenonophosphate and triisoamyl phosphite. Organic phosphites are well known for

thiophosphite.

TABLE	VII. Oil	Analysis	s ог 36-Н Т	our Chev ests	rolet En	GINE OIL	Stability
_	Test 1, Mid-con- tinent SAE 20,	Test 2, Mid-con- tinent SAE 20	Test 3, Mid-con- tinent SAE 20	Test 4, Mid-con- tinent SAE 20	Test 5, Mid-con- tinent SAE 10,	Test 6, Mid-con- tinent SAE 10	Test 7, Mid-con- tinent SAE 10 + Com-
Test Hours	No Additive ^a	$\operatorname{Additive}^{+}$	Additive °	Additive ^d	No Additive ^e	+ Additive/	mercial Additive Eg
0		Neu	tralization	No., Mg. K	OH/Gram o	f Oil	
8	0	0.11	0.11	0.32	0.05	$0.06 \\ 0.28$	0.60
$\frac{16}{24}$	1.77	0.64	0.43	0.75	5.65	$0.39 \\ 0.67$	0.45
36	2.43	1.02	0.86	1.50	3.75	0.73	0.45
n		0	-Viscosity	Increase at	100° F., %-	0	0
8 16	17.6	ŝă	5' 7	÷	97 1	5.0	÷:3
$\frac{24}{36}$	33.8	22.3	14.7	18.5	118.7	$15.7 \\ 15.5 \\ 19.5$	11.87
			_				
0			Benz	ene Insolub	ole, %		
$\cdot \frac{8}{16}$	0.46	0.33	0.34	0.36	0.34		0.40
$\frac{24}{36}$	0.7 1	0.65	0.58	0.60	0.43	•••	0.68
			Normal	Pentane In	eolublee		
0	·						
16	0.58	0.44	0.48	0.37	0.87	• • •	0.55
$\frac{24}{36}$	i.i9	0.91	1 00	0.85	1.96	• • •	0.96
			I	nsoluble Res	sins		
0 8	· · · ·			•••			
$\frac{16}{24}$	0.12	0.11	0.14	0.01	0.53		0.15
36	0.45	0.26	0.42	0.25	1.54		0.29
0		0.31	-Ramsbotto	om Carbon	Residue, %		
8	i'ie	0.34	0.34	0.35		•••	
24	1,40	0.89	0.75	0.73			
30	2.11	1.63	1.45	1.36		•••	
0		0.05	Ash In	organic Inso	luble, % —	0.01	
8 16	0.22	0.00	0.00	0.04		0.20	
24	0.33	0.27	0.20	0.20	• • •	0.29	
50	0.47	0.45	0.40	0.44	• • •	0.50	
0	~~~~		-Conrads	on C <mark>ar</mark> bon I	Residue, %-	0.00	0.22
8	•••				1 20	0.35	0.22
24		• • •		• • •	1.69	0.53	0.60
30	•••	• • •		•••	2.17	1.10	0.88
0				htha Insolui	ole, %	0.05	
8		• • •	•••			0.29	
24			••••		· · ·	$0.56 \\ 0.73$	
36						1.13	• • •
Ω				oform Insolu	ıble, 🤭 —	0 20	
8	•••	• • •	••••	• • •	••••	0.46	• • •
24	• • •	• • •	• • •	• • •	• • •	0.71	•••
20			••••		•••	0.98	• • •
0			P	recipitation	No	0.00	
8 16					•••	0.10	• • •
24		••••		•••	• • • •	0.18	• • •

^a Test No. 1, mid-continent SAE 20 base oil (from refinery D), no additive. ^b Test No. 2, mid-continent SAE 20 base oil (from refinery D) + 0.60% tributyl seleno-nophosphate (this corresponds to 0.145% Se) (sample 2). ^c Test No. 3, mid-continent SAE 20 base oil (from refinery D) + 0.60% tributyl selenon-phosphate (sample 2) + 0.25% Ortholeum 202. ^d Test No. 4, mid-continent SAE 20 base oil (from refinery D) + 0.60% tributyl selenon-nophosphate (sample 2) + 0.50% Ortholeum 202. ^e Test No. 5, mid-continent SAE 10 base oil (from refinery B), no additive. ^f Test No. 6, mid-continent SAE 10 base oil (from refinery B) + 0.15% Se as triisoamyl selenonophosphate. ^g Test No. 7, mid-continent SAE 10 base oil (from refinery B) + 1.5% of a commercial additive E.

tion that conversion of phosphites to selenonophosphates produces more effective antioxidants for lubricating oils.

The conditions of the stirring rods from the Indiana stirring oxidation tester, after 72 hours, for several representative tests are shown in Figure 3.

OXYGEN ABSORPTION RATE

The effect of tributyl selenonophosphate (sample 1) in reducing the rate of oxygen absorption was determined for a Pennsylvania SAE 30 base oil and for a mid-continent solvent-refined base oil. The data, summarized in Table IV, obtained by this test method, showed that very small amounts of selenium (0.015% by weight) as tributyl selenonophosphate substantially decrease the oxygen absorption rates of both types of base oils. It is also observed that the neutralization number and viscosity increase are greatly reduced.

LAUSON ENGINE TESTS

Tributyl selenonophosphate, although not the most outstandingly effective selenonophosphate, according to the Indiana stirring oxidation tests, was selected for Lauson engine tests because of the commercial availability of tributyl phosphite, an intermediate in its preparation. The results of the Lauson engine studies are summarized in Table V. In addition, five well-known commercial additives, obtained from five of the major producers of lubricant additives, were tested in the same oil, an SAE 20 Pennsylvania base, under the same operating conditions. The results at the end of 250 hours for all six tests are summarized in Table VI, which reveals that the oil containing tributyl selenonophosphate was slightly better than the average of the other five, based on total demerits. It was, however, outstandingly better than all of the others in preventing skirt lacquer. A study of the used-oil analysis reveals that it was slightly better than the average in preventing viscosity increase, but was much better than the other five additives in naphtha insolubles and precipitation number. The tributyl selenonophosphate did not inhibit bearing corrosion to the extent expected from results of preceding tests.

CHEVROLET 36-HOUR ENGINE TESTS

A series of Chevrolet 36-hour engine tests (Coordinating Research Council, C.R.C. designation L-4-545) was conducted to determine the effectiveness of the selenonophosphates as additives to lube oils, under full scale engine-operating conditions. A total of seven such tests were conducted. The results obtained are summarized in Tables VII, VIII, and IX, and Figures 4 through 7 Selection of tributyl selenonophosphate sample 2 (unpurified) for use in these tests was based on the excellent (except for bearing corrosion) data shown in Table I. Ortholeum 202, obtained from E. I. du Pont de Nemours & Co., Inc., Wilmington, Del., was used in conjunction with the tributyl selenonophosphate as a bearing-corrosion inhibitor in two test runs. In addition, one run was made using triisoamyl selenonophosphate in a mid-continent SAE 10 base oil. The data indicate



Rocker arm and push rod covers from Chevrolet engine test Upper. No additive Lower. 0.15% selenium as triisoamyl selenonophosphate

an over-all improvement in performance with the use of tributyl selenonophosphate and triisoamyl selenonophosphate as additives to the oil. The improvement is much greater in the case of triisoamyl selenonophosphate in mid-continent SAE 10 base oil for C.R.C. rating and oil deterioration than in the case of tributyl selenonophosphate in mid-continent SAE 20 oil. As is to be expected, SAE 10 base oil (control) has undergone a much greater deterioration during the test than has SAE 20 base oil (control). The greatest effectiveness of the selenonophosphates appears in oils with the greatest susceptibility to oxidation. However, both selenonophosphate additives allow undesirably high bearing corrosion in the absence of a bearing-corrosion inhibitor. Ortholeum 202 effects a very marked decrease in bearing corrosion (tests 3 and 4) when added to blends containing tributyl selenonophosphate, only 0.25% Ortholeum 202 being sufficient to reduce bearing corrosion to an entirely satisfactory level. Addition of 0.50%Ortholeum 202 results in no further significant improvement. Oil deterioration is slightly greater with 0.50% than with 0.25% Ortholeum 202. However, engine clean liness is slightly better at the 0.50% level (C.R.C. rating 89.00 versus 87.50) than at the 0.25% level. In the case of runs using tributyl selenonophosphate in mid-continent SAE 20 base oil, the varnish deposit rating was not improved over that recorded for the oil without additive. However, the sludge deposit rating was improved in every case. In the case of triisoamyl selenonophosphate in a mid-continent SAE 10 oil, improvement in both varnish and sludge ratings was significant.

TABLE	IX. Copper Chevrole	-Lead Bea t Engine (ARING COR DIL STABILI	rosion in ty Tests	36-Hour
Test No.ª	Bearing No.	Top Section Loss, Gram	Bottom Section Loss, Gram	Total Whole Bearing Loss, Gram	Av. Loss per Whole Bearing, Gram
1	3	0.48	0.54	1.02	0.96
2	4	$0.39 \\ 0.43 \\ 0.10$	$ \begin{array}{c} 0.51 \\ 0.51 \\ 0.33 \end{array} $	$0.90 \\ 0.94 \\ 0.43$	0.69
3	2	0.02	0.02	0.04	0.04
4	1	0.02	0.01	0.03	0.03
5	3	0.362	$0.02 \\ 0.515$	0.03	0.885
6	42	0.407 0.181	$0.485 \\ 0.323$	$0.892 \\ 0.504$	0.568
7	5 3 4	$\begin{array}{c} 0.269 \\ 0.014 \\ 0.014 \end{array}$	$0.363 \\ 0.033 \\ 0.023$	$0.632 \\ 0.047 \\ 0.037$	0.042

^a See footnotes at end of Table VII.

DISCUSSION

The data presented herein demonstrate that the class of oilsoluble compounds known as selenonophosphates function as antioxidants in lube oils. Their effectiveness is dependent upon the nature of the base oil in which they are incorporated. In the case of a solvent-treated mid-continent SAE 20 base oil, L-4 Chevrolet engine tests indicate only moderately improved over-all engine cleanliness. However, in the case of a solvent-treated mid-continent SAE 10 base oil (from a different refinery), the over-all improvement was very marked. The selenonophosphates reduce

	Test 1, Mid-con- tinent SAE 20, No Additive ^a	Test 2, Mid-con- tinent SAE 20 + Additive	Test 3, Mid-con- tinent SAE 20 + Additive	Test 4, Mid-con- tinent SAE 20 + Additive	Test 5, Mid-con- tinent SAE 10, No Additive	Test 6, Mid-con- tinent SAE 10 + Additive	Test 7, Mid-con- tinent SAE 10 + Com- mercial Additive E
Varnish deposit rating Piston skirts Rocker arm cover Push rod cover plate Cylinder walls Crankcase oil pan	$\begin{array}{c} 8.25 \\ 10.00 \\ 9.00 \\ 9.50 \\ 9.00 \end{array}$	$7.25 \\10.00 \\10.00 \\8.50 \\9.50$	$\begin{array}{c} 7.00 \\ 10.00 \\ 8.50 \\ 9.50 \\ 9.50 \end{array}$	7.00 10.00 9.00 9.50 9.50	2.0 8.5 9.0 3.0 6.0	$7.1 \\ 10.0 \\ 10.0 \\ 7.8 \\ 8.5$	7.510.010.07.59.5
Varnish total	45.75	45.25	44.50	45.00	28.5	43.4	44.5
Sludge deposit rating Rocker arm assembly Rocker arm cover Push rod cover plate Oil screen Crankcase oil pan	7.00 8.00 6.00 9.00 8.00	8.00 10.00 9.00 9.50 8.00	9.00 8.00 7.00 10.00 9.00	9.00 9.00 8.00 10.00 8.00	5.0 3.0 3.0 8.0 7.5	9.0 9.1 9.0 10.0 9.0	9.5 9.5 * 9.0 9.0 9.0 9.0
Sludge total	38.00	44.50	43.00	44.00	26.5	46.1	46.0
Varnish and sludge total	83.75	89,75	87.50	89.00	55.0	89.5	90.5
a See footnotes at end of '	Table VII.						

TABLE VIII. OIL ANALYSIS OF 36-HOUR CHEVROLET ENGINE OIL STABILITY 1
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bearing corrosion but not to the extent desired for a bearing-corrosion inhibitor. The use of 0.25% Ortholeum 202 in conjunction with tributyl selenonophosphate reduces bearing corrosion to a satisfactory level.

There is an indication that the method of preparation of the selenonophosphates affects their performance as antioxidants and bearing-corrosion inhibitors (see Table I). The manner in which extraneous compounds are formed during the preparation of, and their effect on the performance of, selenonophosphates is not clear. Additional work along these lines is indicated.

ACKNOWLEDGMENT

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Aqueous Nonflammable Hydraulic Fluids

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A number of fires were reported during World War II in hydraulic systems of military equipment operating on petroleum hydraulic fluids. The flammability hazards involved were extensively investigated by the Naval Research Laboratory during the war. Research on a wide variety of less flammable fluids led to the decision in 1943 to emphasize the development of aqueous base fluids. Two such fluids had been developed and were ready for production when the war ended.

Research led to the development of nonflammable hydraulic fluids designated as Hydrolubes, which are defined as polymer-thickened, corrosion-inhibited, aqueous fluids having one or more glycols as major constituents. Of the many classes of polymers investigated for thickening and improving the viscosity-temperature properties, the most suitable were derivatives of the polyalkylene glycols. The large number of metals occurring in present aircraft hydraulic systems posed a difficult problem in cor-

NUMBER of fires were reported during World War II in hydraulic systems of military equipment operating on petroleum hydraulic fluids. The worst fires were caused by the breaking or puncturing of high pressure lines by missiles. In some instances mechanical or packing failures led to oil leakage and subsequent ignition by electrical sparks, incendiaries, or spontaneous ignition on contact with hot parts of the engines. The numerous hydraulic lines distributed throughout the fuselage and wings of modern military planes increase the fire risks.

The flammability hazards involved were extensively investigated by the Naval Research Laboratory early in the war. Petroleum oil sprays or mists such as those formed by the rupture of high pressure hydraulic systems were shown to explode readily in the atmosphere, as did all available hydraulic fluids in aircraft and ship use. Data on the fire hazard involved in the use of such hydraulic fluids in military equipment were not easily collected. Few pilots lived through the serious fires to report or to analyze what had happened. Existing flammability methods were unsatisfactory, making necessary the development of laboratory methods for measuring the flammability of oil mists. Hydraulic fluids in rosion inhibition. However, suitable liquid phase and vapor phase inhibitors were found. Wear-reducing additives were developed of the type forming hydrophobic films on steel.

The results of extensive laboratory and flight tests have indicated that Hydrolube U-4 is the most promising fluid of this class developed to date. Unlike other fire-resistant fluids, it presents no problem with respect to the deterioration of hydraulic packings. With the exception of highmagnesium alloys, it is a safe medium for all the metals commonly found in hydraulic systems. Its resistance to all types of fire hazards has been outstanding. Hydrolube U-4 has been employed in a large number of naval aircraft for three years and has been applied to a wide variety of industrial problems. This development has stimulated widespread interest and research on aqueous lubricants and synthetic organic liquids having high flammability resistance.

use and promising or new fluids were studied, using four laboratory methods of evaluation, and the conclusions relative to their flammability resistance were verified by incendiary firing tests carried out at Dahlgren Proving Grounds through the cooperation of the Bureau of Ordnance. The results of these flammability studies have been presented (14).

Research on a wide variety of fluids led to the decision in 1943 to emphasize the development of aqueous-base hydraulic fluids. Two such fluids had been developed and were ready for production for fighter planes when the war ended. Production was postponed in order to attempt to improve the fluids for wider use. Following a series of serious fires in commercial and military planes in 1946, interest in these fluids increased, and a Naval Research report (8) summarizing progress in developing nonflammable fluids for aircraft was distributed widely to interested organizations by the Bureau of Aeronautics and the Civil Aeronautics Administration. More recently a bibliographical survey of the problem and research activities related to it has been made by the National Advisory Committee for Aeronautics (17). The purpose of this paper is to present a concise, more accessible, and up-to-date