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Organo-Phosphorus Compounds

for

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Technical Report No. 5

Contract Nos. N9onr-87500 and -87501

Project No. NR 053 205

Period Covered: June 1, 1950 to August 31, 1950

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SHELL DEVELOPMENT COMPANY
EMERYVILLE, CALIFORNIA

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SHELL DEVELOPMENT COMPANY

EMERYVILLE, CALIFORNIA

TELEPHONE OLYMPIC 3-2100

December 12, 1950

COMMANDING OFFICER
U. S. Navy, Office of Naval Research
Branch Office
801 Donahue Street
San Francisco, California

Dear Sir:

Reference: Contract ONR:SF/1.4-3(23) N9onr-87501
Project No. NR 055 205

We enclose two copies of our fifth report under the subject contract which we have issued as Technical Report No. V "Organo-Phosphorous Compounds". This report covers the period June to August 31, 1950.

By copies of this letter, distribution of this report is being made in accordance with prescribed distribution for Technical Reports as listed in the attachment hereto.

Yours very truly,

SHELL DEVELOPMENT COMPANY

T. W. Evans

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Report No. S-13239

⑥ ORGANO-PROSPHORUS COMPOUNDS.

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for

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EMERYVILLE, CALIF. U.S.A.

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Report No. S-13239

SHELL DEVELOPMENT COMPANY
Emeryville, California
October 22, 1950

Contract No. N9onr-87500
-87501

Project No. NR 055 205

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ABSTRACT

The present Technical Report No. V, on the work done under the subject contract, covers the quarter June 1 to August 31, 1950. During this period the synthesis and bench scale evaluation of bis-phosphorus compounds have been emphasized in view of the promising leads disclosed during the first year of work. A few preparations have been repeated either because of anomalous early results or because of desire to investigate certain materials further. Attention is now being given to preparative methods amenable to handling in larger scale to provide samples for Motor Laboratory testing and more comprehensive bench scale evaluation. In particular the testing of products not purified by distillation to avoid the need for tedious molecular distillations, is underway. The total numbers of compounds produced this quarter are as follows: phosphine oxides, 1 (total for five quarters, 10); phosphinates, 5 (19); phosphonates, 14 (35, of which 2 are repeats); phosphates 2 (2); miscellaneous (usually as intermediates in preparative procedures), 5 (10); grand total, 27 (76).

↖
The bench scale evaluation studies discussed in this report cover most of the preparations of the quarter. Acid numbers have, in general, been very low. Pour points below -65 F were possessed by the majority of the new compounds. Viscosity - temperature trends are represented by reasonable straight lines on the ASTM chart (low temperature range); the deviations from linearity are less than those shown by many other synthetic oils. Viscosity indices were high (100) for almost all of these new preparations, as was anticipated since their manufacture was planned on the basis of the previous study. Six of seven bis-phosphonates, for example, had Hardiman and Nissen viscosity indices between 122 and 131. Flash points were usually above 400 F. In general, flammability was considerably lower than that of HS-1 (AMS-3150A reference standard), and thermal stabilities excellent, although the "bottoms" products (not distilled) were poor in this regard. Corrosion and oxidation stabilities are the least satisfactory of the properties measured and there exist wide divergences in the results for given groups of compounds. Caustic treatment for impurity removal has proved helpful in some cases, as has the use of inhibitors. As mentioned in other reports, such promising results were anticipated, and this latter attack on the problem is being actively pursued. Wear and friction studies are reported at some length, but concise generalizations are not readily discernable.

Comparisons of the various properties are drawn, where possible, between both the new materials and earlier ones. These comparisons are made for related groups such as dibutyl "R"-phosphonates where R varies from C₃ to C₁₆, and bis(dibutyl phosphono) compounds.

Motor Laboratory evaluations have been begun using a commercial phosphonate (to spare the costly laboratory preparations) to gain some experience in the use of these novel materials. Pesco gear pump and Lauson engine tests are underway.

PREPARATIONS

I. Introduction and Summary

The review of the properties of the organophosphorus compounds given in Technical Report No. IV has shown that of the phosphine oxides, phosphinates and phosphonates, the last appear to be the most stable. Although the phosphine oxides and dialkanephosphinates are somewhat more thermally stable when heated alone, they are not as stable as the phosphonates when heated under oxidizing conditions.

During the present quarter, even though major emphasis has been placed on the phosphonates, we have synthesized one more phosphine oxide and six dialkanephosphinates in an effort to round-out our knowledge of the behavior of these latter classes.

The phosphine oxide described in this report is different from those prepared earlier, being a diphosphine oxide. The compound, tetrabutylhexamethylenediphosphine oxide, was a solid melting at 98.5-100°C and appeared to be thermally stable. In view of the high melting point (and also poor yield) no evaluation has been made of this product.

By attaching a p-chlorobenzene to the phosphorus atom in place of the benzene group we have prepared a number of phosphinic acid derivatives which may be quite non-flammable in character. Two types of bis-phosphinates have been made; one in which the two phosphorus atoms are connected by a chain containing the P-C linkage, while in the other the phosphorus atoms are connected by P-O-C linkages.

Based on the information obtained heretofore, the phosphonic acid derivatives synthesized during the present quarter were chosen with the objective of improving the physical properties of this class of compounds. Thus, we have made a number of C₈ alkane- and alkenephosphonates. This gives us a direct comparison of the influence of paraffinic and olefinic groups.

As indicated in previous reports, efforts have been made to purify all samples as completely as possible and in general the methods have included distillation through a molecular still. In order to determine whether distillation was necessary to obtain satisfactory material, particularly for larger scale evaluation, we have initiated work on the production of a phosphonate as a bottoms-product. Two preparative methods were used and preliminary results indicate that it is possible to obtain bis-1,6-(dibutyl phosphono)hexane as a bottoms-product comparable to the molecularly distilled sample.

Two phosphonates containing carboxylic acid ester groups were synthesized with the possibility that these carboxylate groups would enhance the low temperature properties of the materials. A myristic acid ester was found to be a solid while an adipic acid ester had good low temperature properties.

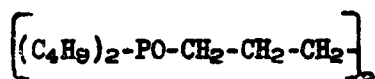
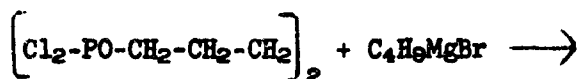
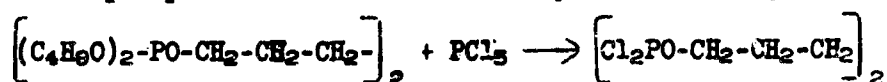
II. Phosphine Oxides

Previous evaluation data on the phosphine oxides have shown that although this class of compounds is quite stable thermally, the materials are not stable when heated in the presence of metals and oxygen. In order to complete this study, one diphosphine oxide was prepared for evaluation.

A. Tetrabutylhexamethylenediphosphine oxide



This diphosphine oxide was obtained by the following reactions:



In the first step of this synthesis bis-1,6-(dibutyl phosphono)hexane was converted to the corresponding tetrachloride by treatment with phosphorus pentachloride¹. The acid chloride was recovered as a dark, viscous liquid that decomposed when distillation was attempted. A small sample of the material was hydrolyzed by refluxing with aqueous hydrochloric acid and 1,6-hexanediphosphonic acid was recovered.

The crude 1,6-hexanediphosphonic tetrachloride was reacted in the usual manner with a large excess of butylmagnesium bromide². On recovery the phosphine oxide was found to be a solid melting at 98.5-100°C after recrystallizing from hot-acid octanes. The reaction of butylmagnesium bromide with the tetrachloride gave only a poor yield of product (23.3 per cent based on the charged chloride) and in view of the fact that the product was a solid, no further effort was made to prepare additional material for bench-scale evaluation. Other properties of the diphosphine oxide are given in Table 1.

III. Phosphinic Acid Derivatives

Two types of phosphinic acid derivatives have been synthesized; one of these consists of compounds containing two phosphorus atoms while the other contains a p-chlorobenzene group attached to a phosphorus atom.

A. 1,5-Pentanediol di(bis-2-ethylhexanephosphinate)



This phosphinic acid ester of 1,5-pentanediol was synthesized by treating the glycol with bis(2-ethylhexane)phosphinic chloride. Those compounds containing two phosphorus atoms, described in earlier reports, have all been joined by alkane groups, or substituted alkane groups. In the

¹ See II - 2, (Technical Report II, p.2).

² Described in II - 2.

Table 1 follows.

Table 1. ORGANO-PHOSPHORUS COMPOUNDS

No.	Formula	M.P. °C.	D. P. 100°/mm.	n _D ²⁰	ANALYSIS					ACID NO.	SOLUBILITY in H ₂ O	Other Notes	
					C, %		H, %		P, %				
					Found	Calcd.	Found	Calcd.					
PHOSPHORIC ACID DERIVATIVES													
197-10	(CH ₃) ₃ PO	15.2	1.553	1.457	1.457	1.457	1.457	1.457	1.457	1.457	1.457	soluble	
197-11	(C ₂ H ₅) ₃ PO	157-160°C at 0.05 mm.	1.119	1.379	1.379	1.379	1.379	1.379	1.379	1.379	1.379	soluble	
197-12	(i-C ₃ H ₇) ₃ PO	149-150°C at 0.4-0.5 mm.	1.098	1.390	1.390	1.390	1.390	1.390	1.390	1.390	1.390	soluble	
197-13	(n-C ₄ H ₉) ₃ PO	146°C at 0.05 mm.	1.190	1.295	1.295	1.295	1.295	1.295	1.295	1.295	1.295	soluble	
197-14	(i-C ₄ H ₉) ₃ PO	131.5°C at 1.5 mm.	1.248	1.248	1.248	1.248	1.248	1.248	1.248	1.248	1.248	soluble	
PHOSPHONIC ACID DERIVATIVES													
197-15	(CH ₃) ₂ POH	197°C at 0.5 mm.	0.995	1.037	1.037	1.037	1.037	1.037	1.037	1.037	1.037	soluble	
197-16	(C ₂ H ₅) ₂ POH	127-128°C at 1.5 mm.	0.987	1.196	1.196	1.196	1.196	1.196	1.196	1.196	1.196	soluble	
197-17	(i-C ₃ H ₇) ₂ POH	146-150°C at 7.5-8.75 mm.	1.041	1.041	1.041	1.041	1.041	1.041	1.041	1.041	1.041	soluble	
197-18	(n-C ₄ H ₉) ₂ POH	124-127°C at 0.5 mm.	1.040	1.040	1.040	1.040	1.040	1.040	1.040	1.040	1.040	soluble	
197-19	(i-C ₄ H ₉) ₂ POH	124-127°C at 0.5 mm.	1.040	1.040	1.040	1.040	1.040	1.040	1.040	1.040	1.040	soluble	
197-20	(C ₂ H ₅) ₂ PO(OH)	124-127°C at 0.5 mm.	1.040	1.040	1.040	1.040	1.040	1.040	1.040	1.040	1.040	soluble	
197-21	(i-C ₃ H ₇) ₂ PO(OH)	124-127°C at 0.5 mm.	1.040	1.040	1.040	1.040	1.040	1.040	1.040	1.040	1.040	soluble	
197-22	(n-C ₄ H ₉) ₂ PO(OH)	124-127°C at 0.5 mm.	1.040	1.040	1.040	1.040	1.040	1.040	1.040	1.040	1.040	soluble	
197-23	(i-C ₄ H ₉) ₂ PO(OH)	124-127°C at 0.5 mm.	1.040	1.040	1.040	1.040	1.040	1.040	1.040	1.040	1.040	soluble	
PHOSPHONIC ACID DERIVATIVES													
197-24	(CH ₃) ₂ PO(OH)	17-18°C at 0.2 mm.	1.040	1.040	1.040	1.040	1.040	1.040	1.040	1.040	1.040	soluble	
197-25	(C ₂ H ₅) ₂ PO(OH)	124-127°C at 0.1 mm.	1.040	1.040	1.040	1.040	1.040	1.040	1.040	1.040	1.040	soluble	
197-26	(i-C ₃ H ₇) ₂ PO(OH)	124-127°C at 0.1 mm.	1.040	1.040	1.040	1.040	1.040	1.040	1.040	1.040	1.040	soluble	
197-27	(n-C ₄ H ₉) ₂ PO(OH)	124-127°C at 0.1 mm.	1.040	1.040	1.040	1.040	1.040	1.040	1.040	1.040	1.040	soluble	
197-28	(i-C ₄ H ₉) ₂ PO(OH)	124-127°C at 0.1 mm.	1.040	1.040	1.040	1.040	1.040	1.040	1.040	1.040	1.040	soluble	
PHOSPHONIC ACID DERIVATIVES													
197-29	(CH ₃) ₂ PO(OH)	124-127°C at 0.05 mm.	0.970	1.056	1.056	1.056	1.056	1.056	1.056	1.056	1.056	soluble	
197-30	(C ₂ H ₅) ₂ PO(OH)	165-166°C at 1.5 mm.	0.960	1.450	1.450	1.450	1.450	1.450	1.450	1.450	1.450	soluble	

subject compound the link joining the phosphorus atoms does not have the P-C_x-P bonding but has a P-O-C_x-O-P bond.

A mixture of 26 g. (0.25 moles) pentamethylene glycol, 79 g. (1.0 moles) of pyridine and 1000 cc. of toluene was cooled to 25°C and there was slowly added with stirring 160 g. (0.519 moles) of bis(2-ethylhexane)phosphinic acid chloride (IV-7). When addition was complete, the reaction mixture was heated at 72°C for 4 hours and then filtered to remove the pyridine hydrochloride. After evaporation of the remaining solvent there was recovered 160 g. of crude ester. This product was distilled through a molecular still and on washing with dilute sodium hydroxide there was recovered a viscous yellow oil with an acid number of 0.02. Other properties of this ester are given in Table 1.

B. Bis-2,2'-(butyl benzenephosphinico)ethyl ether
 $[C_4H_9O(C_6H_5)PO-C_2H_5]_2O$

The sample of bis-2,2'-(butyl benzenephosphinico)ethyl ether described in the last Report (IV-9) was not a pure product, having a very high acid number. This material, obtained in a poor yield (25 per cent), was prepared by reacting tributyl phosphite with 2,2'-dibromoethyl ether at atmospheric pressure. The preparation has now been repeated and a much better product obtained. The method used was that described in the last report, with one exception, and consisted in reacting dibutyl benzenephosphonite with 2,2'-dibromoethyl ether at reduced pressure. (This method of carrying out the Arbuzov reaction at reduced pressure is described in detail later in this report.) The product was recovered in an 84.5 per cent conversion based on the charged dibromoethyl ether. The properties of this preparation are given in Table 1.

C. Butyl p-chlorobenzene(butane)phosphinate
 $C_4H_9OPO(C_4H_9)C_6H_4Cl$

D. Bis-2,2'-(butyl p-chlorobenzene phosphinico)ethyl ether
 $[C_4H_9O(ClC_6H_4)PO-C_2H_5]_2O$

Two phosphinic acid derivatives have been synthesized where one of the groups attached to the phosphorus atom was p-chlorophenyl. A comparison of the properties of these two compounds with those containing the phenyl group should enable us to learn whether an aromatic chlorine atom is beneficial toward lowering the flammability of these liquids. The compounds were all made by reacting dibutyl p-chlorobenzene phosphonite³.

During the preparation of these compounds it has been found that the Arbuzov rearrangement could be carried out very conveniently at reduced pressure when the reacting halide was higher boiling than the liberated

³) See V - 13 of this report for a description of the preparation and properties of this compound.

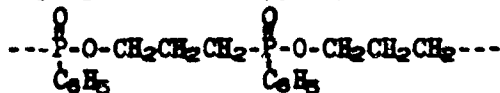
halide. This is illustrated in the following experiment:

Into a flask attached to a short fractionating column was charged 254 g. (0.88 moles) of dibutyl p-chlorobenzenephosphonite. The kettle was heated to 155-165°C at 20 mm. pressure and there was slowly added 85 g. (0.35 moles) of 2,2'-dibromoethyl ether. (b.p. 103-107°C at 20 mm.). The butyl bromide liberated during the reaction was distilled overhead. When no further butyl bromide (b.p. 101°C) was formed the material was fractionated in a molecular still. There was recovered 154 g. (0.29 moles) of product boiling at 160°C at 0.007 mm. pressure. This represented an 82.2 per cent conversion based on the charged dibromoether. The distillate was a colorless viscous oil. After several washings with 50 cc. of 1N sodium hydroxide, the acid number was found to be 0.014.

Similar experiments carried out earlier with refluxing at atmospheric pressure have given yields of product in the neighborhood of 50 per cent of dark and quite acid products. Also, large amounts of high boiling material were formed, while in the experiment just described substantially no bottoms were found.



The polymerization of allyl benzenephosphinate, by means of the addition of the H-P bond to the double bond, could lead to a linear polymeric substituted-propane (benzene) phosphinate.



A compound of this type, a disubstituted phosphinic acid, should be stable and also should have the desirable properties shown by compounds with a high ratio of phosphorus to carbon.

The polymerization could, by reaction of the allyl groups alone, give a phosphinate ester of polyallyl alcohol. However, a mono-substituted phosphinate is quite unstable (IV-33, 2-ethylhexyl benzenephosphinate).

Allyl benzenephosphinate was prepared by adding a mixture of two moles of allyl alcohol and 1 mole of pyridine to an ether solution of benzenephosphonous dichloride. The product was isolated, after filtering off the precipitated pyridine hydrochloride, by distillation at reduced pressure. Yield 20% of theoretical.

The polymerization of allyl benzenephosphinate took place readily when a sample was heated at 120°C in the presence of 1% of di-tert-butyl peroxide. The product was an extremely viscous but clear and colorless material with low solubility in solvents including tributyl phosphate. Polymerization of another sample

of allyl benzenephosphinate with 1-butene gave a product which was quite similar to that just described and it is probable that the butene did not react to any significant extent. Also, exposure of the polymerized material to air for a few days gave a few small crystals at the edge of the material and an odor similar to benzenephosphinic acid. The material was not further evaluated due to its high viscosity and low solubility.

IV. Phosphonic Acid Derivatives

A number of different types of phosphonic acid derivatives were synthesized during the current quarter in order to further study the influence of various substituents on the properties of this class of organophosphorus compounds. This effort has included substituting various hydrocarbon groups, carboxylic acid ester groups and sulfur-containing groups into the phosphonates.

Previous study has shown the bis-1,6-(dibutyl phosphono)hexane to be exceedingly stable. Additional work has now been carried out to determine whether this compound could be prepared as a bottoms-product (not distilled) to eliminate the need for molecular distillation.

During the course of most of the preparations it has been necessary to treat them with sodium hydroxide in order to lower the acid number. In general, this has been done by mixing in a separatory funnel. It has been found that dibutyl butanephosphonate could be refluxed for at least two hours with aqueous 4 per cent sodium hydroxide without undergoing appreciable hydrolysis⁴. This technique proved to be a convenient method of treating the compounds in order to obtain low acid numbers.

The phosphonic acid derivatives in Table I were all made by one of the three general methods described in earlier reports:

- a) the reaction of an alkanephosphonic dichloride with an alcohol,
 - b) the Arbuzov reaction between a trialkyl phosphite and an organic halide, and
 - c) the reaction of sodium dialkyl phosphite with an organic halide.
- A. Dibutyl "isooctans"phosphonate. $(C_4H_9O)_2POC_8H_{15}$
 - B. Dibutyl "isooctans"phosphonate. $(C_4H_9O)_2POC_8H_{17}$
 - C. Dibutyl 2-ethylhexanephosphonate. $(C_4H_9O)_2POC_8H_{17}$
 - D. Dibutyl n-octanephosphonate. $(C_4H_9O)_2POC_8H_{17}$

This is a series of phosphonates containing a C_8 hydrocarbon group. In each case the di-n-butyl ester was made.

⁴ No wetting or solubilizing agents, e.g. alcohol, were used during this hydrolysis test. The experiment is described under the preparation of bis-1,6-(dibutyl phosphono)hexane.

Dibutyl "isooctene"phosphonate was obtained by treating "isooctene"-phosphonic dichloride⁵ with an excess of butyl alcohol in the presence of pyridine. The product was a light yellow liquid and after distilling from a Claisen flask (in the presence of sodium hydroxide) it had an acid number of 0.036.

A sample of this compound was hydrogenated at 1600 psig. pressure using Raney nickel as the catalyst. At 100°C this was found to take place easily⁶. The recovered, saturated ester, was a water-white liquid with an acid number of zero.

Dibutyl 2-ethylhexanephosphonate and dibutyl n-octanephosphonate respectively were obtained by treating 2-ethylhexyl bromide and n-octyl bromide with an excess of sodium dibutyl phosphite in n-heptane solution. The products were isolated as water-white liquids by washing with water to remove the by-product sodium bromide and distilling the organic phase (in presence of sodium hydroxide) at reduced pressure.

The properties of these compounds are given in Table 1.

E. Bis(3,5,5-trimethylhexyl) "isooctene"phosphonate.
 $(C_8H_{16}O)_2POC_8H_{15}$

Previous work in this Laboratory has shown that certain carboxylic acid esters of 3,5,5-trimethylhexanol are more oxidation stable and less corrosive than the corresponding 2-ethylhexanol esters. Bis(3,5,5-trimethylhexyl) "isooctene"phosphonate has been synthesized and evaluation results by the Lubricants and Fuels Department have shown this phosphonate to have many properties that are superior to those of the bis(2-ethylhexyl) ester. (See the following section of this report). The dinonyl ester was prepared by reacting "isooctene"phosphonic dichloride with the alcohol in the presence of pyridine⁷. Its properties are described in Table 1.

F. Dibutyl Butoxyethoxyethanephosphonate.
 $(C_4H_9O)_2PO-C_2H_4OC_2H_4OC_4H_9$

Dibutyl butoxyethoxyethanephosphonate was prepared by heating 4 moles of butoxyethoxyethylchloride and 5 moles of tributyl phosphite to approximately 210°C. The butyl chloride formed by the reaction was slowly distilled with the boiling range 87 to 120°C. The residue was distilled at reduced pressure from sodium carbonate with a yield of 43% of theory. This product was twice distilled from sodium carbonate to reduce the acid number; b.p. 144-6°/0.5 mm.; n_D^{20} 1.4408. Its properties are described in Table I.

⁵ Obtained from the Victor Chem. Works. "Isooctene" is 2,4,4-trimethylpentene.

⁶ IV - 10

⁷ See IV - 13 for details of a similar preparation.

G. Bis(7-methyl-4-thiaoctyl) "isooctene" phosphonate.
 $(C_8H_{11} \cdot S \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot O)_2 \cdot PO \cdot C_8H_{15}$

Another sulfur containing phosphonate has been prepared so that we may gain additional information regarding this class of compounds. The last report (IV-12) described the preparation and properties of bis(7-methyl-4-thiaoctyl) benzenephosphonate which appeared quite interesting, and so we have now synthesized bis(7-methyl-4-thiaoctyl) "isooctene" phosphonate for evaluation. In addition to gaining further information on the sulfur-containing phosphonates, we will be able to compare the influence of "isooctene" and benzene groups. The method of synthesis was that described in IV-12. Its properties are described in Table 1.

H. Bis-2,2'-(dibutyl phosphono)ethyl ether.
 $[(C_4H_9O)_2 \cdot PO \cdot CH_2 \cdot CH_2 \cdot]_2 O$

By reacting tributyl phosphite with bis(2-bromoethyl) ether we were able to prepare bis-2,2'-(dibutyl phosphono)ethyl ether. In view of the fact that this compound contains two phosphorus atoms its properties will be compared with those of bis-1,4-(dibutyl phosphono)butane and bis-1,6-(dibutyl phosphono)hexane.

The Arbuzov reaction between tributyl phosphite and bis(2-bromoethyl) ether was carried out at reduced pressure (see description earlier) and the product was recovered in an 89.5 per cent conversion. Its properties are described in Table 1.

I. Bis-1,4-(dibutyl phosphono)butane. $[(C_4H_9O)_2 PO \cdot CH_2 \cdot CH_2 \cdot]_2$

Since the sample of bis-1,4-(dibutyl phosphono)butane described in IV - Table 3 appeared to have anomalous properties, the preparation of another sample of this material was undertaken in order to insure the identity of the compound. This sample was prepared by reacting an excess of sodium dibutyl phosphite with 1,4-dibromobutane in n-heptane solution. The product was isolated in 42% yield by washing with water, removing the solvent (in presence of sodium hydroxide) at reduced pressure, and distilling through a molecular still. Properties are listed in Table 1.

J. Bis-1,5-(dibutyl phosphono)pentane. $[(C_4H_9O)_2 PO \cdot CH_2 \cdot CH_2 \cdot]_2 CH_2$

This compound was prepared in order to aid in the comparison of the properties of the next lower derivative, bis-1,4-(dibutyl phosphono)butane, and the next higher derivative, bis-1,6-(dibutyl phosphono)hexane. Bis-1,5-(dibutyl phosphono)pentane was synthesized by treating 1,5-dibromopentane with an excess of sodium dibutyl phosphite and then distilling the product through a molecular still. Properties are shown in Table 1.

K. Bis-1,6-(dibutyl phosphono)hexane. $[(C_4H_9O)_2 PO \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot]_2$

In view of the promising properties shown by the sample of bis-1,6-(dibutyl phosphono)hexane described in IV-12, it was suggested that this material be investigated further. The original sample was synthesized by

treating sodium dibutyl phosphite with 1,6-dibromohexane, followed by distillation through a molecular still. Additional work has consisted in preparing this bis-phosphonate by two methods:

- a) The reaction of sodium dibutyl phosphite with 1,6-dibromohexane, and,
- b) the Arbuzov reaction between tributyl phosphite and 1,6-dibromohexane.

The ester from each of the two experiments was recovered as a bottoms-product (not distilled).

In the first experiment (using sodium dibutyl phosphite), there was obtained a 62.1% conversion to bottoms-product. This material was quite acid, acid number 1.36, but on treatment with aqueous sodium hydroxide the value was lowered to 0.10.

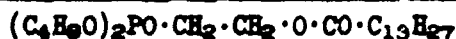
The second run using tributyl phosphite and 1,6-dibromohexane gave an almost quantitative conversion to bottoms-product. The experiment was performed by heating the tributyl phosphite to 150-160°C at 40 mm. pressure, then slowly adding the 1,6-dibromohexane. At the same time the butyl bromide which formed was condensed in a cold trap. The bottoms-product, stabilized at 170°C and 0.1 mm., was recovered in a 95% conversion. A portion of this material was fractionated in a molecular still with the following results:

1.14 per cent light-ends
90.0 per cent product
8.86 per cent heavy-ends

The bottoms-product after stabilization at 170°C and 0.1 mm. had an acid number of 0.545. This number was decreased by refluxing the ester with 2N sodium hydroxide for 2 hours. Titration of the sodium hydroxide indicated that no further alkali was consumed after one hour of refluxing. This treated ester had an acid number 0.02 and a Gardner Color of 2 (very light yellow). Physical properties of both compounds are given in Table I.

L. Bis-1,4-(dibutyl phosphonomethyl)benzene
 $(C_4H_9O)_2PO \cdot CH_2 - C_6H_4 \cdot CH_2PO(OC_4H_9)_2$

With the possibility that the presence of a benzene ring in the chain connecting two phosphonate groups might give a very stable compound, bis-1,4-(dibutyl phosphonomethyl)benzene has been synthesized. The product obtained by the reaction of sodium dibutyl phosphite with bis-1,4-chloromethylbenzene, was found to be a white crystalline solid melting at 45-50°C. Its physical properties are given in Table I. Analysis of this bis-phosphonate indicated that it contained about 1.5 per cent chlorine. In view of the fact that the sample was small, no work has been done to remove this impurity. Further, because of the physical properties, additional work does not appear justified.

M. 2-(Dibutyl phosphono)ethyl myristateN. Bis[2-(dibutyl phosphono)ethyl] adipate

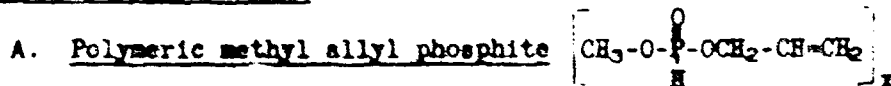
It is well known that certain carboxylic acid esters have very favorable properties when inhibited and used as a hydraulic fluid or lubricating oil. With the possibility that such an ester group would contribute improved properties to a phosphonate, we have synthesized two such compounds. One of these was an ester of myristic acid, the other an adipic acid ester. The method used is as follows:

2-Bromoethyl myristate was prepared by refluxing a mixture of 494 g. (3.95 moles) of ethylene bromohydrin, 798 g. (3.50 moles) of myristic acid and 600 cc. of toluene in the presence of 10 g. p-toluenesulfonic acid. When no further water separated, the reaction mixture was washed and after stabilization was distilled through a Claisen flask. There was recovered 1130 g. (3.14 moles) of ester boiling at 163°C at 0.3 mm. On standing, the distillate solidified to a wax-like material melting at about 50°C.

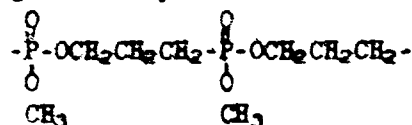
Report No. IV (page 12) describes the reaction of the ester with sodium dibutyl phosphite where the product isolated was not the expected monophosphonate but was bis-1,2-(dibutyl phosphono)-ethane.

The present successful experiment was performed by heating the bromoester with tributyl phosphite. Into a kettle attached to a short column was placed 335 g. (1.0 moles) 2-bromoethyl myristate and 350 g. (1.4 moles) of tributyl phosphite. On heating to about 165°-175°C the reaction set in and there was slowly evolved butyl bromide which was removed as it formed. When no further reaction took place, the unchanged starting materials were removed and the residue was distilled through a falling-film molecular still. There was recovered 291 g. (0.635 moles) of product whose properties are given in Table I.

The adipate ester was prepared in a similar manner and its properties are also given in Table I.

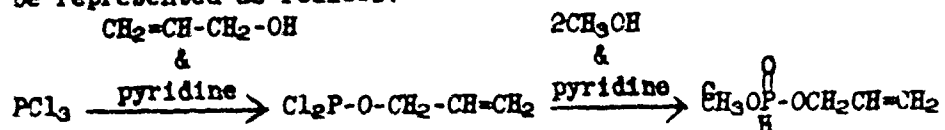
V. Miscellaneous PreparationsA. Polymeric methyl allyl phosphite

The polymerization of methyl allyl phosphite could possibly take place in two manners, namely, the one where the H-P bond reacts with the allyl group to give a polymeric substituted-propanephosphonate



and the other where a homopolymerization of the allyl group takes place to give a phosphite ester of polyallyl alcohol.

Methyl allyl phosphite was prepared by adding a mixture of one mole of allyl alcohol and one mole of pyridine to an ether solution of one mole of phosphorus trichloride at 0°C and then after that addition was completed, a mixture of two moles of methyl alcohol and one mole of pyridine were added. The expected reaction may be represented as follows:



The product was isolated by distillation at reduced pressure after the pyridine hydrochloride had been removed by filtration. Only a small fraction was obtained which had the equivalent weight corresponding to the expected ester; the other fractions were probably contaminated with dimethyl phosphite.

Polymerization of the small yield of pure methyl allyl phosphite for 16 hours at 120° with 1% of di-tert-butyl peroxide as the catalyst gave a clear slightly resilient solid which upon exposure to air for a few days liquified. When the fractions containing dimethyl phosphite contaminant were treated in a like manner, viscous liquid products were obtained. These were apparently insoluble in hydrocarbon solvents but miscible with water and after exposure to air for a few days they became more fluid. Copolymerization with 1-butene did not change the properties of the product to a marked degree. No further work was contemplated because of the instability of the products.

B. Phosphonous Acid Derivatives.

In order to prepare certain of the phosphinates described above, it has been necessary to make p-chlorobenzenephosphonous dichloride and dibutyl p-chlorobenzenephosphonite. This latter compound reacted readily with butyl bromide to form the phosphinates.

1. p-Chlorobenzenephosphonous dichloride $\text{Cl}\cdot\text{C}_6\text{H}_4\cdot\text{PCl}_2$

This compound was prepared by reacting chlorobenzene with phosphorus trichloride in the presence of aluminum chloride. The product was recovered by complexing the aluminum chloride catalyst with phosphorus oxychloride and separating⁵.

A mixture of 1126 g. (10 moles) of p-chlorobenzene, 1374 g. (10 moles) of phosphorus trichloride and 139 g. (1.04 moles) of aluminum chloride was refluxed for 11.5 hours. After the mixture

⁵ This method was described by W. T. Lye, Jr., in N. R. L. Report P-3044, Dec. 1946.

was allowed to stand at room temperature until cool there was added 160 g. of phosphorus oxychloride, then the clear solution was diluted with petroleum ether until no more precipitate formed. The supernatant liquid was separated and the partially crystalline residue was extracted a number of times with petroleum ether. The petroleum ether was flash-distilled and the residue fractionated. There was recovered 259 g. of benzenephosphonous dichloride boiling at 73-80°C at 1 mm. This represents a conversion of 12.2 per cent.

2. Dibutyl p-chlorobenzenephosphonite $\text{Cl-C}_6\text{H}_4\text{-P(OC}_4\text{H}_9)_2$

On treatment of p-chlorobenzenephosphonous dichloride with an excess of n-butyl alcohol in the presence of pyridine, dibutyl p-chlorobenzenephosphonite was formed, a clear liquid boiling at 122°C at 0.1 mm. Its physical constants are given in Table 1.

3. Dibutyl benzenephosphonite · Cuprous chloride complex.

4. Dibutyl p-chlorobenzenephosphonite · Cuprous chloride complex.

It is well known that tributyl phosphite will form complexes with certain metal salts, e.g., cuprous halides and silver halides.⁹ Samples of dibutyl benzenephosphonite and dibutyl p-chlorobenzenephosphonite were treated with cuprous chloride and they were found to undergo an exothermic reaction to form complexes. After filtration of the reaction mixture the complex was recovered as a clear oily liquid which appeared to be quite stable on standing (no copper salts separated nor did green color develop). No further work is planned on them at this time. Properties of the complexes along with certain analyses are given in Table 1.

C. Phosphoric Acid Derivatives

The phosphonic acid derivatives used for comparison purposes in the prior reports have been commercially available materials. For further comparisons we have synthesized a bis-phosphate and a phosphoric amide.

1. 1,5-Pentanediol di(bis-2-ethylhexyl phosphate).

$$\left[(\text{C}_8\text{H}_{17}\text{O})_2\text{-POO-CH}_2\text{-CH}_2\text{-} \right]_2 \text{CH}_2$$

This bis-phosphate was obtained by treating 1,5-pentanediol with bis(2-ethylhexyl) chlorophosphate¹⁰ in the presence of pyridine. The ester was recovered by distilling through a molecular still and was found to be a clear oily liquid. Other properties are shown in Table 1.

Prior to the experiment described above, an attempt was made to obtain this compound by reacting 1,5-pentanediol with POCl_2 then treating this mixture with butyl alcohol and pyridine.¹¹ No diphosphate was recovered

⁹ See Fox & Lockhart, The Chemistry of Organo-Phosphorus Compounds, N.R.L. Report C-3323, July 6, 1948.

¹⁰ Secured from Victor Chem. Works.

¹¹ This method of preparing mixed phosphates is described by Oliver, Wiederhom and Mesrobian, Ind. Eng. Chem. 42, 488(1950).

upon distillation of the reaction product.

2. Bis(2-ethylhexyl) N,N-diisopropylphosphoric amide.
 $(C_8H_{17}O)_2POH(C_3H_7)_2$

This ester-amide was made in order to compare its properties with those of the phosphonic and phosphinic amides evaluated earlier. The compound was prepared as follows:

To a solution of 689 g. (5.3 moles) of 2-ethylhexanol in 500 cc. of toluene was added 74 g. (3.2 moles) of sodium. When all the sodium had reacted there was slowly added 335 g. (1.53 moles of diisopropylamidophosphoric dichloride (see II - 3 for preparation of this compound) at a temperature of 110-120°C. The reaction was stirred at 120°C for 19 hours.

After the mixture had cooled to room temperature, water was added to dissolve the separated sodium chloride. The water phase was separated and the toluene solution dried and stabilized to remove the toluene. The amide product was distilled through a Claisen flask with the product boiling at 165-166° at 1.5 mm. There was recovered 439 g. of material which represented a 70.7 per cent conversion based on the charged diisopropylamidophosphoric dichloride. The material is described in Table I.

BENCH SCALE EVALUATIONS

I. Introduction and Summary

This section summarizes the results of laboratory evaluations of the new organo-phosphorus compounds prepared since those listed in Technical Report No. IV. The new compounds include nine monophosphonates, ten bisphosphonates, two bisphosphinates, a bisphosphate and a phosphoric amide. One of the bisphosphonates was prepared by several different methods and finishing treatments and altogether five samples of this compound have now been evaluated, of which four are included in this report.

In the section on Correlations the data are summarized for all the dibutyl "R"phosphonates $(C_4H_9O)_2POR$, including those reported previously and covering the range where "R" varies from C_3 to $C_{16}O_2$. Similar summaries are made for the di-"R" isooctenephosphonates with four different R groups, bis-(dibutyl phosphono) compounds, where the phosphorus atoms are separated by groups ranging from C_2 to $C_{10}O_4$. Several bisphosphinates and one bisphosphate are also included.

Additive studies on a limited number of organo-phosphorus compounds have included the effects of several oxidation-corrosion inhibitors as well as miscibilities with alkyl methacrylate or styrene polymers. Promising leads were obtained in both phases.

II. Evaluation

A. Summaries of Specific Properties

The properties of the compounds, examined since the previous report, are summarized in Table 2. The data will be discussed in terms of the specific properties.

1. Acidities

All of the acid neutralization numbers (mg KOH/g) of the compounds as secured for test were less than 0.1 except for the Victor Chemical dibutyl benzenephosphonate, the two carboxylate esters (myristate and adipate) and an overhead fraction from a molecular distillation of one of the topped preparations of bis-1,6-(dibutyl phosphono)hexane. While the latter had an acidity of only 0.26, it was very corrosive; caustic treatment dropped this corrosion to a low value. It will be recalled that the distilled high-purity product, previously reported in Technical Report No. IV, was only mildly corrosive. Moderate acidity in a compound does not always result in high corrosivity. For example, the commercial dibutyl benzenephosphonate, on the other hand, had an acidity of 0.44 yet was only moderately corrosive.

The myristate was much less corrosive than the adipate ester, although the original acidities of both products were the same.

2. Four Points

The only compounds in the table which did not have excellent pour points, below -65°F , were the myristate ester discussed above, bis-1,4-(dibutyl phosphonomethyl)benzene, bis-2,2'-(butyl benzenephosphinico)ethyl ether and 1,5 pentanediol di(bis-2-ethylhexanephosphinate). However, the latter had a very low pour point (-60°F) for the high viscosity of this compound.

3. Viscosities

Straight lines on the ASTM viscosity-temperature chart (low temperature range) appear to give reasonably good approximations for the change of viscosity over the temperature range, -40° and 210°F for most of the organo-phosphorus compounds studied. The small deviations which were obtained were less than those shown by many other synthetic oil types.

Viscosities were run at 100°F and 210°F on all the compounds in Table 2 for the purposes of determining VI and slope. On most of the compounds with low pour points, viscosity at -40°F was also determined. In a few selected cases, viscosity at -60°F was also obtained to ascertain whether indications of deviations from a straight line on the ASTM chart were confirmed.

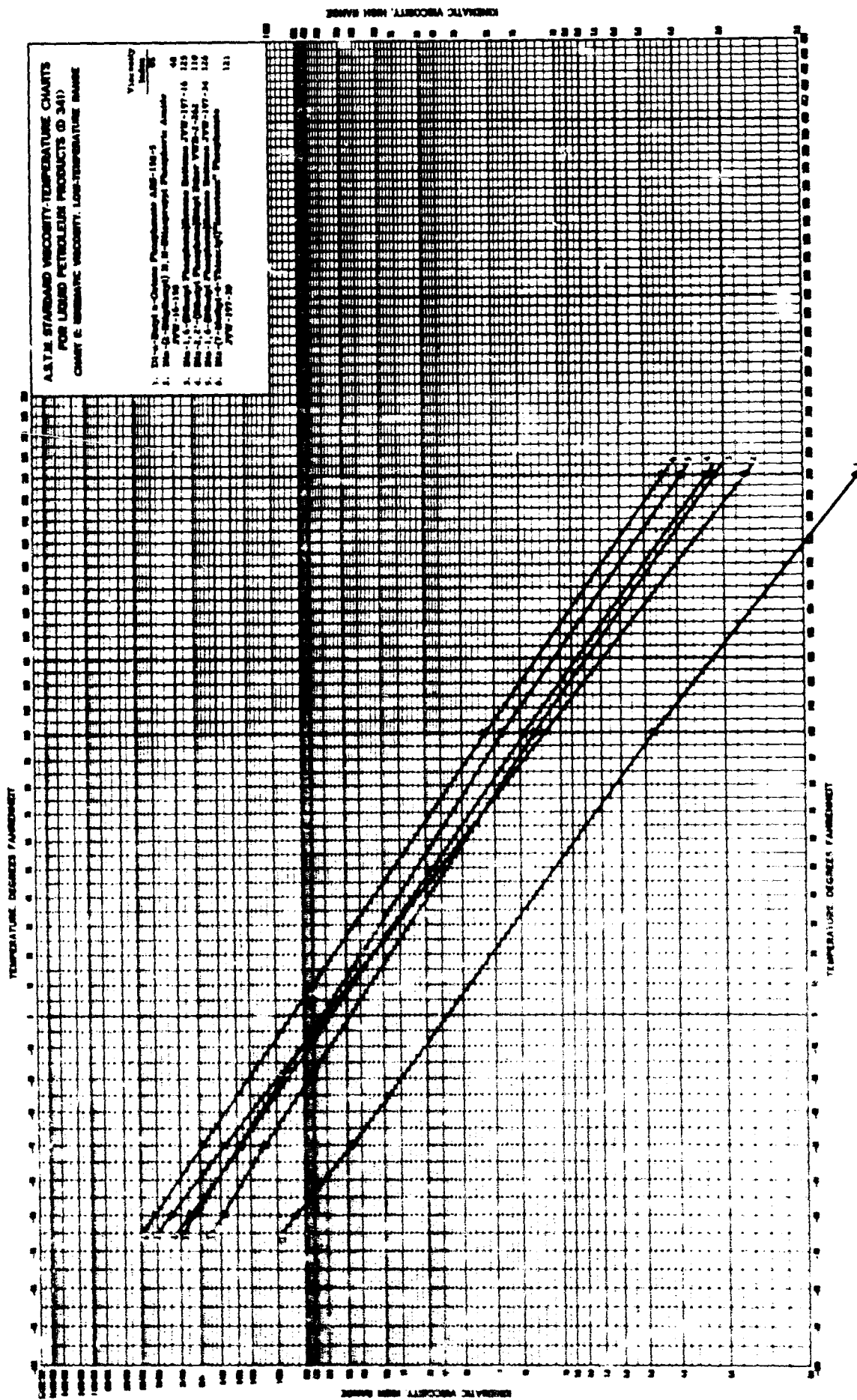
Most of the determined viscosities at -40°F fell slightly below the values obtained by extrapolation from 100°F and 210°F . Exceptions were the bis(3,5,5-trimethylhexyl) "isooctene"phosphonate and Victor Chemical's dibutyl benzenephosphonate in which cases viscosities were 70 and 20 per cent, respectively, higher than the extrapolated values. The six experimentally determined viscosities at -60°F were very close to the values predicted by extrapolation from -40°F and 100°F . Four samples gave values 5 to 10 per cent below the predicted values, while two were 10 to 15 per cent above the predicted values at -60°F . In one case, bis-1,4-(dibutyl phosphono)butane, the sample solidified in the viscometer at -60°F even though the pour point was below -65°F .

The viscosities for the six compounds which were run at four temperatures are plotted on an ASTM chart in Figure 1. The phosphoric amide and the thiooctyl phosphonate gave points which follow straight lines while the ethyl ether bisphosphono compounds show one point not on a straight line. The other three samples show a slight increase in slope with increasing temperature above 100°F , i.e., 210°F viscosities are lower than predicted from viscosities at 100°F and lower.

The viscosity levels of most of the bis-phosphinates and bis-phosphate were of the order of SAE 20. The higher molecular weight "isooctene"phosphonates and the myristate ester were in the hydraulic fluid viscosity range (15-20 cs. at 100°F).

Figure 1 follows.

Figure 1. VISCOSITY TEMPERATURE RELATIONSHIPS OF
 SEVERAL ORGANO-PHOSPHORUS COMPOUNDS



4. Viscosity Ratio and Index

The viscosity ratio and viscosity index by both Dean and Davis (ASTM) and the Hardiman and Nissan systems are given in Table 2. The viscosity ratio will be referred to later in connection with polymer (Acryloid) blends. Hardiman and Nissan VI and Dean and Davis VI are very nearly equal for the more viscous preparations but, in the low viscosity products, such as the dibutyl C₆-phosphonate series, the H and N VI gives such the higher value. The H and N VI and viscosity ratio would rate this series of compounds in the same order. The 2-ethylhexanephosphonate has the highest VI and lowest ratio and the "isooctene"phosphonate is at the other end of the scale. The latter rates even poorer than the benzenephosphonate.

In the higher level of viscosity, the bis(7-methyl-4-thiaoctyl) "isooctene"phosphonate had a VI very nearly equal to the corresponding bis(7-methyl-4-thiaoctyl) benzenephosphonate reported previously. Thus there is little choice between isooctene or benzene in a phosphonate from the VI standpoint. This finding was further confirmed by the data on Victor Chemical's dioctyl "isooctene"phosphonate and dioctyl benzenephosphonate, both of which were reported in Technical Report No. IV. In both instances, the "isooctene"phosphonate is more viscous than the benzenephosphonate at 100°F and 210°F. In the case of the dioctyl derivatives, however, the viscosity at -40°F was lower for the "isooctene"phosphonate than for the benzene derivative. Consequently, at low temperatures, an isooctene derivative would be more desirable than the one containing benzene.

The phosphonoethyl myristate with the highest VI (D and D) in Table 2 also had a high pour point as was the case with the hexadecanephosphonate reported previously. While the phosphonoethyl adipate ester had both high VI and low pour point, its corrosion was very high and thermal stability poor. These latter deficiencies may be due to the fact that traces of the bromoethyl adipate remained in the sample.

5. Flammability

The two flammability tests, the semi-micro open cup flash point apparatus and the pipe cleaner test (see Technical Reports Nos. II and III) were used for these compounds for which sufficient sample was available. Most of the more viscous compounds (viscosity at 100°F over 10 cs.) had flash points above 400°F and the pipe cleaner results were considerably higher than NF-1, the flammability standard for AMS-3150A, interim type aviation hydraulic fluid.

The micro-flash point for the new preparation of bis-2,2'-(butyl benzenephosphinico)ethyl ether was over 500°F. It is thus the highest of any compound tested to date. The bis(7-methyl-4-thiaoctyl) "isooctene"phosphonate had the highest non-flammability of any of the monophosphorus compounds tested and was equal to that of most of the bisphosphono compounds.

The phosphoric amide had a lower flash for its viscosity than most of the other compounds shown in the table.

In the dibutyl C₈ phosphonate series, the n-octane was the least flammable, while the "isooctene"phosphonate was the most flammable in spite of having the highest viscosity of the four compounds in this series.

6. Thermal Stability

Eleven of the new compounds showed excellent thermal stability when heated for 24 hours at 150°C in the presence of carbon dioxide while three were borderline (about 5% viscosity change) and four were poor.

The two topped or "not-distilled" products of bis-1,6-(dibutyl phosphono)hexane, the bis-1,4-(dibutyl phosphonomethyl)benzene and bis[2-(dibutyl phosphono)ethyl] adipate showed poor thermal stability while 1,5 pentanediol di(bis-2-ethylhexanephosphinate), bis-1,4-(dibutyl phosphono)butane and 2-(dibutyl phosphono)ethyl myristate were borderline cases giving about 5% change in viscosity at 210°F during the test.

7. Corrosion and Oxidation Stability

This test, described in Report No. III, is a semi-micro version of the Federal Specification test for light mineral oils, VV-L-791d, test 530.81. The modified test uses the same five metals as catalysts, air circulation and a test temperature of 250°F. The duration of the test was decreased from 168 hours to 71 hours to provide an average level of oxidation equivalent to that obtained in the full-scale test.

The bis(3,5,5-trimethylhexyl) "isooctene"phosphonate was the only compound to give no oxidation or corrosion under the conditions of this test and thus is comparable to the results reported previously for dibutyl butanephosphonate and butyl dibutanephosphinate. Compounds showing moderately low corrosion or oxidation were: dibutyl benzenephosphonate, 2-(dibutyl phosphono)ethyl myristate, bis-1,4-(dibutyl phosphono)butane, bis-2,2'-(dibutyl phosphono)ethyl ether, bis-1,6-(dibutyl phosphono)hexane (bottoms products) (although poor thermal stability was evidenced here), bis-2,2'-(butyl benzenephosphinico)ethyl ether, 1,5-pentanediol di(bis-2-ethylhexanephosphinate) and bis(2-ethylhexyl) N,N-diisopropylphosphoric amide.

All of the preparations of the dibutyl C₈-phosphonate series gave high corrosion. Of the series, the dibutyl "isooctene"phosphonate was the most stable from the standpoint of acid neutralization number, viscosity increase and corrosion. This high corrosion was surprising since the dinonyl "isooctene"phosphonate and the dibutyl butanephosphonate were both non-corrosive.

It is apparent that most of the organo-phosphorus compounds would require inhibitors in applications. The wide variation in corrosion due to small traces of impurity is evidenced by the data for the two distillate samples of bis-1,6-(dibutyl phosphono)hexane (JWV-197-34, cuts 2,3,4 and 5 and 197-49). The heart cut from the molecular distillation of preparation JWV-197-34 had an acid number of 0.26. This material was tested both as distilled and after caustic treatment. The treatment consisted of refluxing

with an excess of 1N caustic until no more caustic reacted (2 hrs. at 102 C in this case). The acidity was reduced to 0.02. The copper corrosion before treatment was 84.2 mg/cm², after treatment 0.52 mg/cm². The viscosity increase dropped from 63% to 3.5% after treatment. Similarly the acid neutralization number of the used oil dropped from 27.1 to 0.27 by this relatively simple treatment. However, in other preparations, caustic treatment does not show this phenomenal improvement and an initial low acidity is no guarantee of low corrosion. Corrosion and oxidation inhibitors are discussed in a later section.

8. Wear and Friction

Wear and friction studies of some of the organo-phosphorus compounds described in this report and in Report No. IV were determined in the Four-ball apparatus.¹² The conditions employed in the present studies are: 2-hour test at 7 kg. load, 80°C and 600 rpm. Since the compounds tested include a number reported previously and only a part of them are included in Table 2, the friction and wear data are summarized separately in Table 3.

While the number of compounds of each class are as yet insufficient to warrant extensive conclusions, the following tentative observations may be made:

a) The phosphates are superior to other types of phosphorus derivatives of comparable structure examined thus far. Tributyl phosphate gives low wear while dibutyl butanephosphonate, butyl dibutanephosphinate and tributylphosphine oxide all give high wear. Aliphatic phosphates as a class are superior to aromatic phosphates.

b) With a series of dibutyl alkanephosphonates, increase in chain length of the alkane group reduces wear as illustrated in Figure 2. The dibutyl hexadecanephosphonate gave the lowest wear obtained to date. The low wear for dioctyl methanephosphonate appears to be an exception. This effect of variation of chain length appears to hold also for the phosphine oxides (see Figure 2).

Changing the chain length of the alkyl groups in phosphonates also changes wear but to a much smaller extent than does a similar change in the alkane group. Thus, changing from butyl to 2-ethylhexyl or 3,5,5-trimethylhexyl groups, in the di-R"isoctene"phosphonates, decreased wear very little, i.e., from 0.52 to 0.42-0.44 while increasing the chain length to 7-methyl-4-thiooctyl gave only 0.46. The thioether chain may be considered comparable to the ether linkage in giving higher wear than an equivalent hydrocarbon chain. Dibutyl butoxyethoxyethanephosphonate has a wear value comparable to a 5 carbon chain (see Figure 2).

c) Unsaturation usually favors lower wear. Examples of both olefinic and aromatic unsaturation indicate increase in wear after hydrogenation in both phosphine oxides and phosphonates. A corollary to this tentative

¹² A description of this test is given by R. G. Larsen in Lubrication Engineering, p. 35 (August 1945).

Fig. 2 and Table 2 follow.

**Figure 2. VARIATION IN WEAR WITH CHAIN LENGTH
OF LONGEST CHAIN IN ALKANE GROUP**

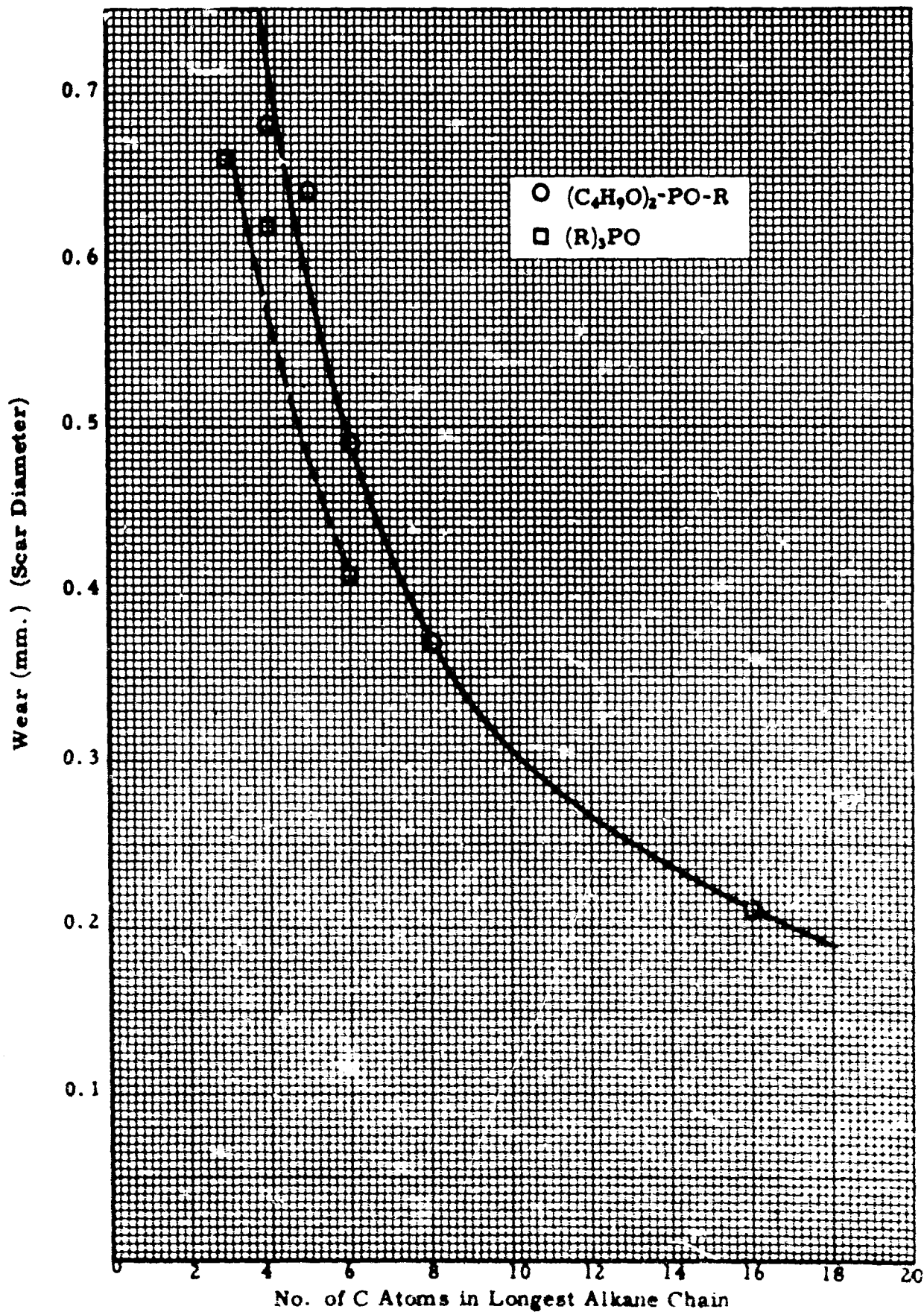


Table 3. Wear and Friction of Organo-Phosphorus Compounds (Cont.)

7 kg. load, 80°C, 600 rpm

Name	Formula	Refer.	Wear Scar Dia. mm.	Coefficient of Friction
<u>Phosphine Oxides</u>				
Tri-n-butylphosphine oxide	$(n-C_4H_9)_3PO$	JW 16-508	0.62	0.13
Tri-sec. butylphosphine oxide	$(Sec. C_4H_9)_3PO$	JW 16-84	0.56	0.11
Ethylbutylisooctylphosphine oxide	$C_2H_5(C_4H_9)(iso C_5H_{11})PO$	JW 15-248	0.66	0.11
Tri(2-ethylhexyl)phosphine oxide	$(C_8H_{17})_3PO$	JW 15-232	0.41	0.11
Bis(2-ethylhexyl)phenylphosphine oxide	$(C_8H_{17})_2(C_6H_5)PO$	JW 16-52	0.37	0.10
Bis(2-ethylhexyl)cyclohexylphosphine oxide	$(C_8H_{17})_2(C_6H_{11})PO$	JW 15-85	0.45	0.12
<u>Phosphinates</u>				
Butyl n-octanephosphate	$(C_4H_9O)HPO(C_8H_{17})$	Stiles	0.24	0.07
Butyl dibutanephosphate	$(C_4H_9O)PO(C_4H_9)_2$	Stiles	0.71	0.11
Butyl benzene(2-propane)phosphate	$(C_4H_9O)PO(C_3H_5)(C_6H_5)$	VPR 2-90	0.67	0.08
Butyl benzene(butane)phosphate	$(C_4H_9O)PO(C_4H_9)(C_6H_5)$	YB 2-182	0.59	0.14
Butyl benzene(methoxymethane)phosphate	$(C_4H_9O)PO(C_6H_5)(CH_2OCH_3)$	VPR 2-108	0.59	0.04
Allyl bis(2-ethylhexane)phosphate	$(C_3H_5O)PO(C_8H_{17})_2$	JW 16-127	0.60	0.13
N,N-Diisopropyl dibutanephosphinic amide	$(C_3H_7)_2NPO(C_4H_9)_2$	JW 16-14	0.51	0.08
Bis-2,2'-(butyl benzene)phosphinicoethyl ether	$[(C_4H_9O)(C_6H_5)POC_2H_5]_2O$	YBB 2-260	0.54	0.11
<u>Phosphonites</u>				
Diallyl benzene phosphonite	$(C_3H_5O)_2PC_6H_5$	YBB 2-2	0.54	0.14
<u>Phosphites</u>				
Diallyl diisopropylaldehyde phosphite	$(C_3H_5O)_2(C_3H_7)_2NP$	YBB 2-164	0.59	0.04
Dibutyl diisopropylaldehyde phosphite	$(C_4H_9O)_2(C_3H_7)_2NP$	YBB 2-150	0.55	0.12
<u>Phosphates</u>				
Tributyl phosphate	$(C_4H_9O)_3PO$	Commercial Solvents	0.25	0.12
Tri(2-ethylhexyl)phosphate	$(C_8H_{17O})_3PO$	Carbide & Carbon Chem.	0.31	0.11
Diphenyl 2-ethylhexyl phosphate	$(C_6H_5O)_2(C_8H_{17O})PO$	Monsanto	0.34	0.13
Triocetyl phosphate	$(C_{17}H_{35O})_3PO$	Celanese	0.46	0.10

(Cont.)

Table 3. Wear and Friction of Organo-Phosphorus Compounds (Cont.)

7 kg. load, 80°C, 600 rpm.

Name	Formula	Refer.	Wear Scar Dia. <u>mm.</u>	Coef. of Fric.
<u>Phosphonates</u>				
Dibutyl butanephosphonate	$(C_4H_9O)_2PO(C_4H_9)$	JW 15-254	0.68	0.12
Dibutyl "isooctane"phosphonate	$(C_4H_9O)_2PO(C_8H_{15})$	JW 197-11	0.52	0.13
Dibutyl "isooctane"phosphinate	$(C_4H_9O)_2PO(C_8H_{17})$	JW 197-28	0.64	0.12
Dibutyl 2-ethylhexanephosphonate	$(C_4H_9O)_2PO(C_8H_{17})$	MS 158-11A	0.49	0.12
Dibutyl n-octanephosphonate	$(C_4H_9O)_2PO(C_8H_{17})$	MS 158-5	0.37	0.13
Dibutyl butoxyethoxyethanephosphonate	$(C_4H_9O)_2PO(C_2H_4OC_2H_4OC_4H_9)$	Stiles	0.60	0.13
Diethyl ethanephosphonate	$(C_2H_5O)_2POC_2H_5$	Stiles	0.39	0.13
Diethyl "isooctane"phosphonate	$(C_2H_5O)_2POC_8H_{15}$	Victor Chen.	0.42	0.13
Dibutyl hexadecanephosphonate	$(C_4H_9O)_2POC_{16}H_{33}$	JW 16-123	0.21	0.08
Diethyl benzenephosphonate	$(C_2H_5O)_2POC_6H_5$	Victor Chen.	0.55	0.14
Diethyl styrenephosphonate	$(C_2H_5O)_2PO(C_8H_7)$	Victor Chen.	0.31	0.10
Diethyl 2-cyclohexylethanephosphonate	$(C_2H_5O)_2PO(C_8H_{15})$	JW 16-82	0.55	0.14
Allyl diisopropylaldehydebutanephosphonate	$(C_3H_5O)(C_3H_7)_2NPO(C_4H_9)$	YB 2-174	0.73	0.17
Butyl diisopropylaldehyde(2-propano)phosphonate	$(C_4H_9O)(C_3H_7)_2NPO(C_3H_5)$	YB 2-158	0.60	0.14
Butyl diisopropylaldehyde(butano)phosphonate	$(C_4H_9O)(C_3H_7)_2NPO(C_4H_9)$	YB 2-160	0.72	0.09
Dibutyl 2-dimethylaminoethanephosphonate	$(C_4H_9O)_2POC_2H_4N(C_2H_5)_2$	YB 2-172	0.57	0.08
Dibutyl 2-morpholineethanephosphonate	$(C_4H_9O)_2POC_2H_4NC_4H_7$	YB 2-196	0.55	0.15
Bis(3,5,5-trimethylhexyl)"isooctane"phosphonate	$(C_9H_{19}O)_2POC_8H_{15}$	JW 197-14	0.44	0.12
Bis(7-methyl-4-thioctyl)"isooctane"phosphonate	$(C_9H_{11}SO_2H_9O)_2POC_8H_{15}$	JW 197-30	0.46	0.12
2(Dibutyl phosphono)ethyl acrylate	$(C_4H_9O)_2PO(C_2H_4OOC_2H_3CH_2)$	JW 16-182	0.40	0.05
<u>Bisphosphonates</u>				
Bis-1,4-(dibutyl phosphono)butane	$[(C_4H_9O)_2PO-C_2H_4]_2$	MS 158-118	0.75	0.12
Bis-2,2'-(dibutyl phosphono)ethyl ether	$[(C_4H_9O)_2POC_2H_4]_2O$	YB 2-262	0.73	0.12
Bis-1,6-(dibutyl phosphono)hexane	$[(C_4H_9O)_2POC_3H_7]_2$	JW 197-16 bottom	0.70	0.14
Bis-1,6-(dibutyl phosphono)hexane	$[(C_4H_9O)_2POC_3H_7]_2$	JW 197-34 bottom	0.71	0.11
Bis(2-ethylhexyl) N, N-diiisopropylphosphoric acid	$(C_8H_{17}O)_2(C_3H_7)_2NPO$	JW 16-158	0.38	0.10

finding would indicate that aromatic groups are better than aliphatic or naphthenic groups in lowering wear with compounds other than phosphates. Thus bis(2-ethylhexyl)phenylphosphine oxide is lower than either tris(2-ethylhexyl)phosphine oxide or bis(2-ethylhexyl)cyclohexylphosphine oxide. Also bis-2,2'-(butyl benzenephosphinico)ethyl ether is considerably better than bis-2,2'-(dibutyl phosphono)ethyl ether.

d) Low friction was obtained with only a few compounds, notably 2-(dibutyl phosphono)ethyl myristate, dibutyl hexadecanephosphonate and the reaction product of tributyl phosphite and epichlorohydrin, all of which gave relatively low wear also.

e) High wear was obtained with the bis(dibutyl phosphono) compounds whether the connecting group between the phosphorus was a four to six carbon chain or an ethyl ether linkage. This high wear was comparable to that obtained with an undoped mineral oil (Houston 100 HVI neutral). However, the epichlorohydrin-tributyl phosphite reaction product mentioned above, which should be a mixture of $(C_4H_9O)_2PO-CH_2-CH(OC_4H_9)-CH_2-PO-(OC_4H_9)_2$ and $(C_4H_9O)_2PO-CH_2-CHOH-CH_2-PO-(OC_4H_9)_2$ did give low wear and friction.

Short chain (C_4 or shorter) diisopropylamido phosphonates gave high wear, while the corresponding amidophosphites and phosphinic amide gave intermediate wear values. A longer chain (2-ethylhexyl) phosphoric amide gave the lowest wear of the nitrogen-phosphorus compounds. This compound, bis-(2-ethylhexyl) diisopropyl phosphoric amide, was the most attractive of the amides from an all around standpoint.

The amines appeared to give lower wear than amides of comparable molecular weight.

Correlation of four-ball wear data with wear in hydraulic pumps (see Motor Laboratory Evaluations) has been unsatisfactory. Dioctyl "styrene"phosphonate, which gave low wear in the four-ball apparatus at either 7 or 40 kg. load, gave high wear (a ten-fold increase) in the Pesco gear pump in comparison to mineral oil. A recheck will be made with a new set of gears.

B. Correlations between Properties and Molecular Structure.

1. Dibutyl "R"-phosphonates $(C_4O)_2-PO-R$ where R is $C_3, \dots, C_{16}, C_{16}O_2$

A large number of dibutyl R-phosphonates have been prepared in which the R group varies from C_3 to $C_{16}O_2$. The data are summarized in Table 4 for a systematic comparison of properties.

There is surprisingly little variation in VI with increasing viscosity from 1 cs. at 210°F for the 2-propenephosphonate to 1.75 cs. for the butoxyethoxyethanephosphonate. The lowest and the highest VI (D and D) for this group are for the "isooctene"phosphonate and the (hydrogenated) "isooctane"phosphonate, respectively. For this group of compounds, the viscosity of -40°F varies between 55 and 400 cs. with the highest viscosity possessed by the compound with the lowest VI.

The two C_{16} -phosphonates, dibutyl n-hexadecanephosphonate and 2-(dibutyl phosphono)ethyl myristate, have very high VI, but unfortunately the pour points are also high, $+45^{\circ}\text{F}$ (Table 3, Report IV) and $+79^{\circ}\text{F}$ (Table 2 this report). Both had excellent nonflammability in comparison with other monophosphonates of equal viscosity or molecular weight (such as the dioctyl "isooctene"phosphonate). The n-hexadecane derivative gave the lowest wear of any of the phosphorus compounds tested to date in the four-ball apparatus. The phosphonoethyl myristate, on the other hand, gave the lowest friction of any of the pure compounds. It also gave moderately low wear. The friction with the hexadecanephosphonate was lower than for most of the other phosphorus compounds (see the section on Wear for further discussion).

Of the group of dibutyl " C_8 "-phosphonates, the n-octanephosphonate gave the lowest wear and best nonflammability. The "isooctane"phosphonate gave the highest VI and highest wear while the "isooctene"phosphonate had the best oxidation resistance but lowest VI and poorest nonflammability in spite of the highest viscosity. The 2-ethylhexanephosphonate had the best low temperature viscosity as well as the lowest viscosity at 100°F or 210°F , and the highest oxidation and corrosion.

Although the oxidation and corrosion of many of the compounds shown in this table were very high, it is believed that inhibitors could probably correct these properties.

2. The Di-R "isooctene"phosphonates $(\text{RO})_2\text{-PO-C}_8\text{H}_{15}$, where R is C_4 , C_6 , C_5SC_3 , and C_9

Four "isooctene"phosphonates are available for comparison. The dioctyl (actually 2-ethylhexyl) "isooctene"phosphonate was obtained from Victor Chemical Works. The others, the dibutyl, the bis(3,5,5-trimethylhexyl), and the bis(7-methyl-4-thiaoctyl)"isooctene"phosphonates were prepared at Emeryville. Their properties are compared in Table 5.

The bis(3,5,5-trimethylhexyl)"isooctene"phosphonate had the best oxidation-corrosion resistance of any of the phosphorus compounds tested in this program. This compound also had a relatively high VI, higher viscosity at 100°F than most of the other phosphonates, good nonflammability and good thermal stability. Viscosity at low temperatures may present a problem.

The bis(7-methyl-4-thiaoctyl)"isooctene"phosphonate, in comparison with the above nonyl derivative, had a higher viscosity, higher VI, better nonflammability, and adequate thermal stability. Although copper corrosion was very high, oxidation remained at a relatively low level. Viscosity at -40°F of this compound is superior to that for the dinonyl "isooctene"phosphonate above.

Although not included in this group a few notes on the bis(7-methyl-4-thiaoctyl) benzenephosphonate, previously reported in Technical Report No. IV, are pertinent. The benzenephosphonate had better oxidation-corrosion stability than the "isooctene"phosphonate prepared from the 3-hydroxypropyl isoamyl sulfide. The viscosity, VI and nonflammability of the

Tables 4 and 5 follow.

Table 4. PROPERTIES OF DIBUTYL R-PROPHONATES WHERE R VARIES FROM C₄ TO C₁₄

Formula	Reference	Viscosity, cs.		Viscosity Index D and D/H and M	Flammability Micro Open Cup Pipe Cleaner No. of Cycles		Corrosion, wt. loss mg./cm. ²			Oxidation % Inc. V100	mg. KOH/g. Acid Neut. No.	2 Hr. 1/2-Ball Test 7 kg. Load, 80°C Wear 600 rpm. Friction Coar. mm. Diam.				
		-40°F	100°F		210°F	Flash Fire	Flash Fire	Cu	Mg				Cd			
(C ₄ H ₉ O) ₂ PO-C ₃ H ₅	VWB-2-74	56.5	2.52	1.00	76	-	295	340	7	11	0	+0.04	0	0.20	0.68	0.12
(C ₄ H ₉ O) ₂ PO-n-C ₄ H ₉	JW-15-254	76.2	2.90	1.10	73	-	320	360	8	13	0.04	0.12	15.8	13.1		
(C ₄ H ₉ O) ₂ PO-C ₂ H ₅ COOC ₃ H ₅	JW-15-252	251.4	4.82	1.56	77	147	350	415	10	14	28.3	0.16	0.12	2.03		
(C ₄ H ₉ O) ₂ PO-C ₃ H ₅	Victor Chems.	312	4.92	1.58	74	145	350	435	11	19	3.35	0.16	0.12	2.03		
(C ₄ H ₉ O) ₂ PO-CH ₂ -C(CH ₃) ₂ -CH ₃	JW-197-11	399	5.55	1.69	66	134	310	390	7	11	34.3	4.26	7.52	9.69	0.52	0.13
(C ₄ H ₉ O) ₂ PO-CH ₂ -CH(CH ₃)-CH ₃	JW-197-28	187	4.43	1.51	88	160	340	405	8	14	82.6	0.68	7.16	12.8	0.64	0.12
(C ₄ H ₉ O) ₂ PO-CH ₂ -CH(CH ₃)-C ₂ H ₅	ARS-158-11A	175	4.05	1.40	80	162	340	410	10	15	48.3	8.20	7.56	45.3	0.49	0.12
(C ₄ H ₉ O) ₂ PO-n-C ₃ H ₇	ARS-158-5	188	4.78	1.56	85	155	365	415	10	18	24.2	2.32	6.16	46.2	0.37	0.13
(C ₄ H ₉ O) ₂ PO-C ₂ H ₅ -O-C ₂ H ₅ -O-C ₄ H ₉	ARS	313	5.65	1.75	81	143	415	460	15	19	84.8	7.45	0.12	37.7	0.60	0.13
(C ₄ H ₉ O) ₂ PO-n-C ₁₂ H ₂₅	JW-16-123	11.76	3.15	149	149	149	455	530	17	19	20.7	0.08	0.24	5.3	0.21	0.08
(C ₄ H ₉ O) ₂ PO-C ₂ H ₅ COOC ₁₃ H ₂₇	JW-16-182	15.48	3.75	151	150	151	450	530	17	21	3.20	0.52	7.20	1.74	0.40	0.05

Table 5. PROPERTIES OF DI R-"ISOOCTENE"PROPHONATES WHERE R IS C₄, C₈, C₈ OR C₈E

C ₈ H ₁₅ PO-(OC ₈ H ₁₅) ₂	JW-197-11	399	5.55	1.69	66	134	310	390	7	11	34.3	4.26	7.52	22	9.69	0.52	0.13
C ₈ H ₁₅ PO-(O-CH ₂ -CH-C ₈ H ₁₅) ₂	Victor Chems.	3695	11.91	2.73	66	110	385	465	14	16	4.39	0.22	7.74	37	37.7	0.45	0.13
C ₈ H ₁₅ PO-(O-C ₂ H ₅ -CH-CH ₂ -C ₈ H ₁₅) ₂	JW-197-14	14700	18.49	3.75	99	115	425	490	18	22	0	0.04	0	1.5	0.05	0.44	0.12
C ₈ H ₁₅ PO-(O-C ₂ H ₅ -S-C ₂ H ₅ -CH-CH ₂ -C ₈ H ₁₅) ₂	JW-197-30	85.59	22.30	4.39	121	121	455	510	24	25	43.1	0	2.0	16	15.0	0.46	0.12

benzenephosphonate were slightly lower than those of the "isooctene"phosphonate. The viscosity at 100°F of the benzenephosphonate was about equal to that of the dinonyl "isooctene"phosphonate, but viscosity at -40°F was almost one-half that of the nonyl derivative.

The dioctyl "isooctene"phosphonate of Victor is intermediate in viscosity, nonflammability and corrosivity between dibutyl "isooctene"phosphonate and the nonyl and thiooctyl derivatives discussed above. Viscosity at -40°F is less than one-half that for the thiooctyl derivative and one-fourth that for the nonyl derivative. However, a dioctyl 2-ethylhexanephosphonate would probably have even better low temperature properties. The VI of the "isooctene"phosphonate was poor as was oxidation stability. This compound is being used for further inhibitor studies since the level of oxidation is rather high.

Although the dibutyl "isooctene"phosphonate exhibits high corrosion to copper, the oxidation level was relatively low. The viscosity at -40°F was about one-ninth that of the dioctyl derivative, although the viscosity at 100°F was only one-half that for the dioctyl "isooctene"phosphonate.

3. Bis(dibutyl phosphono)compounds
 $(C_4O)_2-PO-R-PO-(OC_4)_2$ where $_4$ is C_2 , C_2O , ----- C_1O_4

During the last quarter major emphasis has been placed on the bisphosphono compounds since viscosity, VI and nonflammability have generally been high in this group. The data on new preparations of previously reported compounds as well as on new compounds are summarized in Table 6. Pertinent data from previous reports are also included.

The viscosities of the ethane, methyl ether, butane, pentane, and ethyl ether derivatives fall in the range of 12 to 15 cs. at 100°F and viscosity indices between 95 and 110. The viscosity at -40°F increases from about 1400 cs. for the methyl ether to 2000 cs. for the butane, 2150 cs. for the pentane and 2500 cs. for the ethyl ether derivatives. The viscosities of the preparations of the hexane derivative are considerably higher at 100°F, 17 to 20 cs., with one exception, JW-197-16 bottoms. The low value of this product, 12.94 cs., is attributed to some lower viscosity impurity. The viscosity at -40°F on the hexane derivative ranged from 134 cs. on the very low viscosity product to 3550 cs. on the highest viscosity overhead heart-cut.

The other compounds, in order of increasing viscosity at 100°F, are ethyl-bis-2,2'-(dibutyl phosphono)ethylamine, 22 cs.; ethyl adipate derivative (JW-16-173), 25.7 cs.; and the dimethylbenzene derivative (VWB-2-246), 36.1cs. This last product has the lowest VI and the highest pour point and so is not so attractive from the physical properties standpoint, although nonflammability was excellent. The adipate ester had the highest VI, low pour point, good nonflammability but very high oxidation and corrosion. Nonflammability for the group was generally high but the ethylamine derivative was low in micro flash and fire for its high viscosity. The pipe cleaner tests on this latter compound were better than would be expected from the micro open cup apparatus.

Table 6 follows.

Table 6. SUMMARY OF BIS(DIBUTYL PHOSPHONO) DERIVATIVES

Formula	Reference	Viscosity, ce.		Viscosity Index D and D/H and W	Flammability Micro Open Cup Pipe Cleaner No. of Cycles		Corrosion, mg./cm. ²		Oxidation 5 Inc. Final Acid VIOPV Neut. No.	Wear 2 hr 4-Ball Test 7 kg. load, 80°C, 600 rpm. Scar mm. Diam.	Friction µ	
		-40°F	100°F		210°F	Flash Fire	Flash Fire	Cu				Co
(C ₈ H ₁₇ O) ₂ PO-CH ₂ -CH ₂ -PO-(OC ₄ H ₉) ₂	JWV-16-126	-	12.75	3.02	102	127	17	23	9.4	1.16	2.0	
(C ₈ H ₁₇ O) ₂ PO-CH ₂ -O-CH ₂ -PO-(OC ₄ H ₉) ₂	ARS- DH-10-26	1382	12.05	2.89	97	126	445	560	27.4	11.0	5.8	
(C ₈ H ₁₇ O) ₂ PO-C ₂ H ₅ -C ₂ H ₅ -PO-(OC ₄ H ₉) ₂	ARS- ARS-158-11B	2004 2045	13.27 13.42	2.97 3.08	78 95	114 122	450 430	550 550	4.84 1.56	0.36 1.0	2.5 1.11	0.62 0.75
(C ₈ H ₁₇ O) ₂ PO-C ₂ H ₅ -O-C ₂ H ₅ -PO-(OC ₄ H ₉) ₂	WVB-2-262	2575	14.47	3.31	110	127	475	550	2.96	0.64	1.03	0.73
(C ₈ H ₁₇ O) ₂ PO-C ₂ H ₅ -N(C ₂ H ₅) ₂ -PO-(OC ₄ H ₉) ₂	WVB-2-222	-	22.02	4.25	110	116	400	445	22.0	2.48	77	
(C ₈ H ₁₇ O) ₂ PO-C ₂ H ₅ -CH ₂ -C ₂ H ₅ -PO-(OC ₄ H ₉) ₂	ARS-156-7	2131	13.95	3.22	106	127	465	560	53.1	40.1	26.7	
(C ₈ H ₁₇ O) ₂ PO-CH ₂ -C(CH ₃) ₂ -PO-(OC ₄ H ₉) ₂	WVB-2-246	-	36.1	5.44	91.5	95	480	555	30.8	13.5	18.6	
(C ₈ H ₁₇ O) ₂ PO-C ₂ H ₅ -C ₂ H ₅ -PO-(OC ₄ H ₉) ₂	JWV-16-119	3550	19.86	4.17	131	128	475	560	1.16	0.44	0.77	
(C ₈ H ₁₇ O) ₂ PO-C ₂ H ₅ -C ₂ H ₅ -PO-(OC ₄ H ₉) ₂	JWV-197-16 Bottoms	1340	12.94	3.18	125	137	475	560	2.28	0.32	0.30	
(C ₈ H ₁₇ O) ₂ PO-C ₂ H ₅ -C ₂ H ₅ -PO-(OC ₄ H ₉) ₂	JWV-197-34 Bottoms	2894	18.21	3.91	126	127	485	570	3.40	0.12	0.55	0.14
(C ₈ H ₁₇ O) ₂ PO-C ₂ H ₅ -C ₂ H ₅ -PO-(OC ₄ H ₉) ₂	JWV-197-34 Cuts 2,3,4,5	-	17.40 17.75	3.84 3.90	132 133	131 131	84.16	0.64	1.48	0.64	27.1	0.71
(C ₈ H ₁₇ O) ₂ PO-C ₂ H ₅ -C ₂ H ₅ -PO-(OC ₄ H ₉) ₂	JWV-197-49	-	25.69	5.11	141	131	24.1	22.9	0.52	+0.26	0.27	
(C ₈ H ₁₇ O) ₂ PO-C ₂ H ₅ -OOC-C ₂ H ₅ -PO-(OC ₄ H ₉) ₂	JWV-16-173	7154	10.44	10.68	21	22	515	550	3.84	3.35	1.79	
(C ₈ H ₁₇ O) ₂ PO-C ₂ H ₅ -O-C ₂ H ₅ -PO-(OC ₄ H ₉) ₂	WVB-2-260	-	60.82	7.77	100	99	1.28	0	0.28		0.78	
(C ₈ H ₁₇ O) ₂ PO-OC ₂ H ₅ -O-PO-(OC ₄ H ₉) ₂	JWV-197-22	-	30.53	5.77	139	131	2.25	0.04	0.76		2.26	

Other Bis Phosphorus Compounds

The general level of oxidation and corrosion stability was rather low on most of these compounds with the exception of the hexane derivatives which were excellent. The one hexane preparation which did give high corrosion was readily corrected by refluxing with 1 N caustic as previously noted. As a class, the bis(dibutyl phosphono) compounds gave high wear in the four-ball apparatus. Since undoped mineral oils also give comparable high wear, the significance of this factor remains to be assessed more thoroughly. Data for several bis-phosphinates and a phosphate are also given at the bottom of Table 6 for comparison. Of these, bis-2,2'-(butyl benzenephosphinico)ethyl ether had the highest viscosity of any of the non-polymeric compounds prepared to date, the best nonflammability and relatively low oxidation and corrosion. However, its VI is low, 21 or 22.

The two 1,5-pentanediol derivatives had higher viscosity than most of the bis(dibutyl phosphono) derivatives at the top of Table 6 since these two preparations contained octyl groups in place of the butyl groups. The phosphinate had a higher viscosity and lower VI than the phosphate, a trend noted earlier with the butyl dibutanephosphinate and tributyl phosphate. Corrosion and oxidation were relatively low in either case with the phosphinate being slightly better. In line with its higher viscosity, the phosphinate has a higher nonflammability but the difference is slight.

4. Diethyl Diisopropylphosphoric Amide and Diethyl "Isocetene"phosphonate

The phosphoric amide, for which data are given in Table 2, has the lowest pour point and highest VI of any of the amides (not counting the amido phosphites of very low viscosity which were reported in Technical Report No. IV). The viscosity at 100°F coincided with that for the diethyl "isocetene"phosphonate and consequently useful comparisons can be made between the two products. Substitution of the $(C_3H_7)_2N$ for the C_6H_{15} attached to the phosphorus atom increases viscosity at -40°F, lowers VI, reduces nonflammability slightly, and lowers oxidation and corrosion. As pointed out above, the viscosities at -60°, -40°, 100°, and 210°F fell on a straight line on the ASTM chart for the amide.

C. Additive Studies

1. Corrosion and Oxidation Inhibitors

Since most of the compounds prepared under this contract do not have as high oxidation and corrosion resistance as would be required for many applications, it is important to find satisfactory inhibitors before attempting an extensive larger-scale evaluation program. Even the compounds which were quite stable in the purified form would probably require inhibitors in larger scale production. The conventional inhibitors for mineral oils for the most part are not generally satisfactory in these organo-phosphorus compounds. Inhibitors that are successful with phosphates appear to show promise with phosphonates and possibly phosphinates.

The first inhibitor studies were made using Victor Chemical Works diethyl "styrene"phosphonate. This compound, without inhibitor, is being tested in the Motor Laboratory as the first phosphorus compound for evaluation

on a large scale (see following Section). Although this product gave relatively low corrosion and oxidation, in comparison with most of the high-purity samples prepared under this contract, the corrosion was sufficient to give concern in actual use.

The small scale laboratory oxidation and corrosion test was used to test a series of inhibitors and combinations. The data are given in Table 7. Whereas the conventional inhibitors for mineral oil, phenyl alpha-naphthylamine or 2,6-di-tertiary-butyl-4-methylphenol, gave increased oxidation or copper corrosion in dioctyl "styrene"phosphonate, the combination of glycidyl phenyl ether with disulfide reduced oxidation and corrosion. An investigation of inhibitor concentrations with the combination using bis(methylene tolyl sulfide) in place of the wax disulfide indicated that 1% inhibitor appeared to be optimum. Blend 1604 was tested in the Pezco gear pump (see Motor Laboratory Evaluations). The bis(methylene tolyl sulfide) looked more attractive than benzyl disulfide at the same concentrations. It also has an advantage over the wax disulfide of miscibility with the glycidyl phenyl ether. Phenothiazine, which is satisfactory with some synthetic oils, did not give any improvement with dioctyl "styrene"-phosphonate.

This same combination of glycidyl phenyl ether and either wax disulfide or bis(methylene tolyl sulfide) was tested in a bis-1,1'-(dibutyl phosphono)methyl ether, a bis(3,5,5-trimethylhexyl) "isooctene"phosphonate thickened with polymer, and in a bis-1,6-(dibutyl phosphono)hexane-polymer blend. The data are given in Table 8.

The methyl ether derivative (DH-10-26) gave high copper corrosion and moderate acidity. Phenothiazine had little effect, dropping acidity but increasing corrosion. The glycidyl phenyl ether-wax disulfide on the other hand, lowered copper corrosion but increased acidity. The thickened blend, containing dinonyl adipate to solubilize the polymer in this base stock, was inhibited with the glycidyl phenyl ether and bis(methylene tolyl sulfide). Copper corrosion on this blend was less than one-half that of the original while acidity was about the same as the original.

With the dinonyl "isooctene"phosphonate, the low-corrosion and oxidation was greatly increased by the addition of polymer but the inhibitor combination then brought the oxidation and corrosion back below the original low level.

In the very corrosive bis-1,6-(dibutyl phosphono)hexane, the inhibitor combination gave a small decrease in oxidation and corrosion but caustic treatment of the original, described above, was more effective, reducing it to a very low value (see JWV-197-49).

Subsequent inhibitor studies will be made with Victor's dioctyl "isooctene"phosphonate as a base. This compound is less stable than the dioctyl styrene phosphonate and should be more sensitive to inhibitor action.

Tables 7 and 8 follow.

Table 7. INHIBITOR STUDIES IN DI(Octyl) "STYRENE" PHOSPHONATES

Test No. P.V. Almond No.	212	222	213 1598 0.7% Pheno- thiazine	214 1599 1% OPE 0.1% wax disulfide	217 1602 0.8% OPE 0.17% benzyl disulfide	218 1603 0.8% OPE 0.17% Pheno- thiazine	219 1604 0.8% OPE 0.17 bis (methylene tolyl sulfide)	231 1612 1.66% OPE 0.34% bis methylene tolyl sulfide	237 1618 1.2% OPE 0.2% bis (methylene tolyl sulfide)	230 1611 1.66% OPE 0.34% benzyl disulfide	220 1605 1% TEMP b)	221 1606 1% Pan a)
Via. ca., 100°F	27.13		27.33	26.18	26.07	26.38	26.17	25.48	25.85	25.47	27.65	27.75
210°F	4.00											
VI D and D	-5											
Acid No.	0.77		0.80	0.72	0.55	0.78	0.80	0.77	0.82	0.79	0.80	0.84
% Oil Loss	2.1	2.6	1.1	1.0	1.6	0.5	1.0	2.7	2.7	1.6	2.1	1.6
% Inc. V100	13	14	17	16	17	17.5	15.5	17	16	15	17.5	20
Acid Meant. No.	1.88	2.25	1.99	1.04	0.81	1.13	0.91	1.13	1.42	1.11	4.21	2.55
Cu	4.6	6.71	5.95	1.20	3.32	4.2	1.32	1.04	1.76	2.4	4.24	10.8
Mg	0.04	0.12	0	0.08	0.08	0.12	0.20	0	0.08	+0.04	0.12	0.08
Weight Loss mg./cm. ²	0.16	0.12	0	0.08	0.08	0.12	0.08	0	0.56	+0.04	0.12	0.08
Ca	1.04	0.50	11.2	0.24	0.12	0.28	0.16	0.04	0.24	0.12	0.12	0.12
Al	0	0.08	0	0.24	0.08	0.08	0.12	+0.04	0.08	0	0.08	0.08

OPE - glycidyl phenyl ether
a) phenyl o-naphthylamine
b) 2,6-tertiary butyl 4-methylphenol

Table 8. INHIBITOR STUDIES ON OTHER PHOSPHONATES

Test No. P. V. B.	215 Bis- (dibetyl phosphono) methyl ether (DM-10-26)	261 1601 0.2% Phos- phono in DM-10-26	216 1600 1% CPE 0.1% var dimulfide in DM-10-26	256 1617 16.7% Xylene B 4.17% A-EPB125 0.6% CPE 0.1% MCTS in DM-10-26	290 Bis(5,5-tri- methylhexyl) "isocostene" phosphonate JVM-197-14	253 1619 5% A-EPB125 in JVM-197-14	268 1620 4.5% A-EPB125 0.8% CPE 0.17% MCTS in JVM-197-14	296 Bis-1,6- (dibetyl phosphono) hexane JVM-197-34	264 1622 5% A-EPB125 0.8% CPE 0.17% MCTS in JVM-197-34
Vis., ca. at 100°F	12.57	12.79	12.27	15.35	17.61	29.0	27.35	17.40	24.24
at 210°F	3.01				3.64	6.05		3.84	
VI (D and D)	105				98	194		132	
Acid No.	0.05		0.18		0.05		0.07	0.26	0.48
Per Oil Loss	0	1.5	1.5	2.5	0.6	1.1	1.7	0.5	1.6
% Inc. V100	5	8.5	16	12	5	41.5	4	65	52
Acid Meq. No.	3.15	2.85	4.90	3.42	0.48	28.5	0.24	27.1	24.8
	9.64	10.99	5.56	4.44	1.32	12.8	1.24	84.16	64.16
	0.68	1.40	0.57	0.56	0	0.08	0.40	0.64	1.60
Weight Loss mg./cm.²	0	0.04	0.04	0	0	0	0.04	0.04	0.80
	0	1.16	1.08	0.56	2.64	0	0.82	1.48	0.96
	0	0	0	0	0	0	0.48	0	0.12

MCTS - bis(methylene tolyl sulfide)
CPE - glycidyl phenyl ether
A-EPB125 - styrolid EPB125 (methacrylate polymer in 300° flash mineral oil)
Xylene B - bis(5,5-trimethylhexyl) adipate

2. Viscosity Index Improvers

Since the majority of the compounds prepared under this contract have had relatively low viscosities, it is of interest to examine their response to the use of thickeners to raise viscosity and VI. Accordingly, a preliminary examination has been made of the miscibility of the conventional VI improvers with a few organo-phosphorus compounds. The data are given in Table 9.

Based on earlier work with phosphates and other synthetic oils, the greatest increase in VI for a given increase in viscosity is usually obtained with the alkyl methacrylate polymers or copolymers (Acryloids). Other thickeners of commercial importance are alkylated styrene polymer (Santodex) and polyisobutylene or polybutenes (Paratone, Vistanex, Indopols). In some instances Santodex shows better miscibility over Acryloid for phosphates. Most of the present work was done with Acryloids, either HF855 or HF8125. In one instance with bis(dibutyl phosphono)ethyl ethers when one of the compounds was immiscible with Acryloid, a Santodex blend was tried but was also immiscible.

Addition of Acryloid to either the dioctyl or the dinonyl "isooctene"phosphonate (blends 1386 or 1619) gave a large increase in VI but only a small drop in ratio of viscosity at 100°F to viscosity at 210°F. With the dioctylphenylphosphine oxide both the VI improvement and drop in ratio were large but the original VI was so low that the final VI of 33 was still lower than most of the organo-phosphorus compounds.

With the bis(dibutyl phosphono) compounds, Acryloid was not miscible with either methyl or ethyl ether derivatives but was miscible with both butane and hexane derivatives. Santodex was also not miscible (at 5% concentration) in the ethyl ether derivative. Both of the immiscible bis-phosphono ethyl ether blends with Acryloid or Santodex could be solubilized with about 25% of dioctyl "isooctene"phosphonate as shown by blends 1627 and 1629. The VI improvement and decrease in viscosity ratio was greater for the Acryloid blend than with the Santodex although the concentration of the latter was slightly lower.

The bis-1,4-(dibutyl phosphono)butane-Acryloid blend (No. 1626) showed a greater increase in VI and drop in ratio than the corresponding blend in bis-1,6-(dibutyl phosphono)hexane (No. 1638).

As pointed out above, the addition of polymer to these compounds often necessitates the simultaneous addition of oxidation-corrosion inhibitors to give stable products.

Table 9 follows.

Table 9. POLYMER BLENDS IN ORGANO-PHOSPHORUS COMPOUNDS

Compound	Reference	Viscosity, ce.		Viscosity 100% D and B and H	Ratio Via 100 Via 2107	F.V. Blend Wt. %	In Polymer Blend	Viscosity, ce.		Viscosity 100% D and B and H	Ratio Via 100 Via 2107	Remarks
		1007	2107					1007	2107			
Dibutyl (1-oxo-2-oxaphosphorin-2-ylidene)phosphine Oxide	Victor Chem.	11.91	2.73	66	4.37	1386	3A-48755	16.21	3.74	136	4.34	Big increase in VI, small drop in ratio.
Dibutylphosphorophosphine Oxide	JF 16-32	71.82	3.29	-118	13.37	1307	3A-487125	100.1	8.29	33	12.09	Big increase in VI, large drop in ratio.
Di-(1,3,5-trisubstituted)phosphine Oxide	JW-137-13 Cuba 2,5,4	17.61	3.64	98	4.84	1619	3A-487125	29.0	6.05	142	4.81	Big increase in VI, small drop in ratio.
Di-(diethyl phosphino)phosphine Oxide	PM-10-86	14.27	3.01	105	4.17	1616	3A-487125	Immiscible				
Di-(2,2'-diethyl phosphino)phosphine Oxide	PM-3-260	14.47	3.11	110	4.37	1605	6A-487125	Immiscible				
Di-(1,3,5-trisubstituted)phosphine Oxide	AS-138-118	14.40	3.25	123	4.43	1606	3A-487125	Immiscible				
Di-(1,3,6-trisubstituted)phosphine Oxide	JW-171-24 Cuba 2,5,4,2	17.40	3.24	132	4.25	1638	3A-487125	24.70	5.67	166	4.36	Big increase in VI, large drop in ratio.
Di-(2,2'-diethyl phosphino)phosphine Oxide	PM-3-260			131		1607	4, 3A-487125	16.36	4.46	172	4.16	Big increase in VI, large drop in ratio.
Di-(1,3,5-trisubstituted)phosphine Oxide	Victor Chem.	13.28	3.11	120	4.44	1629	3, 08 Santolux	17.92	4.15	141	4.24	Smaller increase in VI, smaller drop in ratio.

MOTOR LABORATORY EVALUATIONSI. Introduction

In addition to dioctyl "styrene"phosphonate, the commercial preparation discussed previously (IV-36), the Motor Laboratory has obtained a light mineral oil (HVI 100 Neutral, Houston stock - Reference designation, K-1500) to use as a further orientation aid in evaluating the materials prepared under the Contract. A list of physical properties of the two reference fluids is provided in Table 10 following, from which it may be seen that the two materials possess certain rather similar characteristics:

Table 10. Properties of Reference Fluids

Name	Fluid No.	Source	Viscosity		V.I. D.A.D. ¹	Acid No. mg.KOH/g.	Pour Point °F	Micro ²⁾	
			100°F	210°F				Flash Point °F	Fire Point °F
Dioctyl "styrene" phosphonate	K-1508	Victor Chem.	27.13	4.02	-1	0.8	-55	435	505
HVI 100 Neutral	K-1500	Shell Oil Co.	21.78	4.11	96	0	+10	400	445

- 1) Dean and Davis.
- 2) See Report III-18 for description of test.

II. Preliminary EvaluationA. Pesco Gear Pump Studies

The Pesco aircraft hydraulic pump, Model AP-349, has been chosen for wear and fluid deterioration evaluation of those of the Contract materials that are operable in this equipment. The test stand employs a simple recirculating system with reservoir, pump, loading valve, heat exchanger, filter, and the necessary gages and control equipment. Table 11 summarizes the operating conditions and lists the results of initial tests of the two reference fluids. Changes in viscosity and acid number were nominal in the seven tests completed to date (Table 11), but the pump wear, as measured by the weight losses of the gears and their supporting bushings, was notably higher with the phosphonate (Test WI-151) than with the mineral oil (Test WI-150). Preliminary attempts to achieve more satisfactory wear values by means of either anti-oxidation and corrosion or anti-wear additives in the phosphonate (Tests WI-154 and 155) were unsuccessful.

More additive studies are contemplated for the Pesco apparatus, as well as wear investigations of additional commercial phosphorous compounds, before work is initiated with compounds synthesized under the Contract.

B. Lauson Engine Test

An engine test of the EVI 100 Neutral reference oil has been started in a single-cylinder, liquid-cooled, four-stroke cycle gasoline engine (Lauson Model LF; bore 2.6 in., stroke 2.5 in.). Satisfactory operation has been obtained despite the low viscosity of the oil. The complete test results, together with a full description of the equipment and procedure, will be reported later. The dioctyl "styrene"phosphonate is also scheduled to be run in the Lauson engine.

WEV:fhb

William E. Vaughan
as Coordinator

Appendices A and B

Table II. Composition and Test Results of Fluids Investigated in the High Pressure Gear Pump

Test Designation: PF-81
 Pump Model: Peaco 1P-340
 Test Conditions: 1,000 psi. Outlet Pressure 750 psi. Fluid Charge
 200°F Inlet Temperature 13 hr. Duration
 Pump Speed: 1,800 rpm.

Test No. PPo	Fluid No.	Composition (%)	Duration (hours)	Per Cent Viscosity Change (at 100°F)	Acid No. (mg. KOH/g.)		Sludge Used Oil	Gear Set No.	Weight Losses (mg.)		Remarks
					New Oil	Used Oil			Gears (Steel)	Bushings (Brass)	
VI-150	K-1500	HWI 100 Neutral	13	-2.2	0	0	None	19	5.0	2.0	Mineral oil reference run.
VI-151	K-1508 (Victor Chas. Victor)	Diocetyl styrene ² phosphonate	13	3.4	0.84	0.87	None	19	58.8	5.8	Commercial phosphonate reference run. Gear unexpectedly high.
VI-152	K-1500	HWI 100 Neutral	13	-2.4	0	-	None	19	2.0	0.5	Low wear may indicate presence of anti-wear "phosphorus film".
VI-153	K-1508 (Victor)	See Test No. 151	13	-4.4	0.84	0.93	None	19	22.5	2.5	Lower wear level than in Test 151. Probably the result of "searing in".
VI-154	FW-1604	99.0 K-1508 0.83 SFE 0.17 B(MTS)	13	-1.2	0.60	0.36	None	19	22.1	2.4	Additives unsuccessful in reducing wear.
VI-155	FW-1623	99.0 K-1508 1.0 TCP	13	-1.2	0.94	0.90	None	19	19.0	-	Anti-wear additive ineffective.
VI-156	K-1500	HWI 100 Neutral	13	-0.1	0	0	None	19	1.5	-	Mineral oil reference run

* Key to Abbreviations used: SFE - Glycidyl phenyl ether
 ICF - Tricresyl phosphate
 K-1508 - Diocetyl styrene² phosphonate
 B(MTS) - Bis(methylene tery sulfide)

APPENDIX A

Personnel

Following is a list of the professional personnel who have been actively associated with the contract work to date (including both full- and part-time participants):

Preparations

S. A. Ballard
V. W. Buls
R. C. Morris
A. R. Stiles
J. L. Van Winkle
W. E. Vaughan, Coordinator

Bench Scale Evaluations

R. G. Larsen
W. F. Ross
S. K. Talley
R. E. Thorpe
F. J. Watson

Motor Laboratory Evaluations

A. G. Cattaneo
A. R. Isitt
J. E. Weigel

Electrical Properties


J. N. Wilson

Analytical Work

G. W. Bond
F. R. Brooks
A. E. O'Donnell
E. D. Peters

APPENDIX B

Formula Index with Cross Reference to Preparations^{a)}

Empirical Formula	Name	Structural Formula
C ₄ H ₉ O ₂ P	methyl allyl phosphite	(CH ₃ O)(C ₃ H ₅ O)POH
C ₆ H ₄ Cl ₃ P	p-chlorobenzene phosphonic dichloride	Cl·C ₆ H ₄ ·PCl ₂
C ₉ H ₁₁ O ₂ P	allyl benzenephosphinate	(C ₃ H ₅ O)OPH(C ₆ H ₅)
C ₁₄ H ₂₂ ClO ₂ P	butyl p-chlorobenzene (butane) phosphinate	ClC ₆ H ₄ (C ₄ H ₉)OP(OC ₄ H ₉)
C ₁₄ H ₂₂ ClO ₂ P	diethyl p-chlorobenzene phosphonite	ClC ₆ H ₄ P(OC ₂ H ₅) ₂
C ₁₄ H ₂₃ O ₃ P	diethyl benzenephosphonate	(C ₂ H ₅ O) ₂ (C ₆ H ₅)PO
C ₁₆ H ₃₃ O ₃ P	diethyl "isooctene" phosphonate	(C ₄ H ₉ O) ₂ (C ₈ H ₁₅)PO
C ₁₆ H ₃₅ O ₃ P	diethyl "isooctene" phosphonate	(C ₄ H ₉ O) ₂ (C ₈ H ₁₇)PO
C ₁₈ H ₃₅ O ₃ P	diethyl 2-ethylhexane phosphonate	(C ₄ H ₉ O) ₂ (C ₈ H ₁₇)PO
C ₁₈ H ₃₅ O ₃ P	diethyl n-octane phosphonate	(C ₄ H ₉ O) ₂ (C ₈ H ₁₇)PO
C ₁₈ H ₃₅ O ₃ P	diethyl butoxyethoxyethane phosphonate	(C ₄ H ₉ O) ₂ (C ₄ H ₉ OC ₂ H ₄ OC ₂ H ₄)PO
C ₁₈ H ₄₀ O ₇ P ₂	bis(diethyl phosphono)methyl ether	[(C ₂ H ₅ O) ₂ POCH ₂] ₂ O
C ₁₈ H ₄₈ O ₂ P ₂	tetraethylammonium ethylenediphosphine oxide	(C ₂ H ₅) ₂ OP-(CH ₂) ₂ PO(C ₂ H ₅) ₂
C ₂₀ H ₄₄ O ₆ P ₂	bis-1,4-(diethyl phosphono)butane	[(C ₂ H ₅ O) ₂ PO-CH ₂ -CH ₂] ₂
C ₂₀ H ₄₄ O ₇ P ₂	bis-2,2'-(diethyl phosphono)ethyl ether	[(C ₂ H ₅ O) ₂ PO-C ₂ H ₄] ₂ O
C ₂₁ H ₄₈ O ₆ P ₂	bis-1,5-(diethyl phosphono)pentane	[(C ₂ H ₅ O) ₂ PO-C ₂ H ₄] ₂ CH ₂
C ₂₂ H ₄₈ O ₃ P	bis(2-ethylhexyl)N,N diisopropylphosphoric amide	(C ₈ H ₁₇ O) ₂ (C ₃ H ₇) ₂ NPO
C ₂₂ H ₄₈ O ₆ P ₂	bis-1,8-(diethyl phosphono)hexane	[(C ₂ H ₅ O) ₂ POC ₃ H ₆] ₂
C ₂₄ H ₃₆ O ₆ P ₂	bis-2,2'(butyl benzenephosphinico)ethyl ether	[(C ₄ H ₉ O)(C ₆ H ₅)POC ₂ H ₄] ₂ O
C ₂₄ H ₄₄ O ₆ P ₂	bis-1,4-(diethyl phosphonoethyl)benzene	(C ₂ H ₅ O) ₂ PO-CH ₂ -  -CH ₂ -PO(OC ₂ H ₅) ₂
C ₂₄ H ₄₉ O ₃ P ₂	bis(7-methyl-4-thioacetyl)"isooctene" phosphonate	(C ₅ H ₁₁ S-C ₃ H ₇ -O) ₂ (C ₈ H ₁₅)PO
C ₂₄ H ₄₉ O ₅ P	2-(diethyl phosphono)ethyl myristate	(C ₂ H ₅ O) ₂ PO(C ₂ H ₄ COOC ₁₃ H ₂₇)
C ₂₆ H ₅₂ O ₁₀ P ₂	bis [2-(diethyl phosphono)ethyl] adipate	[(C ₂ H ₅ O) ₂ POC ₂ H ₄ COOC ₂ H ₄] ₂
C ₂₆ H ₅₃ O ₃ P	bis(3,5,5-trimethylhexyl)"isooctene" phosphonate	(C ₉ H ₁₉ O) ₂ (C ₈ H ₁₅)PO
C ₃₇ H ₇₈ O ₄ P ₂	1,5-pentanediol di(bis-2-ethylhexane phosphinate)	[(C ₈ H ₁₇) ₂ PO-OC ₂ H ₄] ₂ CH ₂
C ₃₇ H ₇₈ O ₆ P ₂	1,5-pentanediol di(bis-2-ethylhexyl phosphate)	[(C ₈ H ₁₇ O) ₂ PO-OC ₂ H ₄] ₂ CH ₂

a) For Technical Report No. V (see also IV - Appendix C)