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FINAL REPORT

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WATER-BASE FIRE-RESISTANT HYDRAULIC FLUID FOR SUBMARINES

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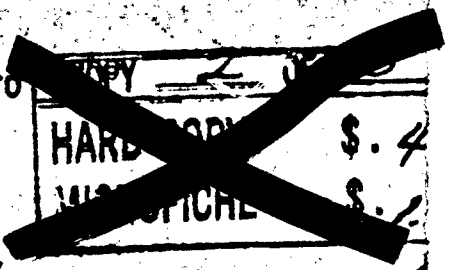
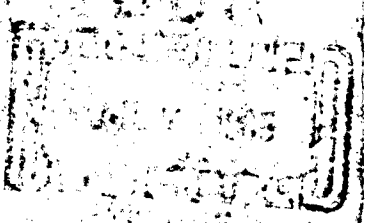


TO
BUREAU OF SHIPS
DEPARTMENT OF THE NAVY
WASHINGTON 25, D. C.



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ABSTRACT

Syntheses of over 40 phosphorus esters and ester salts and numerous intermediates are reported.

The ability of organic phosphorus electrolytes, as water-soluble pour-point depressants, to satisfy the tentative specifications of this contract is characterized by measurements and comparisons of solubility, flammability (AIT, Flash, Fire), hydrolytic stability, sonic shear stability, compatibility with commercial thickeners (35), sea water, paint, Buna N, and corrosivity to eight metal alloys. Some flammability property comparisons of phosphorus compounds with compounds containing boron, nitrogen and sulfur are made.

This study supports the premise that for the additive package of a water-base fluid to have an AIT >900°F., the thickener must also possess an AIT in the 900°F. range.

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I. INTRODUCTION

Serious surface shipboard explosions in 1953 and 1954, attributed to flammable hydraulic fluids, precipitated a research program by the Navy to develop fire-resistant hydraulic fluids. The program resulted in the development of water glycol-based hydraulic fluids for hydraulically operated catapults, and aryl phosphate ester-type fluids for elevator hydraulic systems, for which better load-carrying capacity was required. The adequate performance of the phosphate ester-type fluid in the elevator hydraulic systems of surface ships led to a strong effort to adapt the fluid to submarine use. After an extensive testing program by the Navy, an aryl phosphate ester fluid was employed on a submarine.

This installation of an aryl phosphate fluid on a submarine has now been withdrawn and replaced with flammable petroleum oils. The failure of MIL-H-19457 type fluids in submarine use, in spite of previous success in aircraft carriers, is attributable to the more complex and extensive hydraulic systems on submarines compared to the more localized, less complicated systems on the carriers. The multitude of devices and complex interconnecting systems on a submarine make total elimination of leakage practically impossible. This unavoidable leakage results in an intolerable housekeeping problem and is considered responsible for at least one steering and diving system failure [1,2] resulting from attack on electrical insulation by the fluid.

Moreover, the solvent and plasticizing ability of the phosphate fluids for certain gaskets and O-rings makes them difficult to contain in the hydraulic system, and the resultant spills cause deterioration of electrical insulation, paints, vinyl deck tile, soles of crewmen's shoes, etc. The need, therefore, for a fire-resistant hydraulic fluid that is more manageable and compatible

with insulation, paints, gaskets, etc., is strongly recognized by the Navy as a high-priority project.

To qualify for this urgent Navy application, a molecule must satisfy a myriad of parameters. It must meet simultaneously at least ten bounding properties; namely, specified viscosity; fire resistance; low vapor pressure; hydrolytic stability; compatibility with specific seals, gaskets, and sheathing; noncorrosivity; nontoxicity; and, in some degree, oxidation resistance.

In the contract work (1962-1964) to develop an organic base fire-resistant hydraulic fluid the Navy suggested certain guidance values for viscosity and fire resistance in addition to compatibility with paint and elastomers. The suggested guidance values were much improved in viscosity over MIL-H-19457 and were as follows:

	Viscosity, cs. at °F.		ASTM Slope	AIT	Micro Flash	
	28	150	100°-210°F.	°F.	°F.	Density
Suggested Guidance Values	868	25-31	∿0.65	>1000	>500	ca. 1.6 (max.)
MIL-H-19457	3500	13	0.97	1045	500	

In the period 1962-1964 the Bureau of Ships sponsored six contracts for the development of an organic base fire-resistant hydraulic fluid. These contracts were with Olin-Mathieson Chemical Corporation [3], Monsanto Research Corporation [4], Stanford Research Institute [5] and I. I. T. Research Institute [6].

The major research effort in all of these contracts was directed toward the development of molecules containing a high percentage of fluorine. In Monsanto Research Corporation's two contracts, the fluorine content was considered critical if the organic base fluid was to be compatible with alkyd base paint and elastomers such as

Buna N, neoprene and polyvinyl chloride. As a result of the first year's contract (NObs 86749) effort in which five chemical classes were investigated, the polyfluoroalkyl-substituted aryl phosphates and polyfluoroalkyl-substituted aryl alkyl phosphonates appeared to afford the optimum potential for the development of a fire-resistant hydraulic fluid base stock for submarine use. In the second year's effort (NObs 90095), phosphoramidate compounds were synthesized that possess properties superior to the currently available MIL-H-19457 fluid (trixylyl phosphate). For example, phenyl 1H,1H,7H-dodecafluoroheptyl N-methyl-N-(2-cyanoethyl)-phosphoramidate (Cpd. 512) and 3-trifluorophenyl 1H,1H,7H-dodeca-fluoroheptyl N-methyl-N-(2-cyanoethyl)phosphoramidate (Cpd. 515) have better ASTM slopes and far superior paint and elastomer compatibility, while retaining comparable fire resistance.

	Viscosity, cs., °F.		ASTM	AIT	Micro Flash,	Micro Fire,
	28	150	Slope	°F.	°F.	°F.
Cpd. 512	4000	22.8	0.89	1020	532	No fire to 671
Cpd. 515	4600	24.0	0.89	1005	511	No fire to 662
Guidance Values	868	25-31	~0.65	>1000	>500	-

These molecules, although superior to MIL-H-19457, do not satisfy the suggested viscosity guidance values and they are relatively expensive to produce, as are all organic molecules containing a high percentage of fluorine.

Therefore, the broad objective of this Water Base Hydraulic Fluid Program (Contract NObs 90270) is the development of a hydraulic fluid in which the nonaqueous phase is fire resistant. Hopefully, such a fluid should be more economical to produce than the organic-based fluids described above and the viscosity guidance values more

readily met by the use of appropriate thickeners.

To have the nonaqueous phase fire-resistant is important in systems operating at 5000 psi where the aqueous phase in certain segments of the system may, under certain circumstances, evaporate, thereby leaving a hazardous explosive residue or where spray leaks may develop explosive flammable residues to ignition sources.

Presumably a water base fluid would contain 30% or more of water, a pour point depressant, a thickener to obtain the desired viscosity, and corrosion inhibitors. Specifications for the most part are the same as that of the organic base fluid except that the AIT is specified as greater than 900°F., pour point 0°F. (maximum), with stability to -20°F. and compatible with 10% sea water.

Here again, we believe that a water-soluble organic molecule as a pour point depressant must contain either halogen or phosphorus or both with a minimum of aliphatic content to possess a high degree of fire resistance. Also, unless the thickener has an AIT of >900°F. the pour point depressant must be above this value.

In this contract the greatest amount of synthesis effort was in the search for a pour point depressant with a 900°F. AIT or better although a great number of commercial thickeners were investigated and some corrosion studies were made.

II. SUMMARY

Synthesis was essentially confined to water-soluble phosphorus c pounds in a search for a pour point depressant with an AIT of 90 or better.

In the broad class of organic phosphorus acid salts, the dialkyl potassium phosphates, alkyl potassium alkylphosphonates and potassium dialkylphosphinates in concentrations of 30-40%, all produce freezing points of -20°F. or better. These compounds po essed AIT's in the 850°F. range.

The monopotassium aroylated phosphorus compounds, as exemplified by potassium alkyl arylphosphonates, potassium aroxyalkyl phos- phates, and potassium diaryl phosphates, although somewhat highe in AIT than the above alkyl compounds (850°F.) do not possess sufficient useful solubility.

Dipotassium alkyl phosphates and dipotassium alkyl- and aryl- phosphonates have much higher AIT's than the monopotassium salts of close analogs, but were eliminated because of their severe attack on copper and aluminum.

Triesters of phosphoric acid, diesters of phosphonic acid and th aryl esters of either acid were not used as depressants because of their hydrolytic instability. The alkali dialkyl phosphates and alkali alkyl alkylphosphonates and the dialkali alkyl phosph all pass the "coke bottle" hydrolysis test. However, in this te the dipotassium alkyl phosphates and alkylphosphonates show seve attack on copper.

All of the phosphates, phosphonates and phosphinates (40% soluti are compatible with sea water.

Dipotassium alkylphosphonates show severe attack on aluminum. Potassium dialkyl phosphates showed no attack on aluminum on heating at 200°F. for two weeks.

A series of compatibility tests were run on eight specified alloys using a phosphate, phosphinate and phosphonate as depressants in a tentative water base fluid formulation heated 48 hrs. at 200°F. The monopotassium salts of the ethyl analogs were used since they were previously shown to be less corrosive to metals and more compatible with certain thickeners.

Some general conclusions on the corrosivity of the three formulations toward metals can be drawn from these data: (1) the silver base, nickel-copper and aluminum alloys were not attacked by any of the three formulations; (2) copper and copper alloys with a high percentage of copper acquired a heavy tarnish in the vapor phase indicating a need for a vapor phase inhibitor with these materials; (3) the phosphonate and phosphinate formulations attacked copper alloys more severely than the phosphate formulation; (4) the phosphate formulation appeared to attack steel alloys the most severely of the three formulations with the phosphinate formulation showing no attack.

Aqueous solutions (40%) of alkali alkyl phosphorus compounds soften paint sufficiently so that it can be scratched with the finger nail while wet. On drying, there appears to be little if any paint damage.

Potassium diethyl phosphate was the pour point depressant of choice because of its solubility, hydrolytic stability, better average compatibility properties, cost, and its AIT approached 900°F. (850°F.).

The generic classes of thickeners tested were the polyvinyl alcohols, polyethylene oxides, polyethylenimine, polyacrylates, polyvinylpyrrolidone, guar gum, polyoxypropylene-polyoxyethylene copolymers,

ethylene diamine/polyoxypropylene/polyoxyethylene copolymers, and hydroxyethylcellulose.

The Elvanols (polyvinyl alcohol) and Acrysols (polyacrylates) wer eliminated because of gellation by electrolytes; the PVP-series (polyvinylpyrrolidone) is hydrolyzed by alkali; the Jaguars (guar gum), being natural products, would be subject to bacterial degra tion; the Pluronics (polyoxypropylene/polyoxyethylene copolymers) and the Tetronics (ethylenediamine/polyoxypropylene/polyoxyethyle copolymers) formed stable foams; the Q-P series (Cellosizes; hydroxyethylcelluloses) were pituitous and did not dissolve completely.

The polyethylene oxide polymer class of thickeners was the most c patible with the potassium diethyl phosphate and specifically the WSR N-series was considered the most promising because of complet water-solubility, and superior viscosity-temperature properties.

A tentative water-base fluid formulation containing potassium diethyl phosphate as the depressant (39.1%) and Ucar Polyox resin WSR N-80 (5.85%; average m.w. 175,000-200,000) as a thickener, exhibited very poor sonic shear stability. This sonic shear instabi ity at this molecular weight was not unexpected and suggests a low molecular weight thickener such as WSR N-10 in a higher percentage but with a concomitant greater detrimental effect on AIT.

The attack on Buna N of the tentative water-base fluid described above was tremendously improved over MIL-H-19457 but slightly inferior to BuShips 2110-H. This small inferiority to 2110-H could probably be corrected by additives.

This study supports the premise that for the additive package of a water-base fluid to have an AIT of >900°F. the thickener must also possess an AIT in the 900°F. range. To improve shear stability of the thickener, the molecular size must be kept to a minimum

and therefore a higher concentration is required which further indicates a need for fire-resistance in the thickener.

III. PHYSICAL TESTING

The suggested, tentative specifications for a water-base hydraul fluid, in which the non-aqueous phase is fire-resistant, are: AIT >900°F.; flash point >450°F.; fire point >550°F. The non-aqueous phases of currently-used, water-base hydraulic fluids consist of two major components: (a) a flammable pour point depressant, to meet the low temperature specifications; and (b) a flammable polymeric thickener, to meet the viscosity specifications [7].

Therefore, for the non-aqueous phase of a water-base hydraulic fluid to be fire resistant (AIT >900°F.) the pour point depressa must possess sufficient AIT to compensate for any lowering from additives and/or the thickener must be fire-resistant. Initiall it appeared that the best approach was to use a commercially ava able flammable polymeric thickener in conjunction with a non-fla mable freezing point depressant.

The lower alkyl potassium phosphorus ester-salts were investigat first as non-flammable pour point depressants because of their high solubility, and hopefully, a fire resistance of 900°F. or above. Flammability data on a variety of alkyl and/or aryl potassium phosphorus ester-salts are listed in Table I.

Table II gives the flammability data on blends of commercially a able thickeners and alkyl and/or aryl potassium phosphorus ester salts.

Table III contains flammability data on miscellaneous compounds, including boron and nitrogen-containing compounds, which were te in the program.

A. FLAMMABILITY PROPERTIES

1. PHOSPHORUS COMPOUNDS (Table I)

To possess an AIT appreciably above 900°F. (Table I), two broad generalizations on molecular structure can be made regarding phosphates and phosphonates: (a) an organic phosphate can contain no alkyl moiety (compare Cpds. 25, 26, 27 and 28 with 39, 1 and 9), and (b) an aromatic phosphonate or lower alkyl phosphonate and their salts can contain no alkyl ester groups (compare Cpds. 33, 35 and 39). Several water-soluble compounds (Cpds. 10, 20, 30, 33 and 39) had AIT's which approached or slightly exceeded 900°F., but they offer little advantage economically over diethyl potassium phosphate (Cpd. 3). It is noteworthy that the AIT's of the ethyl and methylphosphonic acids (compare Cpds. 30 and 31, 34 and 35), were materially increased on conversion to the dipotassium salts.

The AIT of an alkali dialkyl phosphate can be raised by admixing with a phosphate which has a much higher AIT (see Cpds. 3, 27, 49, 50 and 51). However, the fire point of the mixture is considerably below that of the compound with the lowest fire point. If one compares Compounds 51, 52, 53 and 54, it appears that the AIT of certain blends is raised by the addition of water.

Incorporation of stabilized aliphatic halogen into an alicyclic phosphate failed to raise the AIT significantly (compare Cpds. 15 and 16).

The introduction of two beta α-pyridyl groups into diethyl potassium phosphate did not alter the AIT (compare Cpds. 3 and 24); two beta phenoxy groups (Cpd. 20) and presumably two phenyl groups (Cpd. 18) raised the AIT 40-50°F.

Table I

PHOSPHORUS COMPOUNDS

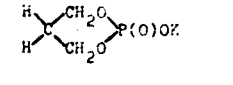
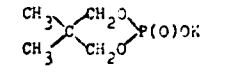
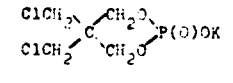
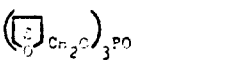
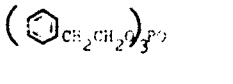
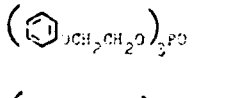
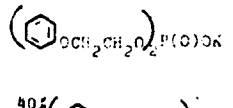
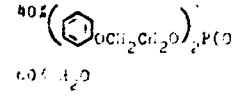
Compound No.	MRC No.	Compound	AIT °F.	AIT Time Lag Sec.	Micro Flash, °F.	Micro Fire, °F.
1	437	$(C_2H_5O)_3PO$	840	5	-	-
2	481	$(ClCH_2CH_2O)_3PO$	850	3	518	608
3	468	$(C_2H_5O)_2P(O)OK$	850	7	547	676
4	-	40% $(C_2H_5O)_2P(O)OK$, 60% H_2O	850	40	-	-
5	441	$(C_2H_5O)_2P(O)ONa$	830	9	493	608
6	502	$(C_2H_5O)_2P(S)OK$	535	47	-	-
7	488	$C_2H_5OP(O)(OK)_2$	880	24	NO	No fire 75
8	455	$(CH_3O)_3PO$	725	13	-	-
9	484	$(CH_3O)_2P(O)OK$	845	25	522	No fire 75
10	443	$CH_3OP(O)(OK)_2$	925	18	-	-
11	668	$(HOCH_2CH_2OCH_2CH_2O)_2P(O)OK$	730	12	-	-
14	727		750	33	-	-
15	493		800	10	-	-
16	640		845	13	-	-
17	637		600	12	-	-
18	674		800	10	-	-
19	678		920	14	-	-
20	691		900	22	-	-
21	-	40%  , 60% H_2O	900	22	-	-

Table I, Continued

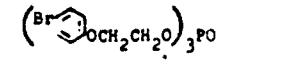
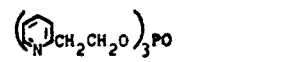
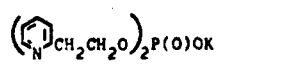
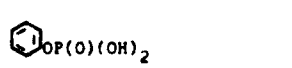
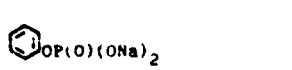
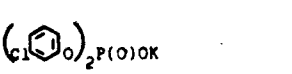
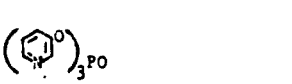
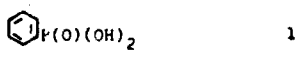
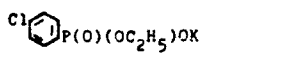
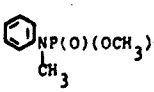
Compound No.	MRC No.	Compound	AIT °F.	AIT Time Lag Sec.	Micro Flash, °F.	Micro Fire, °F.
22	680		825	11	-	-
23	676		850	7	-	-
24	692		855	21	-	-
25	433		1165	4	370	No fire 682
26	634		1150	8	-	-
27	591		1270	5	NO	No fire 752
28	677		1200	5	-	-
29	486	$C_2H_5P(O)(OC_2H_5)OK$	860	14	590	No fire 752
30	476	$C_2H_5P(O)(OH)_2$	910	2	750	No fire 752
31	490	$C_2H_5P(O)(OK)_2$	1040	19	NO	No fire 752
32	467	$CH_3P(O)(OCH_3)_2$	700	22	-	-
33	485	$CH_3P(O)(OCH_3)OK$	890	15	707	No fire 752
34	487	$CH_3P(O)(OH)_2$	1075	4	-	-
35	489	$CH_3P(O)(OK)_2$	1180	17	NO	No fire 752
36	444	$NCCH_2CH_2P(O)(OCH_2CH_2Cl)_2$	805	5	507	No fire 581
37	447	$CH_2=CHP(O)(OCH_2CH_2Cl)_2$	745	6	-	-
38	651		1175	14	-	-
39	631		895	27	-	-
40	749	$(CH_3)_2P(O)OH$	825	18	-	-
41	434		1160	4	594	No fire 743
42	438	$(HOCH_2)_3PO$	625	4	464	500
43	423	$[(CH_3)_2N]_3PO$	485	9	265	360
44	462	$[(CH_3)_2N]_2P(O)OCH_3$	495	5	-	-

Table I, Continued

Compound No.	MRC No.	Compound	AIT °F.	AIT Time Lag Sec.	Micro Flash, °F.	Micro Fire, °F.
45	460	$(CH_3)_2NP(O)(OCH_3)_2$	500	10	-	-
46	739	$H_2NP(O)(OCH_3)_2$	640	10	-	-
47	766		820	27	-	-
48	481	$(CH_3)_2NP(O)(OC_6H_4Cl)OK$	820	22	-	-
49	619	35% $(C_2H_5O)_2P(O)OK$ 65% $(ClC_6H_4O)_2P(O)OK$	1015	9	541	563
50	620	50% $(C_2H_5O)_2P(O)OK$ 50% $(ClC_6H_4O)_2P(O)OK$	995	15	543	567
51	625	65% $(C_2H_5O)_2P(O)OK$ 35% $(ClC_6H_4O)_2P(O)OK$	925	25	505	550
52	743	20% $(C_2H_5O)_2P(O)OK$ 10% $ClC_6H_4P(O)(OC_2H_5)OK$ 70% H_2O	950	45	-	-
53	744	20% $(C_2H_5O)_2P(O)OK$ 10% $(ClC_6H_4O)_2P(O)OK$ 70% H_2O	1215	7	-	-
54	745	20% $(C_2H_5O)_2P(O)OK$ 10% $(CH_3)_2NP(O)(OC_6H_4Cl)OK$ 70% H_2O	950	22	-	-
55	753	$(CH_3)_2P(O)OK$	1075	34	-	-

Replacement in a dialkyl potassium phosphate of an alkyl group by a secondary amido group appreciably lowers the AIT (compare Cpds. 3, and 43 thru 48, inclusive).

2. PRELIMINARY BLENDS OF PHOSPHORUS COMPOUNDS WITH REPRESENTATIVE COMMERCIAL THICKENERS (Table II)

Flammability properties of some preliminary blends of commercial thickeners and ester potassium phosphorus salts are described in Table II. The data represents an attempt to gain insight into the concentration effect of various types of flammable thickeners on the AIT of diethyl potassium phosphate. Diethyl potassium phosphate was chosen as a model compound because its AIT approached 900°F., and it could be readily and cheaply synthesized. In general, the polymer concentration, rather than the chemical constitution, appears to have the greater effect on the flammability properties of the blends of commercial thickeners.

The poor flammability properties of thickeners synthesized from the lower polyglycols and phosphorus oxychloride were discouraging (mixtures 14, 15 and 16). This suggests that for the phosphorus to be effective in imparting fire resistance to a phosphorus-containing thickener, a critical ratio of phosphorus to aliphatic content must not be exceeded.

The data in Table II further points up a definite need for a fire-resistant thickener if an AIT >900°F. is to be realized in the presence of an appreciable concentration of thickener. The desirable phosphorus-containing pour point depressants tested (Tables I and II) do not have an AIT sufficient to compensate for the lowering by flammable thickeners. Such fire-resistant thickeners would require a synthesis study, since none are available commercially.

Table II

FLAMMABILITY PROPERTIES OF PRELIMINARY BLENDS OF PHOSPHORUS COMPOUNDS AND WATER-SOLUBLE POLYMERIC THICKENERS

Mixture No.	MRC No.	Composition, %	Mixture	AIT °F.	AIT Time Lag, Sec.	Viscosity, cs., °F. 28°	Viscosity, cs., °F. 150°
1	662	56.5 7.5 36.0	$(C_2H_5O)_2P(O)OK$ Gelvatol 20-30[a] H_2O	845	49		
2	666	39.8 45.3 15.1	$(C_2H_5O)_2P(O)OK$ Carbowax 600[b] H_2O	780	10	820	18.5
3	756	40.0 40.0 20.0	$(CH_3)_2P(O)OH$ Carbowax 600 H_2O	820	3		
4	759	36.1 27.1 9.1 27.7	$(C_2H_5O)_2P(O)OK$ Carbowax 4000[c] Urea H_2O	<<900	(2)		
5	748	34.1 9.8 2.4 53.7	$(C_2H_5O)_2P(O)OK$  QP-3[d] H_2O	860	32		
6	682	40.6 0.5 58.9	$(C_2H_5O)_2P(O)OK$ WP-4400 H_2O	850	47		
7	731	40.7 0.5 58.8	$(CH_3O)_2P(O)OK$ WP-4400 H_2O	870	63		
8	689	39.0 2.4 58.5	$(C_2H_5O)_2P(O)OK$ WSR-205[e] H_2O	845	9		
9	675	37.2 3.0 2.9 56.9	$(C_2H_5O)_2P(O)OK$ WSR-205 $Co(OOCCH_3)_2$ H_2O	860	64		
10	764	40.1 3.5 56.4	$(C_2H_5O)_2P(O)OK$ WSR N-750[f] H_2O	865	36		
11	765	39.2 1.8 59.0	$(CH_3O)_2P(O)OK$ WSR N-750 H_2O	905	25		
12	767	39.4 3.5 2.6 54.5	$(C_2H_5O)_2P(O)OK$ WSR N-750 PEI[g] H_2O	890	32		
13	768	39.4 2.7 5.1 52.8	$(C_2H_5O)_2P(O)OK$ WSR N-750 PEI H_2O	890	47		

Table II, Continued

Mixture No.	MRC No.	Composition, %	Mixture	AIT °F.	AIT Time Lag, Sec.	Viscosity, cs., °F. 25°	Viscosity, cs., °F. 150°
14	679	Neat	Partially hydrolyzed (KOH) 2 $CH_3OP(=O)Cl_2$/3$HOCH_2CH_2OCH_2)_2$ reaction product	575	24		
15	672	Neat	Partially hydrolyzed (KOH) 3$(HOCH_2CH_2OCH_2CH_2)_2O$/2 $POCl_3$ reaction product	750	44		
16	668	Neat	Partially hydrolyzed (KOH) excess $HOCH_2CH_2OCH_2CH_2OH$/$POCl_3$ reaction product	730	12		

Notes:

[a] Polyvinyl alcohol containing ~20% residual polyvinyl acetate;

[b] Polyethylene glycol; number average molecular weight 600;

[c] Polyethylene glycol; number average molecular weight 4000;

[d] Hydroxyethyl cellulose; low viscosity;

[e] Polyethylene oxide; high molecular weight;

[f] Polyethylene oxide; high molecular weight;

[g] Polyethyleneimine.

3. MISCELLANEOUS COMPOUNDS (Table III)

Table III lists the flammability properties of compounds of elements other than phosphorus, such as boron, nitrogen and sulf which elements have a negative flame coefficient and thus should impart fire resistance.

From the data it appears that neither organoboron nor organic nitrogen compounds possess fire resistance equal to organic phosphorus compounds. For example: (a) phenylboronic acid (Cpd 6) has an AIT 400°F. lower than that of phenylphosphonic acid (C 7); (b) triethanolamine borate (Cpd. 4), a compound containing both boron and nitrogen, has an AIT over 200°F. lower than triet phosphate (Cpd. 5), and 65-100°F. lower than a glycol (Cpds. 1 a 2); (c) methylphosphonic acid appears to be about equal to bori acid in imparting fire resistance to triethanolamine as shown by the AIT (see mixtures 10 and 11). However, methylphosphonic aci has the advantage of being infinitely more water-soluble than boric acid which is eliminated as a pour point depressant becaus of its low solubility.

Incorporation of sulfur as a sulfonic acid in an aromatic molecu raised the AIT by 55°F. (compare Cpds. 8 and 9). The utility as a pour point depressant of this class from the corrosivity and s bility properties has not been investigated. Polyglycols such a Ucon Hydrolube CP-150 are not promising thickeners for use with diethyl potassium phosphate because of their low contribution to solution viscosity and their lowering of the AIT (see Cpds. 12 a 13). The AIT of boric acid, 10% in polyglycol 2000, was too low to be of any interest (Cpd. 14).

Compounds 15 illustrates that the aliphatic portion of any molec must be kept to a minimum if the AIT is to be above 900°F.

Table III

FLAMMABILITY PROPERTIES OF MISCELLANEOUS MATERIALS

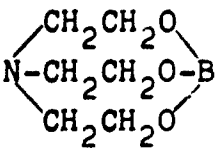
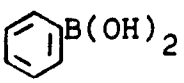
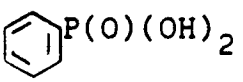
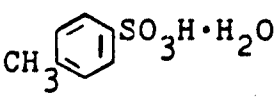
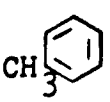
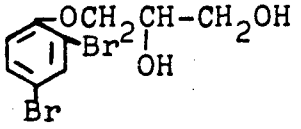
Compound or Mixture No.	MRC No.	Composition, %	Compound or Mixture	AIT °F.	AIT Time Lag, Sec.
1	650	-	$(HOCH_2CH_2OCH_2CH_2)_2O$	690	5
2	648	-	Polyglycol P-2000	725	4
3	645	-	$(HOCH_2CH_2)_3N$	610	26
4	224	-		625	8
5	437	-	$(C_2H_5O)_3PO$	840	5
6	681	-		775	7
7	651	-		1175	14
8	752	-		1085	19
9	687	-		1030	60
10	646	40.0 (15.0 $CH_3P(O)(OH)_2$; 25.0 $(HOCH_2CH_2)_3N$)	60.0 H_2O	750	4

Table III, Continued

Compound or Mixture No.	MRC No.	Composition, %	Compound or Mixture	AIT °F.	AIT Time Lag, Sec.
11	644	16.0	H_3BO_3	750	26
		55.0			
		39.0	$(HOCH_2CH_2)_3N$		
		45.0	H_2O		
12	702	-	Ucon Hydrolube CP-150	830	45
13	703	40.0	$(C_2H_5O)_2P(O)OK$	820	8
		60.0	Ucon Hydrolube CP-150		
14	649	10.0	H_3BO_3	715	37
		90.0	Polyglycol P-2000		
15	497	-		775	70

B. VISCOSITY AND ELECTROLYTE COMPATIBILITY STUDIES

The proposed tentative specifications for viscosity are 850 cs. (maximum) at 28°F. and 25-31 cs. at 150°F. These values correspond to an ASTM slope (~0.61) which is equivalent to a currently-used glycol-water base hydraulic fluid (MIL-H-22072; ASTM slope 0.63).

The proposed viscosity-temperature properties cannot be achieved in a water-base fluid without a thickener. It seemed advantageous to first qualitatively determine the viscosity properties, solubility characteristics, thickening ability, foaming and gelling tendencies, pituitousness and electrolyte compatibility on a number of commercially available, water-soluble thickeners. The results are shown in Table IV.

The thickeners which appeared most promising in the preliminary screening were then further evaluated in blends containing electrolytes and other additives, with emphasis on viscosity properties. The data are given in Table V.

1. WATER-SOLUBLE POLYMERS (Table IV)

Preliminary observations on aqueous solutions of a number of commercial thickeners are shown in Table IV.

The viscosity appraisals in this initial screening were made by visual comparisons with mixture 32 (MRC 666). On this screening test, the three most promising thickener candidates were: the Gelvatols, (polyvinyl alcohol/polyvinyl acetate copolymers, mixtures 1 to 4, inclusive); the WSR N-polymers (polyethylene oxides, mixtures 29 and 30); PEI (polyethylenimine, mixture 31). Of these three types, the WSR N-series was the most promising because of complete water-solubility and superior viscosity-temperature properties. PEI was of interest for comparison with the polyoxy-

Table IV

PROPERTIES OF AQUEOUS SOLUTIONS OF WATER-SOLUBLE POLYMERS

Mixture No.	MRC No.	Mixture	Parts by Weight, g.	Composition, %	Viscosity, cs., 28°F.	Remarks
1	654	Gelvatol 1-60[a] H_2O	8 192	4 96	74.0	
2	655	Gelvatol 20-30[b] H_2O	8 192	4 96	11.2	
3	656	Gelvatol 1-30[c] H_2O	8 192	4 96	8.80	
4	657	Gelvatol 20-30 H_2O	19 81	19 81	1390	
5	-	Elvanol (Med. Vis.; type A)[d] H_2O	0.25 4.75	5 95	87	Gelled with alk potassium phosp solution.
6	-	Elvanol (Med. Vis.; type A) H_2O	0.5 4.5	10 90	2008	Viscosity too h tended to gel p se.
7	-	PVP (Type NP-K20)[e] H_2O	0.5 4.5	10 90	-	
8	-	PVP (Type NP-K20) H_2O	1.0 4.0	20 80	-	
9	-	PVP (Type NP-K20) H_2O	1.50 3.50	30 70	59.10	Molecular weig this PVP too lo
10	-	Acrysol ASE-60[f] H_2O	0.005 27.995	-	-	Viscosity too l
11	700	Acrysol ASE-60 H_2O	0.019 28.0	0.01 99.99	-	Viscosity too l
12	701	Acrysol ASE-60 H_2O	0.287 24.8	1.15 98.85	-	Precipitated on ing alkyl potas phosphate.
13	-	Jaguar 806[g] H_2O	0.05 10.00	0.50 99.5	-	Not completely soluble.
14	-	Jaguar 807 H_2O	0.26 10.00	2.60 97.4	-	Considerable un solved material
15	-	Jaguar 807 H_2O	0.065 10.00	0.65 99.35	-	Solids precipit
16	-	Jaguar 808 H_2O	0.56 10.00	5.60 94.4	-	Viscosity too h
17	-	Jaguar 808 H_2O	0.28 10.00	2.80 97.2	-	Heavy gel-like cipitate came o on standing.
18	-	Jaguar J-2S-1[h] H_2O	0.01 10.00	0.01 99.99	-	Undissolved mat rial still pres
19	-	Jaguar A-20-D H_2O	0.015 10.00	0.015 99.98	-	Same as J-2S-1.
20	-	Pluronics P-88[i] H_2O	0.500 4.50	10.0 90.0	-	Formed stable f
21	-	Pluronics P-88 H_2O	1.00 4.00	20.0 80.0	-	Formed stable f
22	-	Pluronics P-88 H_2O	1.50 3.50	30.0 70.0	-	Formed stable f
23	-	Tetronic 701[j] H_2O	2.00 8.00	20.0 80.0	-	Added 1-ml (0.f stable foam for
24	-	Tetronic 908[k] H_2O	2.00 8.00	20.0 80.0	-	Added 1-ml (0.f foam broke - vi

Table IV, Continued

Mixture No.	MRC No.	Mixture	Parts by Weight, g.	Composition, %	Viscosity, cs., 28°F.	Remarks
25	-	QP-3 H_2O	0.500 4.50	10 90	-	Viscosity too high; contained undissolved solids.
26	-	QP-3 H_2O	0.150 4.85	3 97	-	Viscosity estimated correct; contained undissolved solids.
27	-	QP-300 H_2O	0.250 4.75	5 95	-	Viscosity too high; pituitous; not completely dissolved.
28	-	QP-300 H_2O	0.120 4.75	2.40 97.6	-	Pituitous; not completely dissolved.
29	-	WSR N-10 H_2O	1.00 9.00	10.0 90.0	-	Molecular weight too low; viscosity 9.8 cs. @ 150°F.
30	-	WSR N-750 H_2O	0.380 9.62	3.80 96.2	-	Molecular weight too high; viscosity 54 cs. @ 150°F.
31	-	PEI[1] H_2O	2.0 8.0	20.0 80.0	-	Molecular weight too low.
32	666	Carbowax 600 H_2O $(C_2H_5O)_2P(O)OK$	3.75 1.25 3.30	45.3 15.1 39.8	820 18.5 @ 150°F.	Viscosity at 150°F. somewhat low

Notes:

[a] Polyvinyl alcohol containing ~1% residual polyvinyl acetate; medium high molecular weight (Shawinigan Resin Corporation).

[b] Polyvinyl alcohol containing ~20% residual polyvinyl acetate (Shawinigan Resin Corporation).

[c] Polyvinyl alcohol containing ~1.5% residual polyvinyl acetate (Shawinigan Resin Corporation).

[d] Polyvinyl alcohol (du Pont).

[e] Polyvinylpyrrolidone, low molecular weight (General Aniline and Film).

[f] Acid-containing, crosslinked acrylic emulsion copolymer (Rohm and Haas Company).

[g] Guar gum (Stein, Hall and Company).

[h] Cationic Guar gum (Stein, Hall and Company).

[i] Polyoxypropylene base with polyoxyethylene end groups (Wyandotte Chemical Corporation).

[j] Polyoxypropylene-ethylenediamine with 10-20% polyoxyethylene (Wyandotte Chemical Corporation).

[k] Polyoxypropylene-ethylenediamine with 80-89% polyoxyethylene (Wyandotte Chemical Corporation).

[l] Polyethylenimine; molecular weight 30,000-40,000 (Cary Chemical Corporation).

ethylenes and the polyglycols as a polymeric nitrogen analog. The Gelyatols were of interest because of the C-C chain backbone which presumably would contribute to shear stability.

The Elvanols (polyvinyl alcohol) and Acrysols (polyacrylates) were eliminated because of gellation by electrolytes; the PVP-series (polyvinylpyrrolidone) is hydrolyzed by alkali; the Jaguars (guar gum), being natural products, would be subject to bacterial degradation; the Pluronics (polyoxypropylene/polyoxyethylene copolymers and the Tetronics (ethylenediamine/polyoxypropylene/polyoxyethylene copolymers) formed stable foams; the Q-P series (Cellosizes; hydroxyethyl celluloses) were pituitous and did not dissolve completely.

2. MIXTURES OF WATER-SOLUBLE POLYMERS AND PHOSPHORUS SALTS (Table V)

The most promising of the commercial thickeners was determined by preliminary screening in section 1 (Table IV). The compatibility of these candidate thickeners with aqueous ester phosphate salt solutions was then determined as the finished fluid must contain a high percentage of the fire-resistant pour point depressant in order to achieve the desired low temperature properties. Table V gives the viscosity and compatibility data on aqueous solutions of candidate polymeric thickeners in the presence of high concentrations of fire-resistant pour point depressant electrolytes. Diethyl and dimethyl potassium phosphates were chosen as the model electrolytes as a result of the properties previously discussed. This afforded some comparison of the compatibility of the ethyl and methyl homologs with various thickener types.

If a comparison is made of mixtures No. 14 and 15; 17, 18 and 20; 38 and 39 there appears to be a marginal difference in the compatibility of the methyl and ethyl analogs with the polyethylene oxid

Table V

PROPERTIES OF MIXTURES OF WATER-SOLUBLE POLYMERS AND PHOSPHORUS SALTS

Mixture No.	MHC No.	Mixture	Parts by Weight, g.	Composition, %	AIT °F.	Viscosity, cs., 28°F.	Viscosity, cs., 150°F.	Pour Point, °F.	Remarks
1	-	Acrysol GS[a] H_2O $(C_2H_5O)_2P(O)OK$	0.240 4.18 2.34	3.50 61.8 34.7	-	~230	30	-	Salted out at 28°F. - Value extrapolated.
2	658	Gelvatol 20-30[b] H_2O $(C_2H_5O)_2P(O)OK$	10.0 62.0 48.0	8.35 51.7 40.0	-	1740	-	~-40	Pour point sample gelled on warming.
3	662	Gelvatol 20-30 H_2O $(C_2H_5O)_2P(O)OK$	0.750 3.60 5.65	7.50 36.0 56.5	-	738	-	+15	710 cs. @ 28°F. after 24 hr. Pour point sample gelled on warming.
4	663	Gelvatol 1-30[c] H_2O $(C_2H_5O)_2P(O)OK$	0.750 3.60 5.65	7.50 36.0 56.5	-	Gelled	-	-	Made for comparison of Gelvatol 1-30 and 20-30 (662).
5	-	Gelvatol 1-30 H_2O $(CH_3)_2P(O)OK$ Urea	0.600 4.56 2.69 0.250	7.40 56.6 32.2 3.10	-	-	-	-	Mixture gelled at room temperature.
6	664	Carbowax 600[d] H_2O $(C_2H_5O)_2P(O)OK$	4.75 0.250 3.30	57.3 3.00 39.8	-	-	-	-	Carbowax crystallized from solution.
7	665	Carbowax 600 H_2O $(C_2H_5O)_2P(O)OK$	4.50 0.500 3.30	54.2 6.00 39.8	-	Gelled	-	-	-
8	666	Carbowax 600 H_2O $(C_2H_5O)_2P(O)OK$	3.75 1.25 3.30	45.3 15.1 39.8	780	820	18.5	-30	Viscosity at 150°F. somewhat low.
9	667	Carbowax 600 H_2O $(C_2H_5O)_2P(O)OK$	4.75 0.83 3.30	53.5 9.4 37.2	-	2640	-	-	-
10	-	Carbowax 6000[e] H_2O $(C_2H_5O)_2P(O)OK$	0.410 4.49 2.78	5.34 58.5 36.2	-	-	-	-	Thickening action not proportional to molecular weight.
1	755	Carbowax 600 H_2O $(CH_3)_2P(O)OK$	5.61 4.90 3.51	40.0 35.0 25.0	890	-	-	-	AIT too low.
2	756	Carbowax 600 H_2O $(CH_3)_2P(O)OK$	2.82 1.41 2.81	40.0 20.0 40.0	820	-	-	-	AIT too low.
3	-	Carbowax 600 Carbowax 1540 H_2O $(CH_3)_2P(O)OK$ $HOCH_2CH_2OH$	0.704 1.05 2.12 2.81 0.352	10.0 15.0 30.0 40.0 5.00	-	-	-	-	Mixture gelled on cooling; sterilized.
4	737	Carbowax 1500[f] H_2O $(C_2H_5O)_2P(O)OK$	3.75 2.27 4.00	37.5 22.7 40.0	-	394	-	-	Complete initial solution. Carbowax gradually crystallized from solution.
5	732	Carbowax 1500 H_2O $(CH_3O)_2P(O)OK$	4.00 2.53 3.75	36.5 24.6 38.9	-	-	-	-	Incomplete solution-precipitate increased on standing.

Table V, Continued

Mixture No.	MRC No.	Mixture	Parts by Weight, g.	Composition, %	AIT °F.	Viscosity, cs., 28°F.	Viscosity, cs., 150°F.	Pour Point, °F.	Remarks
16	-	Carbowax 1540[g] H_2O $(C_2H_5O)_2P(O)OK$	3.85 3.22 4.00	34.8 29.1 36.2	-	234	-	-	Solution remained clear.
17	733	Carbowax 4000[h] H_2O $(CH_3O)_2P(O)OK$	3.00 4.53 3.99	26.0 39.3 34.6	-	-	-	-	Incomplete solution; precipitate increased on standing.
18	736	Carbowax 4000 H_2O $(C_2H_5O)_2P(O)OK$	3.00 3.00 4.01	30.0 30.0 40.0	-	Cryst.	-	-	Complete initial solution. Carbowax gradually crystallized from solution.
19	-	Carbowax 4000 H_2O $(CH_3)_2P(O)OK$	4.20 6.30 3.51	30.0 45.0 25.0	-	-	-	-	Mixture solidified.
20	759	Carbowax 4000 H_2O $(C_2H_5O)_2P(O)OK$ Urea	3.00 3.06 4.00 1.01	27.1 27.7 36.1 9.10	-	350	-	-	Solution remained clear; diethyl phosphates more compatible than dimethyl phosphates (733).
21	-	Carbowax 4000 H_2O $(C_2H_5O)_2P(O)OK$ Urea	3.85 2.21 4.00 1.01	35.0 20.0 36.2 8.80	-	1450	34.0	-	Carbowax slowly crystallized from solution on standing.
22	-	Carbowax 4000 H_2O $(C_2H_5O)_2P(O)OK$ Urea	3.54 2.52 4.00 1.01	32.0 22.8 36.2 9.00	-	808	26.0	-35, s.c.	Mixture solidified on cooling.
23	-	Carbowax 6000[e] H_2O $(C_2H_5O)_2P(O)OK$	0.410 4.49 2.78	5.34 58.5 36.2	-	-	-	-	Viscosity too low.
24	-	Carbowax 6000 H_2O $(C_2H_5O)_2P(O)OK$	0.810 4.49 2.78	10.1 55.5 34.5	-	43.0	-	-	Viscosity too low.
25	-	Carbowax 6000 H_2O $(C_2H_5O)_2P(O)OK$	1.59 4.36 2.70	18.4 50.4 31.2	-	118	-	-	Viscosity too low.
26	-	Carbowax 6000 H_2O $(C_2H_5O)_2P(O)OK$	2.12 3.86 2.40	25.3 46.1 28.6	-	271.2	-	-	Viscosity too low, mixture remained clear.
27	695	Carbowax 6000 H_2O $(C_2H_5O)_2P(O)OK$	3.32 3.86 2.40	34.6 40.3 25.1	-	Gelled	-	-	Crystallized on standing.
28	-	Carbowax 6000 H_2O $(C_2H_5O)_2P(O)OK$	2.50 2.50 2.50	25.0 25.0 25.0	-	Gelled	-	-	Crystallized on standing.
29	696	Carbowax 6000 H_2O $(C_2H_5O)_2P(O)OK$	1.50 1.75 1.75	30.0 35.0 35.0	-	Gelled	-	-	Remained clear at room temperature.
30	694	Carbowax 6000 H_2O $(C_2H_5O)_2P(O)OK$	2.50 5.00 2.50	25.0 50.0 25.0	-	177	-	-	Mixture remained clear; viscosity too low.

Table V, Continued

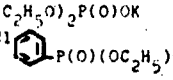
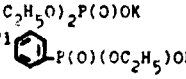
Mixture No.	MRC No.	Mixture	Parts by Weight, g.	Composition, %	AIT °F.	Viscosity, cs., 28°F.	Viscosity, cs., 150°F.	Pour Point, °F.	Remarks
31	-	Carbowax 6000 H_2O $(C_2H_5O)_2P(O)OK$ Urea	3.50 1.50 4.00 1.00	35.0 15.0 40.0 10.0	-	-	-	-	Mixture solidified.
32	-	Carbowax 6000 H_2O $(C_2H_5O)_2P(O)OK$ Urea	3.50 2.50 4.00 1.00	31.8 22.7 36.4 9.1	-	-	-	-	Mixture solidified.
33	747	QP-3[i] H_2O $(C_2H_5O)_2P(O)OK$ 	0.50 5.50 3.50 1.00	4.76 52.4 33.3 9.53	-	-	-	Cryst. -20	Viscosity too low.
34	748	QP-3 H_2O $(C_2H_5O)_2P(O)OK$ 	0.250 5.50 3.50 1.00	2.44 53.7 34.1 9.77	860	-	-	Cryst. -10	Cleared at 0°F.; no improvement in AIT over $(C_2H_5O)_2P(O)OK$
35	-	WP-300[j] H_2O $(C_2H_5O)_2P(O)OK$	0.19 3.60 2.50	3.02 57.2 39.8	-	-	-	-	Would not all dissolve.
36	-	WP-300 H_2O $(C_2H_5O)_2P(O)OK$	0.19 6.60 2.50	2.05 70.2 27.9	-	-	-	-	800 cs. at room temperature - dissolved with difficulty.
37	-	WP-300 H_2O $(C_2H_5O)_2P(O)OK$	0.07 3.60 2.50	1.13 58.3 40.5	-	-	-	-	Formed an insoluble ball.
38	731	WP-4400[k] H_2O $(CH_3O)_2P(O)OK$	0.031 3.619 2.500	0.5 58.8 40.7	870	-	-	-	Would not all dissolve.
39	-	WP-4400 H_2O $(C_2H_5O)_2P(O)OK$	0.19 3.60 2.50	3.02 57.2 39.8	-	-	-	-	All dissolved; Gelled at room temperature.
40	-	WP-4400 H_2O $(C_2H_5O)_2P(O)OK$	0.002 3.69 2.50	0.03 59.5 40.5	-	-	-	-	Viscosity too low.
41	-	WP-4400 H_2O $(C_2H_5O)_2P(O)OK$	0.004 3.69 2.50	0.064 59.6 40.4	-	-	-	-	Viscosity too low.
42	-	WP-4400 H_2O $(C_2H_5O)_2P(O)OK$	0.007 3.69 2.50	0.113 59.5 40.3	-	-	-	-	-
43	-	WP-4400 H_2O $(C_2H_5O)_2P(O)OK$	0.014 3.69 2.50	0.226 59.5 40.3	-	-	-	-	-
44	-	WP-4400 H_2O $(C_2H_5O)_2P(O)OK$	0.021 3.69 2.50	0.338 59.4 40.3	-	-	-	-	Viscosity too low.

Table V, Continued

Mixture No.	MRC No.	Mixture	Parts by Weight, g.	Composition, %	AIT °F.	Viscosity, cs., 210°F.	Viscosity, cs., 150°F.	Pour Point, °F.	Remarks
45	682	WP-4400 H_2O $(C_2H_5O)_2P(O)OK$	0.031 3.69 2.50	0.510 58.8 40.6	850	827	23.5	-	Molecular weight too high.
46	702	Ucon Hydrolube CP-150[l]	100	100	830	-	-	-	AIT low.
47	703	Ucon Hydrolube CP-150 $(C_2H_5O)_2P(O)OK$	4.36 2.91	60.0 40.0	820	214	-	-	Cannot attain sufficient viscosity or AIT.
48	-	WSR-35[m] H_2O $(C_2H_5O)_2P(O)OK$	0.400 4.55 3.06	5.00 56.8 38.2	-	-	-	-	Viscosity too high.
49	697	WSR-35 H_2O $(C_2H_5O)_2P(O)OK$	0.400 10.55 7.06	2.22 58.6 39.2	-	460	-	-	Viscosity too low; solids precipitated from solution.
50	-	WSR-35 H_2O $(C_2H_5O)_2P(O)OK$	0.350 5.49 3.89	3.60 56.4 40.0	-	-	-	-	Solids remained undissolved.
51	-	WSR-35 H_2O $(C_2H_5O)_2P(O)OK$ Urea	0.350 4.49 3.89 1.00	3.50 46.3 40.0 10.3	-	-	-	-	Solids remain undissolved.
52	-	WSR-205[n] H_2O $(C_2H_5O)_2P(O)OK$	0.363 6.000 4.000	3.51 57.9 38.6	-	1734	-	-	Molecular weight too high.
53	-	WSR-205 H_2O $(C_2H_5O)_2P(O)OK$	0.255 4.820 3.212	3.08 58.2 38.8	-	1260	-	-	-
54	-	WSR-205 H_2O $(C_2H_5O)_2P(O)OK$	0.234 4.783 3.186	2.86 58.3 38.9	-	990	-	-	Solids settled causing viscosity lowering.
55	-	WSR-205 H_2O $(C_2H_5O)_2P(O)OK$	0.05 6.00 4.00	0.50 59.7 39.8	-	36	-	-	Viscosity too
56	689	WSR-205 H_2O $(C_2H_5O)_2P(O)OK$	0.25 6.00 4.00	2.40 58.5 39.0	845	733	-	-	Made by [illegible] of a pure solution. [illegible] after [illegible] n = 71
57	698	WSR-205 H_2O $(C_2H_5O)_2P(O)OK$	0.275 6.00 4.00	2.70 58.4 38.9	-	674	-	-	[illegible] Solids [illegible] after [illegible] n = 57
58	-	WSR-205 H_2O $(C_2H_5O)_2P(O)OK$	0.29 5.20 3.66	3.20 56.8 40.0	-	973.2	85	-	[illegible] pitting.
59	-	WSR-205 H_2O $(C_2H_5O)_2P(O)OK$ Urea	0.29 4.20 3.66 1.00	3.17 46.0 40.0 10.9	-	1648	-	-	Very pitting.
60	-	WSR-205 Cobalt-EDTA 11.7% aq. $(C_2H_5O)_2P(O)OK$	0.30 3.00 2.00	- - -	-	-	-	-	[illegible] [illegible] overnight.

Table V, Continued

Mixture No.	MRC No.	Mixture	Parts by Weight, g.	Composition, %	AIT °F.	Viscosity, cs., 28°F.	Viscosity, cs., 150°F.	Pour Point, °F.	Remarks
61	675	WSR-205 H_2O $(C_2H_5O)_2P(O)OK$ Cobalt Acetate	0.16 3.06 2.00 0.15	3.00 57.0 2.90 37.2	860	-	-	-	AIT not sufficiently improved.
62	-	WSR N-10[o] H_2O $(C_2H_5O)_2P(O)OK$	0.312 3.42 4.61	6.00 40.0 54.0	-	-	-	Cryst. -40	Poured at -30°F.; bubble formation interfered with determination of clear point.
63	-	WSR N-10 H_2O $(C_2H_5O)_2P(O)OK$	0.37 2.63 2.00	3.50 52.5 40.0	-	-	-	-	Solution cloudy, viscosity too low.
64	-	WSR N-750[p] H_2O $(C_2H_5O)_2P(O)OK$	0.190 2.31 3.32	3.27 39.7 57.1	-	400	18.8	-	-
65	-	WSR N-750 H_2O $(C_2H_5O)_2P(O)OK$	0.380 4.62 3.32	4.57 55.5 39.9	-	1244	115	-	-
66	764	WSR N-750 H_2O $(C_2H_5O)_2P(O)OK$	0.190 3.07 2.18	3.50 56.4 40.1	865	565	48	Cryst. -20	Cleared at 0°F.
67	-	WSR N-750 H_2O $(CH_3O)_2P(O)OK$	0.190 2.31 1.67	4.55 55.5 40.0	-	-	-	-	Added solid potassium salt to aqueous WSR N-750 solution; formed an insoluble gel.
68	-	WSR N-750 H_2O $(C_2H_5O)_2P(O)OK$	0.152 4.88 3.32	1.81 58.5 39.8	-	-	-	-	Added aqueous potassium salt to aqueous WSR N-750 solution; solution remained clear.
69	-	WSR N-750 H_2O $(CH_3)_2P(O)OK$	0.19 2.31 1.50	4.75 57.8 37.6	-	-	-	-	Phosphorus acid and WSR N-750 compatible; added caustic and insoluble ball formed.
70	-	WSR N-750 H_2O $(CH_3)_2P(O)OK$	0.08 1.65 1.21	2.62 56.2 41.2	-	-	-	-	Aqueous potassium salt added to solid WSR N-750; formed an insoluble ball.
71	-	WSR N-750 H_2O $(CH_3)_2P(O)OK$	0.08 2.37 1.05	2.30 67.8 30.2	-	-	-	-	Aqueous solution of potassium salt added to aqueous WSR N-750; formed insoluble gel.
72	-	PEI[q] H_2O $(C_2H_5O)_2P(O)OK$	0.50 4.50 3.33	6.00 54.0 40.0	-	-	-	-	Viscosity too low; molecular weight too low.
73	-	PEI WSR N-750 H_2O	0.05 0.076 2.02	2.32 3.53 94.5	-	-	-	-	Mixture partially; slight cloudiness.
74	767	PEI WSR N-750 H_2O $(C_2H_5O)_2P(O)OK$	0.050 0.068 1.062 0.767	2.57 3.49 54.8 39.4	890	-	-	-	Partial insolubility.

Table V, Continued

Mixture No.	MRC No.	Mixture	Parts by Weight, g.	Composition, %	AIT °F.	Viscosity, cs., 28°F.	Viscosity, cs., 150°F.	Pour Point, °F.	Remarks
75	768	PEI	0.100	5.14	890	-	-	-	Partial insolub
		WSR N-750	0.053	2.72					
		H_2O	1.027	52.8					
		$(C_2H_5O)_2P(O)OK$	0.767	39.4					
76	-	PEI	0.400	5.66	-	-	-	-	Partial insolub
		WSR N-750	0.190	2.69					
		H_2O	3.37	47.6					
		$(C_2H_5O)_2P(O)OK$	3.12	44.1					
77	-	PEI	0.400	5.27	-	-	-	-	Copper caused separation into two layers. Aqueous phase gradually becam blue.
		WSR N-750	0.190	2.50					
		H_2O	3.37	44.3					
		$(C_2H_5O)_2P(O)OK$	3.12	41.1					
		Mercaptobenzotniazole	0.016	2.10					
		Carbowax 600	0.500	6.58					
78	-	WSR N-80[r]	1.00	10.0	-	-	-	-	Viscosity too h ~800 cs. at 25°
		H_2O	9.00	90.0					
79	-	WSR N-80	0.375	4.50	-	248	22.0	-	Viscosity sligh low.
		H_2O	4.62	55.3					
		$(C_2H_5O)_2P(O)OK$	3.34	40.2					
80	-	WSR N-80	-	7.50	-	534	55.0	-	Viscosity sligr high; need ~6.(WSR N-80.
		H_2O	-	92.5					
81	772	WSR N-80	2.50	5.87	865	466	43.0	Cryst. -40	ASTM slope (100-210°F)=0.1
		H_2O	22.5	52.8					
		$(C_2H_5O)_2P(O)OK$	16.7	39.2					
		Renex 31	0.82	2.00					
		Mercaptobenzothiazole	0.08	0.20					
		KNO_2	0.04	0.10					
		K_3PO_4	0.01	0.025					

Notes:

[a] Sodium polyacrylate (Rohm and Haas Co.).

[b] Polyvinyl alcohol containing ~20% residual polyvinyl acetate (Shawinigan Resins Corp.).

[c] Polyvinyl alcohol containing ~1.5% residual polyvinyl acetate (Shawinigan Resins Corp.).

[d] Polyethylene glycol; number average molecular weight 600 (Union Carbide Corp.).

[e] Polyethylene glycol; number average molecular weight 4000 (Union Carbide Corp.).

[f] Polyethylene glycol; blend of equal parts carbowax 300 and 1540 (Union Carbide Corp.).

[g] Polyethylene glycol; number average molecular weight 1540 (Union Carbide Corp.).

[h] Polyethylene glycol; number average molecular weight 4000 (Union Carbide Corp.).

[i] Hydroxyethyl cellulose; low viscosity; fast dispersion grade (Union Carbide Corp.).

[j] Hydroxyethyl cellulose; medium viscosity (Union Carbide Corp.).

[k] Hydroxyethyl cellulose; medium high viscosity (Union Carbide Corp.).

[l] Fire-resistant hydraulic fluid (Union Carbide Corp.).

[m] High molecular weight polyethylene oxide; medium high viscosity (Union Carbide Corp.).

[n] High molecular weight polyethylene oxide, medium high viscosity (Union Carbide Corp.).

[o] Polyethylene oxide; molecular weight intermediate between the Carbowax series and WSR series (Union Carbide

[p] Polyethylene oxide; molecular weight lower than WSR-35, viscosity equivalent to WSR-35 (Union Carbide Corp.).

[q] Polyethylenimine, molecular weight 30,000-40,000 (Cary Chemical Corp.).

[r] Polyethylene oxide; number average molecular weight 175,000-200,000 (Union Carbide Corp.).

type thickeners. The ethyl analog is the more compatible probably due to a difference in water and/or glycol solubility, and therefore was preferred as a depressant over the methyl analog.

The dimethyl potassium phosphinate was of interest because of its high AIT. Although it was found incompatible with WSR N-750 thickener (mixtures 67, 70 and 71) and with Gelvatol 1-30 (mixture 5) it holds potential as a depressant for attainment of a water-base fluid with an AIT >900° provided a compatible thickener can be found.

The properties of the WSR N-series thickeners (mixtures 62-66 inclusive and 78-80 inclusive), in combination with diethyl potassium phosphate as a depressant, were superior to the other polymer thickener candidates. WSR N-80 (mixture 81), an intermediary member of the WSR N-series, was chosen as the thickener for a two-quart sample of a fire-resistant water base fluid.

Acrysol GS (sodium polyacrylate, mixture 1) was incompatible with the diethyl potassium phosphate at low temperatures; the Gelvatols polyvinyl alcohol/polyvinyl acetate copolymers, mixtures 2-5) formed a gel in the presence of the phosphate depressant.

The Carbowaxes, in general, are compatible with the diethyl potassium phosphate. However, with the higher molecular weight carbowaxes the concentration is critical and does not permit the incorporation of sufficient thickener to produce the desired viscosity. The lower molecular weight carbowaxes, such as Carbowax 600, require the incorporation of over 45% to approach the desired viscosity which in turn has an adverse affect on the AIT (mixture 8).

The QP-3 (hydroxyethyl cellulose, low viscosity) was compatible with combination of phosphate depressants (mixtures 33 and 34). Incorporation of the aromatic chlorine-containing phosphonate depressant

did not improve the AIT over the diethyl potassium phosphate. Th class of thickener is worthy of some further investigation.

WP-300 thickener, as evidenced by solubility and viscosity, has too high a molecular weight (mixtures 35, 36 and 37).

The molecular weights of WP-4400 and of WSR-35 also appear too high for a useful thickener (mixtures 38-45 inclusive, and mixtur 52-61 inclusive, respectively).

Solutions of WSR-205 (polyethylene oxide) were pituitous (mixture 52-61 inclusive).

From these data, WSR N-10 (mixtures 62 and 63) and WSR N-750 (mix tures 64, 65 and 66), both should be usable thickeners with dieth potassium phosphate, and WSR N-10 should be investigated further. However, we considered the molecular weight of WSR N-10 (75,000 - 100,000) somewhat low, thus requiring a sufficiently high concentration as to adversely affect the AIT. The WSR N-750 (m.w. ca. 350,000) is in the shear-instability range.

Polyethylenimine (PEI) appeared too low in molecular weight to be used alone, and as a cothickener with WSR N-750 it showed some partial insolubility. In addition, the solutions of PEI attacked copper.

Urea was added to some of the blends to prevent gellation due to hydrogen bonding, and to increase the solubility of the thickener (mixtures 5, 20-22, 32, 51 and 59) but it was ineffectual. Likewise, the addition of cobalt salts did not raise the AIT (mixture 60 and 61).

C. LOW TEMPERATURE PROPERTIES OF AQUEOUS SOLUTIONS OF PHOSPHORUS SALTS (Table VI)

The suggested tentative low-temperature specifications, in addition to viscosity, for a fire-resistant water base hydraulic fluid are: pour point 0°F. (maximum); stable to storage at -20°F. As previously mentioned in part A, these low-temperature properties cannot be achieved in a water base fluid solely by the use of a thickener but will require a freezing point depressant. To illustrate, 400 g. of ethanol, or 479 g. of ethylene glycol, or 1220 g. of a polyethylene glycol thickener [8], in 1000 g. of water, are required to give a freezing point of 0°F. The amount of a non-ionized material needed to produce a given freezing-point lowering, increases proportionately with molecular weight. The molecular size of a non-ionized molecule which can be used as a freezing point depressant is therefore limited.

Since lowering of the freezing point is dependent upon the number of particles in solution, it seemed that small highly-ionized molecules such as salts, should be investigated. Surprisingly, it was found that very few salts which are relatively non-corrosive, and impart fire resistance, have adequate solubility for use as fire-resistant freezing-point depressants.

Data on the broad class of phosphorus salts, some of which meets the freezing-point depressant specifications, are shown in Table VI. Potassium salts were used because of their greater solubility.

In concentrations of 30 to 40%, the dialkyl phosphates (methyl and ethyl), alkyl alkylphosphonates, alkylphosphonates and the dialkyl phosphinates all produce freezing points of -20°F. (Cpds. 1, 2, 3, and 15). No advantage was evident in the use of mixtures of pure salts (Cpds. 19 and 20).

Table VI

LOW TEMPERATURE PROPERTIES OF AQUEOUS SOLUTIONS OF PHOSPHORUS SALTS

Compound or Mixture No.	MRC No.	Mixture	Composition, %	Freezing Point, °F.	Melting Point, °F.	Solution Cleared, °F.	Storage Stability		Remarks
							Time	Appearance	
1	468	$(C_2H_5O)_2P(O)OK$	50.0	-60	-	-3[illegible]	-	-	-
			40.7	-20	-14	-	-	-	still supercool[illegible]
			40.0	-16	-18	-	5 days	clear	-
			40.7	-20	-14	-	-	-	pH 7.95; compatible with dem water.
			40.7	-20	-14	-	-	-	pH 9.10
			20.0	+20	-	+24	-	-	-
2	484	$(CH_3O)_2P(O)OK$	40.0	-24	-16	- 6	5 days	clear	Compatible with dem water
3	485	$CH_3P(O)(OCH_3)OK$	39.9	-34	-	-20	5 days	clear	Compatible with dem water
4	486	$C_2H_5P(O)(OC_2H_5)OK$	40.0	-36	-	-29	5 days	clear	Compatible with dem water
5	489	$CH_3P(O)(OK)_2$	40.0	-25	-16	-10	5 days	clear	Small amount insoluble with dem water.
6	490	$C_2H_5P(O)(OK)_2$	40.0	-28	-18	-12	5 days	clear	Compatible with dem water
			30.0	-15	-	- 4	-	-	
7	488	$C_2H_5OP(O)(OK)_2$	39.9	-30	-	-16	5 days	clear	Compatible with dem water
8	691	$\left(\bigcirc OCH_2CH_2O\right)_2P(O)OK$	40.0	+30	-	-	-	-	-
9	771	$\left(\bigcirc O\right)_2P(O)OK$	40.0	+59	-	-	-	-	-
10	750	$\left(\bigcirc\right)_2P(O)OK$	10.0	- 5	-	+ 5	-	-	-
		$(C_2H_5O)_2P(O)OK$	20.0						
11	751	$\left(\bigcirc\right)_2P(O)OK$	10.0	-15	-	+40	-	-	-
		$(C_2H_5O)_2P(O)OK$	30.0						
12	754	$(CH_3)_2P(O)OK$	10.0	+16	+18	+21	-	-	-
		$(C_2H_5O)_2P(O)OK$	10.0						
13	754-1	$(CH_3)_2P(O)OK$	8.90	0	+ 2	+ 5	-	-	-
		$(C_2H_5O)_2P(O)OK$	20.0						
14	-	$(CH_3)_2P(O)OK$	14.8	- 2	+ 2	+ 6	-	-	-
		$(C_2H_5O)_2P(O)OK$	20.4						
15	749	$(CH_3)_2P(O)OK$	19.5	+10	+12	+16	-	-	-
			33.8	<-20	-	-	-	-	-
16	746	$Cl\bigcirc P(O)(OC_2H_5)OK$	10.0	-10	- 6	0	-	-	-
		$(C_2H_5O)_2P(O)OK$	31.0						
17	743	$Cl\bigcirc P(O)(OC_2H_5)OK$	10.0	+10	+12	+14	-	-	-
		$(C_2H_5O)_2P(O)OK$	20.0						
18	-	$(CH_3)_2P(O)OLi$	40.0	-	-	-	-	-	Still precipitate after solution.
19	-	$C_2H_5P(O)(OK)_2$	20						
		$C_2H_5P(O)(OC_2H_5)OK$	20	-28	-18	-	-	-	-
		H_2O	60						
20	-	$CH_3P(O)(OK)_2$	20						
		$C_2H_5P(O)(OK)_2$	20	-25	-16	-13	-	-	-
		H_2O	60						
21	-	$C\bigcirc P(O)(OC_2H_5)OK$	40	+10	+1[illegible]	-	-	-	

otassium alkyl arylphosphonate, potassium aroxyalkyl phosphate and otassium diaryl phosphates did not have sufficient solubility for se as freezing-point depressants (Cpds. 8, 9 and 21).

ixtures of potassium aryl and potassium alkyl phosphorus esters howed no improvement over the alkyl esters (Cpds. 10, 11, 16 and 7).

t is noteworthy that a 40% solution of a lithium salt could not e obtained (Cpd. 18).

. HYDROLYTIC STABILITY (Tables VII and VIII)

Hydrolytic stability is an important property of a water base ydraulic fluid. The non-aqueous phase of the water base fluid ust be functional and stable in aqueous solution over the range f the operating temperatures (+25 to 180°F.). The hydrolytic tability of the thickener and inhibitors, which were designed for se in aqueous systems, presented no problem.

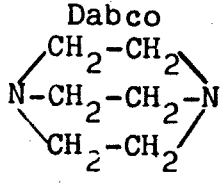
he hydrolytic stability of the phosphorus ester freezing point epressants was open to question. Triesters of phosphoric acid nd diesters of phosphonic acid were eliminated for use as freezing oint depressants because of known [9,10,11,12] hydrolytic instablity in acid, neutral or alkaline media.

hanley [13] reports that monoaryl phosphates are stable to hydrolsis at pH 8, while Plimmer [10] reports that all three, mono-, di- nd triaryl phosphates, are completely hydrolyzed by dilute acid r dilute alkali.

he data in Table VII tends to support Plimmer's contention, that onoaryl esters are hydrolyzed in acid or alkaline media. While t has been reported that diaryl phosphates are more hydrolytically table than the triaryl esters [12], they do hydrolyze very slowly

Table VII

HYDROLYSIS[1] OF AQUEOUS SOLUTIONS OF MONOARYL PHOSPHATES

MRC No.	Compound	Salt	pH	Temp. °F.	Time in Hours	% Hydrolyzed[2]
433	$C_6H_5O-P(=O)-(OH)_2$	None	Acid	167	18	9
	$C_6H_5O-P(=O)-(OH)_2$	Morpholine	7	200	66.5	Complete
	$C_6H_5O-P(=O)-(OH)_2$	Triethylamine	7	200	18	Complete
	$C_6H_5O-P(=O)-(OH)_2$	NaOH	7	200	66.5	Trace
	$C_6H_5O-P(=O)-(OH)_2$	NaOH	8	200	184	30
	$C_6H_5O-P(=O)-(OH)_2$	Benzyltrimethyl-ammonium hydroxide	7	200	66.5	Complete
	$C_6H_5O-P(=O)-(OH)_2$	Dabco 	7	200	18	Complete
	$C_6H_5O-P(=O)-(OH)_2$	Dabco	8	200	24	30

(1) Small-scale experiments

in alkaline media.

The aryl esters were preferred over the alkyl esters because of their greater fire resistance, but as cited above, they were eliminated because of inadequate hydrolytic stability. The aryl esters are also marginal in solubility.

It has been reported [10, 9] that mono- and dialkyl phosphates were exceedingly stable to alkaline hydrolysis.

The hydrolytic stability of alkali alkyl phosphates and alkali alkylphosphonates was investigated in the Coke Bottle Test. Results are shown in Table VIII.

All compounds easily met specifications on total acidity and therefore appear sufficiently hydrolytically stable to be used as fire-resistant, pour point depressants. However, copper corrosion may be a problem with the dipotassium salts.

The weight change of the copper strip is assumed to be related to corrosion. Monopotassium alkyl phosphates (Cpds. 468 and 484) do not appear to be especially corrosive to copper, even without an inhibitor and phosphonates are marginal (Cpds. 485 and 486). However, the dipotassium alkylphosphonates (Cpds. 488, 489 and 490) have questionable utility because of their severe copper corrosion.

. COMPATIBILITY

. PAINT (Table IX)

It was assumed, based on some previous experience, that paint and elastomer compatibility were related and that preliminary evaluations on paint would serve as qualitative estimates of elastomer capability. This contract did not require a paint test, but did specify that the fluid shall be compatible with Buna N rubber,

Table VIII

HYDROLYSIS OF ALKALI ALKYL PHOSPHATES AND ALKALI ALKYLPHOSPHONATES

(Coke Bottle Test MIL Spec MIL-H-19457A) (1)

MRC No.	Compound	Initial pH	Final pH	Total Acidity, (2) mg.KOH/g.	Copper Strip Weight Change (4) $mg./cm^2$	Copper Strip Corrosion	Residue in Solution
484	$(CH_3O)_2\overset{O}{\overset{\|}{P}}OK$	7.91	7.43	0.06	0.041	Stained	None
468	$(C_2H_5O)_2\overset{O}{\overset{\|}{P}}OK$	8.24	7.32	0.10	+1.10	Film on Copper	None
		10.0	-	-	0.09	Copper dark brown, no etching	-
		9.10	8.20	0.039	-	Copper brown, no etching	-
441	$(C_2H_5O)_2\overset{O}{\overset{\|}{P}}ONa$	6.00	-	-	0.571	Appeared etched	-
485	$CH_3\overset{O}{\overset{\|}{P}}(OCH_3)(OK)$	8.03	8.30	0.09 (3)	0.083	Corroded	Very small
486	$C_2H_5\overset{O}{\overset{\|}{P}}(OC_2H_5)(OK)$	7.99	9.45	0.18 (3)	1.45	Corroded	None
489	$CH_3\overset{O}{\overset{\|}{P}}(OK)_2$	8.00	8.00	0	10.1	Heavy film	Moderate

(Continued)

MRC No.	Compound	Initial pH	Final pH	Total Acidity,(2) mg. KOH/g.	Copper Strip: Weight Change(4) mg./cm^2	Copper Strip: Corrosion	Residue in Solution
490	$C_2H_5P(OK)_2$ (O above P)	7.95	7.87	0	13.6	Corroded	Moderate to heavy
488	$C_2H_5OP(OK)_2$ (O above P)	8.08	8.15	0	9.70	Stained	Very heavy
		9.35	8.80	0.039	0.62	Tarnished and etched	-

(1) Standard test conditions, using 100 g. of 40% aqueous solution.

(2) 5.0 mg. KOH/g. is passing for aqueous phase in MIL Spec MIL-H-19457A.

(3) Calculated as mg. HCl/g; back-titrated with HCl.

(4) 0.3 mg./cm^2 is passing in MIL Spec MIL-H-19457A.

MIL spec. MIL-P-5516. Paint test data are shown in Table IX.

The order of increasing compatibility with paint appeared to be: Aromatic-O-P(OH)$_2$<(haloaromatic-O)$_2$P-O-alkali<aromatic-O-P(aliphatic)OH≅[14] Aliphatic-P(OH)$_2$<haloaromatic-P(O aliphatic)O-alkali<(aromatic)$_2$P-O-alkali≅aromatic-O-P(O-alkali)$_2$<<aliphatic-P(O-aliphatic)O-alkali≅aliphatic-P(O-alkali)$_2$≅aliphatic-O-P(O-alkali)$_2$≅aromatic-P(O-alkali)$_2$≅(aliphatic-O)$_2$P-O-alkali. Phosphorus compounds with free acid groups attacked the paint severely. Aromatic groups in general showed greater attack on paint than alkyl groups; halogenation of aromatic groups increased paint attack.

These data suggest (Table IX) that alkali alkyl phosphates are compatible with paint, and probably elastomers. The difference, in paint compatibility, between compound 273, a fluorinated organic phosphorus compound, and compound 486, a potassium salt of an alkyl-phosphonate ester, was minor.

However, it should be pointed out that aqueous solutions of alkali alkyl phosphorus compounds soften paint to the point at which it can be scratched with the fingernail, although only while the treated spot is wet. Immediately after drying there appears to be no detectable damage to the paint. In contrast, paint treated with MIL-H-19457 (Cpd. 92) is permanently softened.

2. SEA WATER (Table X)

Compatibility of a water base hydraulic fluid with sea water is important, for on occasion, the fluid must function satisfactorily in the presence of as much as 10% sea water.

The investigation was carried out with natural sea water, obtained offshore at Marblehead, Massachusetts. The data are listed in Table X.

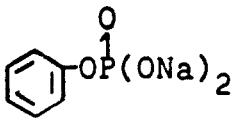
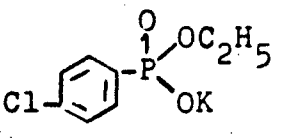
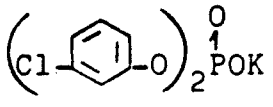
Table IX

EFFECT OF PHOSPHORUS COMPOUNDS ON PAINT

(Formula 20L over Formula 116)

C.	Compound (a)	% Concentration Water Solution	Effect
1	2110-H (Hydrocarbon hydraulic fluid)(b)	-	No apparent effect
3	$\left(CF_3-\langle\rangle-O\right)_3PO$(b)	-	
8	$C_2H_5P(O)(ONa)_2$	40.0	
8	$(C_2H_5O)_2P(O)OK$	40.0	Very slight effect, if any
5	$CH_3P(O)(OCH_3)OK$	40.0	Slight effect
9	$C_6H_5P(O)(ONa)_2$	40.0	
4	$(CH_3O)_2P(O)OK$	40.0	Slightly more damage than above
9	$CH_3P(O)(OK)_2$	40.0	
8	$C_2H_5OP(O)(OK)_2$	39.9	
0	$C_2H_5P(O)(OK)_2$	40.0	Slightly more damage than above
6	$C_2H_5P(O)(OC_2H_5)OK$	40.0	

Table IX, Continued

MRC No.	Compound (a)	% Concentration Water Solution	Effect
634		40.0	Paint softened; light to moderate damage
510	$C_6H_5OP(ONa)_2$	46.0	
511	$(C_6H_5)_2PONa$	39.0	Paint very soft; easily scratched with fingernail
92	MIL-H-19457 (b)	-	
631		40.0	Moderate damage; paint could be removed with fingernail
339	$C_2H_5P(OH)_2$	40.0	Greater damage than above; pieces of paint easily removed
466	$C_4H_9P(OC_6H_5)OH$ (b)	-	
591		40.0	Severe damage, some permanent damage; paint grainy and swelled
433	$C_6H_5OP(OH)_2$	39.8	Test stopped after two days; severe damage; could remove paint with gentle wiping

(a) Listed in order of increasing attack on paint.

(b) Compound used neat, not a solution.

COMPATIBILITY OF ALKYL PHOSPHATES AND ALKYLPHOSPHONATES WITH SEA WATER

MRC No.	Compound	% Conc. in H_2O Solution	pH of H_2O Solution	% Concentration Sea Water (3)	Precipitation	
					No Heat (1)	Boil (2)
484	$(CH_3O)_2\overset{O}{\overset{\|}{P}}OK$	40.0	8.01	10.3	No	No
468	$(C_2H_5O)_2\overset{O}{\overset{\|}{P}}OK$	40.0	7.95	10.2	No	No
485	$CH_3\overset{O}{\overset{\|}{P}}(OCH_3)(OK)$	39.9	8.00	10.0	No	No
486	$C_2H_5\overset{O}{\overset{\|}{P}}(OC_2H_5)(OK)$	40.0	7.96	9.99	No	No
489	$CH_3\overset{O}{\overset{\|}{P}}(OK)_2$	40.0	7.98	10.2	No	No
490	$C_2H_5\overset{O}{\overset{\|}{P}}(OK)_2$	40.0	7.90	9.99	No	Very small amount
488	$C_2H_5O\overset{O}{\overset{\|}{P}}(OK)_2$	39.9	8.01	10.4	No	No

(1) Allowed to stand three days.

(2) Boiled solutions vigorously and allowed to stand two days.

(3) Sea water pH 8.10.

The samples were checked for precipitation at the boiling point, as well as at room temperature, since calcium, barium, and magnesium salts of phosphorus compounds often demonstrate "reverse" solubility wherein they precipitate when heated. A very slight cloudiness appeared upon heating the solution of compound 490; otherwise the compounds were unaffected.

3. METALS (Corrosion)

It is imperative that the water base hydraulic fluid be compatible with the various metal alloys in the submarine hydraulic system. Of the twenty-seven alloys originally included in the contract target objectives, eight alloys were chosen by approval of the U.S. Navy Marine Engineering Laboratory as representative: Grade 1009 steel, QQ-S-698; electrodeposited, galvanized steel, QQ-Z-325a, Type II, Class 1; silver base brazing alloy, MIL-B-15395A, Grade IV; copper, QQ-C-576b; nickel-copper, QQ-N-281, Class A (Monel 400); bronze, MIL-B-16541A (WEP); phosphor bronze QQ-B-750, composition A; and aluminum, QQ-A-250/4b.

Aluminum and copper were chosen for the initial preliminary corrosion tests. Aluminum was chosen because of its sensitivity to alkali, and copper was chosen because of its apparent reaction wit alkali phosphates.

a. Aluminum

Preliminary corrosion tests were carried out for direct comparison of diethyl potassium phosphate and methyl potassium methylphosphonate using aluminum:

RC o.	Compound	pH Before Heating	pH After Heating(a)	Remarks
68	$(C_2H_5O)_2\overset{O}{\overset{\|}{P}}OK$	8.24	6.56	No visible attack
85	$CH_3\overset{O}{\overset{\|}{P}}(OCH_3)(OK)$	8.98	8.22	Aluminum heavily stained; precipitate present in solution

a) heated at 200°F. for 336 hours (2 weeks).

ince aluminum was attacked by methyl potassium methylphosphonate t pH 9.0, the effect of pH on corrosion within three classes of hosphorus compounds was investigated:

RC o.	Compound	pH of 40% solution(a)	Remarks
84	$(CH_3O)_2\overset{O}{\overset{\|}{P}}OK$	8.98 7.20	No visible attack after 5 weeks.
85	$CH_3\overset{O}{\overset{\|}{P}}(OCH_3)(OK)$	8.99	Very slight corrosion at solution-vapor interface (5 weeks).
		7.10	Aluminum stained; precipitate deposited on metal (5 weeks).
89	$CH_3O\overset{O}{\overset{\|}{P}}(OK)_2$	9.00	Became solid after 18 hr.; tentatively identified as an alkali aluminate (b).
		7.15	

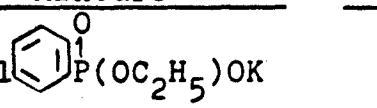
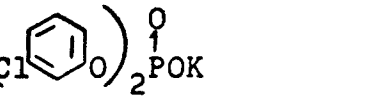
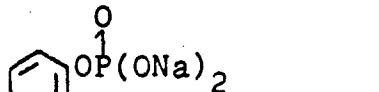
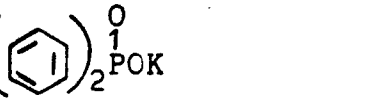
a) Heated at 200°F.

b) Attack at either pH.

hese data show that: (1) dipotassium phosphonates chemically attack luminum; (2) the attack of a partial ester potassium alkylhosphonate on aluminum is pH-sensitive; (3) aluminum is not

attacked by dialkyl potassium phosphates at pH 7 or 9.

The corrosivity of aromatic alkali phosphorus compounds was also determined:

MRC No.	Mixture	Composition, %	pH	Remarks
748		9.8		(Heated at 200°F. fo one month.)
		34.1	8.50	No visible attack o aluminum; solution colorless and clear
	H_2O	53.7		
	QP-3	2.4		
591		40	9.72	Small precipitate present; aluminum not visibly attacke
	H_2O	60		
634		40	9.60	Separated into two layers; lower layer crystallized; vapor phase corrosion of aluminum
	H_2O	60		
434		38	9.05	Heavy precipitate ir solution; aluminum had white coating; not visibly pitted
	H_2O	62		

General conclusions, for the pH specified, can be made from these visual observations: (1) alkali diaromatic phosphorus ester-salts do not appear corrosive to aluminum (Cpd. 591); (2) the dialkali aromatic phosphates appear more corrosive than the monoalkali salts (compare Cpds. 591 and 634); (3) the alkali diarylphosphinates show some type of severe chemical change but do not pit the aluminum (Cpd. 434); (4) inclusion of 10% of an alkyl potassium haloaromatic phosphonate and 2.4% of a thickener in a solution of a dialkyl

›tassium phosphate (mixture 748) apparently did not alter the ›n-corrosivity of the alkyl phosphate.

b. Copper

Copper corrosion data are listed under Section III-D ydrolytic Stability). The dialkali salts of phosphorus compounds used severe corrosion of copper, whereas the monoalkali salts fected it very little. Dimethyl potassium phosphate (Cpd. 484) d methyl potassium methylphosphonate (Cpd. 485) had a very ight, if any, corrosive effect on copper. In contrast, the copper ight change with dipotassium ethylphosphonate (Cpd. 490) was 330 mes that of dimethyl potassium phosphate (Cpd. 484). (See Table II).

lyethylenimine (PEI) was severely corrosive to copper as shown Section III-B, Table V. A 40% solution of PEI was deeply colored thin an hour at 200°F. in the presence of copper. The addition 2% mercaptobenzothiazole (MBT), a copper corrosion inhibitor, d retard PEI corrosion of copper.

c. Corrosion Comparison Studies with Alkyl Phosphates, Phosphinates and Phosphonates (Table XI)

A series of compatibility tests were run on the eight loys (Section III-E-3) using a phosphate, phosphinate and ›sphonate as depressants in a water base fluid formulation. The ›opotassium salts of the ethyl analogs were used since they were ›viously shown to be less corrosive to metals and more compat-le with certain thickeners. The results are given in Table XI.

re general conclusions on the corrosivity of the three formula-›ns toward metals can be drawn from these data: (1) the silver ›e, nickel-copper and aluminum alloys were not attacked by any the three formulations (metals 1, 2 and 8); (2) copper and a

Table XI

CORROSION COMPARISON STUDIES WITH PHOSPHATES, PHOSPHINATES AND PHOSPHONATES[a][b]

No.	Metal	Phosphate Formula (MRC 772)	Phosphinate Formula[c] (MRC 774)	Phosphonate Formula (MRC 775)
1	Silver Base Brazing Alloy MIL-B-15395 A (Ships), Grade IV	Yellow deposit on metal; no visible corrosion	No visible corrosion; yellow particles precipitated.	No visible corrosion; yellow deposit on metal in solution
2	Nickel-Copper, QQ-N-281, Class A (Monel 400)	Moderate yellow precipitate in solution; no visible corrosion.	Slight corrosion at vapor/liquid interface	No visible corrosion; slight yellow precipitate
3	Bronze, MIL-B-16541A (WBP)	Yellow deposit on metal in solution; vapor phase tarnish	Heavy vapor phase tarnish	Moderate vapor phase tarnish; heavy yellow precipitate in solution
4	Electrodeposited, galvanized steel, QQ-Z-325a, Type II, Class 1	Heavy precipitate in solution; heavy black deposit on metal	Few black particles on metal	Heavy vapor phase tarnish, considerable in solution
5	Steel, QQ-S-698, grade 1009	Black precipitate; steel corroded	No visible corrosion	No visible corrosion; some precipitate in solution
6	Copper, QQ-C-576	Heavy vapor phase tarnish; small precipitate in solution	Heavy vapor phase tarnish; some in solution	Heavy vapor phase tarnish; moderate yellow precipitate in solution
7	Phosphor Bronze, QQ-B-750, composition A	Vapor phase tarnish; no visible attack on metal in solution	Heavy tarnish in vapor phase and solution	Heavy vapor phase tarnish; yellow precipitate in solution
8	Aluminum, QQ-A-250/4b	No visible corrosion	No visible corrosion	No visible corrosion

(a) All compositions contained identical percentages of the components. They were:

5.87% WSR N-80
52.8 % Water
39.2 % phosphorus salt [$(C_2H_5O)_2P(O)OK$ (MRC 772), or $(C_2H_5)_2P(O)OK$ (MRC 774), or $C_2H_5P(O)(OC_2H_5)OK$ (MRC 775)]
2.0 % Renex 31
0.2 % MBT
0.1 % Potassium nitrite [d]
0.02% Potassium phosphate [d]

(b) All samples heated 48 hr. @ 200°F.

(c) Polymeric thickener precipitated in all solutions.

(d) Offered some protection to steel.

igh percentage of copper alloys acquired a heavy tarnish in the apor phase indicating a need for a vapor phase inhibitor with hese materials (metals 3, 6 and 7); (3) the phosphonate (MRC 775) nd phosphinate (MRC 774) formulations attacked copper alloys ore severely than the phosphate formulation (MRC 772); (4) the hosphate formulation (MRC 772) appeared to attack steel alloys he most severely of the three formulations with the phosphinate ormulation showing no attack.

he nature of the yellow precipitate which formed in a number of he solutions was unknown. It was not observed previously in queous solutions of the salts and metals, so was assumed to have risen from some ingredients of the formulation in the presence f metals.

wo problems were apparent from the compatibility studies: (1) stable, effective vapor-phase corrosion inhibitor is needed for opper and copper-containing alloys; (2) a compatible inhibitor or the protection of steel is needed if a dialkyl potassium hosphate is used as pour point depressant.

otassium dichromate, nitrite and phosphate have been used [15] as orrosion inhibitors for steel in the presence of brines and salts. teel was completely protected against the corrosivity of a 40% queous solution of diethyl potassium phosphate by addition of 0.25% otassium dichromate. Unfortunately potassium dichromate could not e used as an inhibitor in the formulation (MRC 772) since it tacked both the Renex 31 and WSR N-80. Surprisingly, it did not ffect mercaptobenzothiazole (MBT).

comparison of the steel corrosion of the phosphate formulation 1RC 772) with an aqueous solution of diethyl potassium phosphate owed that the potassium nitrite and phosphate in the formulation ld protect steel to some extent.

IV. TENTATIVE CANDIDATE WATER-BASE HYDRAULIC FLUID

The following tentative fire-resistant water-base hydraulic fluid (2 quarts) designated "Water-Base Fluid 65-04-22-01," was delivered to BuShips on termination of the contractual period:

WATER-BASE FLUID
65-04-22-01

COMPOUND	COMPOSITION, %
A. Diethyl potassium phosphate	39.1
B. Ucar Polyox resin WSR N-80	5.85
C. Renex 31	2.00
D. Mercaptobenzothiazole (MBT)	0.20
E. Potassium nitrite	0.10
F. Potassium phosphate	0.05
G. Water	52.7

The fluid consisted of a (G) water solution of (A) a fire-resistant pour-point depressant, (B) a flammable organic polymeric thickener, (C) a boundary-type lubricant, (D) a liquid-phase corrosion inhibitor for copper and steel, (E) and (F) liquid-phase corrosion inhibitors for steel.

Compatibility of water-base fluid 65-04-22-01 with metals and with Buna N was as follows:

METAL CORROSION

Metals	Wt. Change, mg./cm^2	Corrosion
Aluminum, QQ-A-250/4b	+ 0.01	None
Bronze, MIL-B-16541A	+ 0.16	Yellow Deposit
Copper, QQ-C-576b	+ 0.11	Yellow Deposit
Nickel-Copper, QQ-N-281, Class A (Monel 400)	+ 0.11	Tarnished

METAL CORROSION
(Cont.)

tals	Wt. Change, mg./cm^2	Corrosion
osphor Bronze, QQ-B-750, Composition A	+ 0.03	Yellow Deposit
lver Base Brazing Alloy, MIL-B-15395A, Grade IV	+ 0.08	None
eel, QQ-S-698, Grade 1009	+ 0.03	Sl. Corrosion, edges
eel, galvanized, electro-deposited, QQ-Z-325a, Type II, Class I	+ 0.21	Sl. Tarnish

om these data improved inhibition does not seem insurmountable.
e tests were run at 200°F. for 48 hours as described under
valuation Test Methods."

e Buna N compatibility tests were also run as described under
valuation Test Methods."

Table 12

BUNA N COMPATIBILITY

MRC No.	Fluid	Ultimate Tensile psi	Ultimate Elongation %	Volume Change %	Weight Change %	Hardness Shore "A"
-	Buna N "O" Rings before immersion	1705 (±241)	238 (±30)	-	-	68 (±1)
92	MIL-H-19457	655 (±118)	142 (±16)	87.6 (±4.7)	77.8 (±3.7)	59 (±1)
271	BuShips 2110-H	1815 (±92)	238 (±22)	-4.2 (±2)	-4.0 (±1)	72 (±2)
776	65-04-22-01 Water-Base Hydraulic Fluid	1384 (±134)	169 (±26)	0.6 (±1.2)	0.9 (±1.1)	70 (±2)

compatibility of water-base hydraulic fluid 65-04-22-01 with N was greatly improved over MIL-H-19457 but may be regarded lightly inferior to BuShips 2110-H. However, the somewhat r values for ultimate tensile and elongation may not be sig- cant from an application standpoint since there was no volume ardness change in the Buna N specimens. The small inferiority 110-H in tensile and elongation values could probably be cor- ed by additives.

d 65-04-22-01 became opaque with concomitant formation of a ipitate when cooled during the Buna N compatibility test.

tentative water-base fluid 65-04-22-01 exhibited very poor c shear stability as shown:

SONIC SHEAR STABILITY

Fluid	Irradiation Time	Viscosity @ 100°F.	% Change
H-5606B	0	14.29 cs.	-
"	15 min.	12.92 cs.	-9.58
"	45 min.	11.66 cs.	-18.40
"	60 min.	11.28 cs.	-21.06
"	90 min.	10.67 cs.	-25.33
"	120 min.	10.17 cs.	-28.83
H-22072			
ghtonsafe-271)	0	42.43 cs.	-
"	15 min.	42.55 cs.	+0.28
"	30 min.	42.78 cs.	+0.82
"	60 min.	42.82 cs.	+0.91
"	90 min.	44.00 cs.	+3.70
"	120 min.	44.64 cs.	+5.20
r-Base Fluid No.			
05-05-05)	0	70.55 cs.	-
"	15 min.	24.36 cs.	-65.47
"	30 min.	23.36 cs.	-66.88
"	90 min.	21.86 cs.	-69.01
"	120 min.	20.85 cs.	-70.44

SONIC SHEAR STABILITY, Cont.

Fluid	Irradiation Time	Viscosity @ 100°F.	% Change
Water-Base Fluid (Lot No. 65-05-05-05) (Second Run)	5 min.	35.79 cs.	-49.27
"	10 min.	28.43 cs.	-59.70
"	15 min.	28.09 cs.	-60.18
"	30 min.	27.65 cs.	-60.80
"	60 min.	26.84 cs.	-61.95

The total sonic shear was about 70% in 2 hours; sixty-five percent of which took place in the first 15 minutes.

The molecular size which would be shear stable could easily be established from such data. It was anticipated that thickener WSR N-80 (m.w. 175,000 - 200,000) would not be stable to sonic shear. WSR N-80 was used in preference to a lower molecular weight polymer, such as WSR N-10, in order to keep the AIT at a maximum value.

The results of MIL-H-22072 (Houghtonsafe-271) show viscosity increase of 5.2%. This figure leads us to believe water may have been lost by evaporation during the test.

The following is comparative data on Fluid 65-04-22-01, the additive package for 65-04-22-01, and a MIL-H-22072 fluid. A crystalline solid separated from fluid 65-04-22-01 on standing approximately one month. This precipitate was not investigated further.

PHYSICAL PROPERTIES

	Fluid Sample 65-04-22-01	Additive Package 65-04-22-01	MIL-L-2[illegible]
AIT			
°F.	860	820	730
Time lag (Sec.)	20	10	32
Flammability (°F.)			
Micro flash point	548	545	286
Micro fire point	No fire 626	No fire 626	[illegible]
Viscosity (cs.)			
28°F.	359	-	216.7
100°F.	71.7	-	41.9
150°F.	34.0 (extrapolated)	-	16.8
210°F.	16.5	-	8.59
ASTM Slope			
100-210°F.	0.44	-	0.63
Pour Point			
Crystallized	-35°F.	-	-5°F.
Compatibility with 10% Sea Water	Compatible		Precipitate
Specific Gravity	1.16 at 20°C. (68°F.)	-	-
Stability	Clear at -20°F.; passes <5 micron filter		
Fluid Residues		Completely water soluble	

V. DISCUSSION OF SYNTHESIS AND CHEMISTRY

A. FINAL PRODUCTS

The partial potassium salts, rather than sodium salts, of phosphor esters were used because of their greater solubility in aqueous media. Several variations in method of synthesis were used and ar discussed under each section.

1. PHOSPHATES

This series of compounds was synthesized generally by two methods:

Partial saponification of an ester,

$$(RO)_3\overset{\overset{O}{\|}}{P} \xrightarrow[\substack{18\text{-}37 \text{ hr.}\\ \text{reflux}}]{\substack{KOH\\ EtOH\text{-}H_2O}} (RO)_2\overset{\overset{O}{\|}}{P}OK + ROH,$$

and by hydrolysis of a phosphorochloridate,

$$(RO)_2\overset{\overset{O}{\|}}{P}Cl \xrightarrow[H_2O]{\substack{KOH\\ 0\text{-}10^\circ}} (RO)_2\overset{\overset{O}{\|}}{P}OK + KCl.$$

On completion of hydrolysis, the pH was adjusted to the electrometrically predetermined endpoint of the salt and the solution was evaporated to dryness in vacuo.

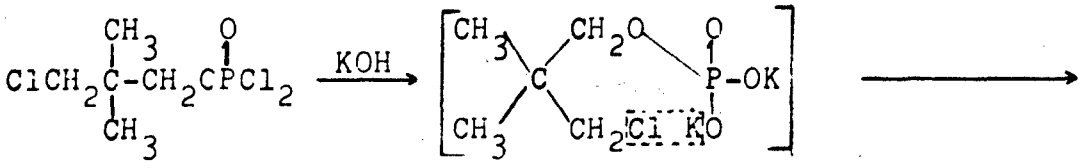
In the ester hydrolysis, pure products were obtained directly in good yields.

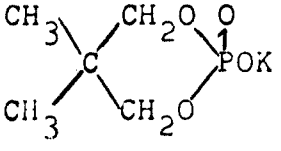
In the phosphorochloridate hydrolysis, the dry salts were dissolved in methanol and then filtered to remove the potassium chloride; evaporation of the methanol solution gave product of high purity in

good yields. Absolute methanol was superior to other solvents for the near-quantitative separation of potassium chloride.

Compound 672, the partially hydrolyzed tetraethylene glycol/phosphorus oxychloride reaction product, (cf. also Cpds. 668 and 679) was obtained by random, partial saponification of the glycol phosphate, made by reaction of the metal dialkoxide with phosphorus oxychloride [16].

The alkaline hydrolysis of 2,2-dimethyl-3-chloropropyl phosphorodichloridate gave 5,5-dimethyl-2-hydroxy-1,3,2-dioxaphosphorinane-2-oxide (Cpd. 493) instead of dipotassium 2,2-dimethyl-3-chloropropyl phosphate:





apparently the potassium salt formed, as expected, but a secondary intramolecular reaction took place between the potassium and γ-chlorine to produce the alicyclic derivative. Although this reaction could be expected to take place under more rigorous conditions, it was somewhat surprising that it occurred under mild conditions.

2. PHOSPHONATES

The half-ester potassium phosphonates (Cpds. 485 and 486) were synthesized by ester hydrolysis as previously described for phosphates:

$$RP(OR')_2 \xrightarrow[\text{Reflux}]{\text{KOH}\ \text{EtOH-}H_2O} RP(OR')(OK) + R'OH$$

The dipotassium phosphonates (Cpds. 489 and 490) were formed by titrating an aqueous solution of the phosphonic acid to an alkaline pH with potassium hydroxide:

$$RP(OH)_2 \xrightarrow[H_2O]{KOH} RP(OK)_2$$

As with the phosphates, the pH was adjusted to the predetermined endpoint for the salt and the solution was evaporated to dryness to give high yields of the pure product.

3. PHOSPHINATES

Dimethylphosphinic acid was synthesized by the following method

$$(CH_3)_2P(S)-P(S)(CH_3)_2 + 3H_2O_2 \longrightarrow 2(CH_3)_2POH + 2S + 2H_2O$$

Because of its extreme solubility in water, dimethylphosphinic acid cannot be prepared as satisfactorily by the usual method [17] which is excellent for the relatively insoluble, higher members of the series:

$$RMgX + (R'O)_2PH \longrightarrow R_2PH \xrightarrow[H_2O]{Br_2} R_2POH$$

The preparation of dimethylphosphinic acid by the hydrogen peroxide oxidation of tetramethyldiphosphine disulfide gives high quality product in high yields in a simple, single-step reaction. The acid retains water so tenaciously that it is very difficult to obtain the anhydrous acid. Thus, this procedure is also favored over the usual method because there is a minimum amount of water present.

A procedure which describes the preparation of the acid under essentially anhydrous conditions (moist benzene) has been published recently [18] and it appears to eliminate many of the solubility problems associated with the isolation of the acid.

4. PHOSPHINE OXIDES

Hoffmann [19] reports the preparation of tris(hydroxymethyl)-phosphine oxide by the action of barium carbonate on tetrakis-(hydroxymethyl)phosphonium chloride identified via the tribenzoate:

$$(HOCH_2)_4PCl \xrightarrow[\text{Reflux}]{BaCO_3,\ H_2O} (HOCH_2)_3P{\rightarrow}O + H_2 + CH_2O + BaCl_2$$

Our experiment (23020) yielded a product which was identified by NMR as 90% $(HOCH_2)_3P{\rightarrow}O$ and 10% of an unidentified phosphorus compound. An attempt (23019) to prepare the tris(hydroxymethyl)-phosphine oxide in one step using potassium hydroxide also yielded 1:1 mixture identified by NMR as $(HOCH_2)_3P{\rightarrow}O$ and $(HOCH_2)_2P(O)OK$.

5. PHOSPHORAMIDATES

Since the P-NR_2 bond is stable to alkali, phosphoramidates were synthesized by methods similar to those used for phosphonates and phosphates:

a. $$R'\text{-}N(R)\text{-}P(O)(OR)_2 \xrightarrow[\text{EtOH-}H_2O,\ 24\text{ hr. @ }80^\circ]{KOH} R'\text{-}N(R)\text{-}P(O)(OR)(OK)$$

b. $$R_2N\text{-}P(O)(OR'')Cl \xrightarrow[H_2O,\ 48\text{ hr. }<25^\circ]{KHCO_3} R_2N\text{-}P(O)(OR'')(OK)$$

Compound 766, methyl potassium N-methyl-N-phenylphosphoramidate ($R=CH_3$, $R'=C_6H_5$), was prepared using method a. Compound 481, m-chlorophenyl potassium dimethylphosphoramidate (method b; $R=CH_3$, $R''=m\text{-}ClC_6H_4\text{-}$) was hydrolyzed under somewhat milder conditions to prevent hydrolysis of the m-chlorophenyl ester moiety.

6. PHOSPHOROTHIONATES

Diethyl potassium phosphorothionate was synthesized by treating potassium diethyl phosphite with sulfur:

$$(C_2H_5O)_2\overset{O}{\overset{\|}{P}}H \xrightarrow{K(metal)} (C_2H_5O)_2\overset{O}{\overset{\|}{P}}K \xrightarrow{S} (C_2H_5O)_2\overset{O}{\overset{\|}{P}}SK \xrightarrow{\Delta} (C_2H_5O)_2\overset{S}{\overset{\|}{P}}OK$$

$$(C_2H_5O)_2\overset{O}{\overset{\|}{P}}SK$$

The expected product, $(C_2H_5O)_2PSK$, is presumed to have rearranged to the thionate during the heating period.

B. INTERMEDIATES

The compounds in this section were prepared mainly as intermediates for the ester-salt preparations, however AIT determinations were made on a number of the ester intermediates prior to hydrolysis.

1. DERIVATIVES OF PHOSPHORIC ACID

a. Phosphates

The phosphates were synthesized from the alcohol and phosphorus oxychloride in the presence of a tertiary amine:

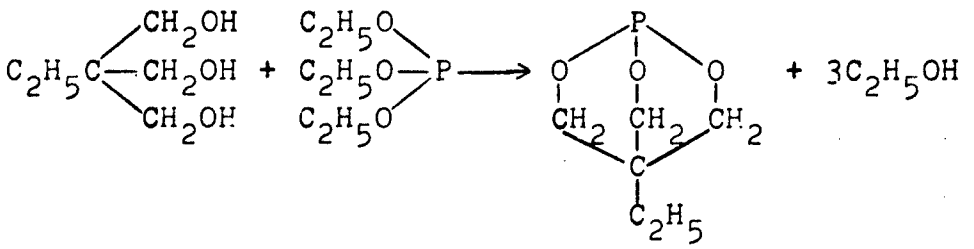
$$POCl_3 + ROH \xrightarrow[\text{Benzene}]{R_3N} (RO)_3\overset{O}{\overset{\|}{P}} + R_3N\cdot HCl$$

The tris(3-pyridyl) phosphate (Cpd. 677; 33841) appeared to be more hydrolytically unstable than other water soluble phospnates and was

not investigated further (31436). Tris(2-phenoxyethyl) phosphate (34804) and the tris[β-(2-pyridyl)ethyl] phosphate (34805) could not be distilled. These are large molecules with low vapor pressures which raised the distillation temperature above the decomposition point.

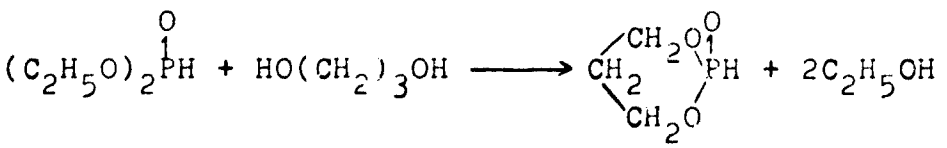
b. Alicyclic phosphates

4-Ethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane was prepared by the reaction of 2-ethyl-2-hydroxymethyl-1,3-propanediol (trimethylolpropane) and triethyl phosphite in the presence of catalytic amounts of triethylamine:



The ethanol must be distilled very slowly (18-20 hrs.) from the reaction mixture in order to obtain yields in excess of 90%. If the ethanol is removed too rapidly, accompanying side reactions materially lower the yield.

A compound believed to be 1,3,2-dioxaphosphorinane-2-oxide was prepared in low yield from 1,3-propanediol and diethyl phosphite by ester interchange following the procedure of U.S. 3,152,164:

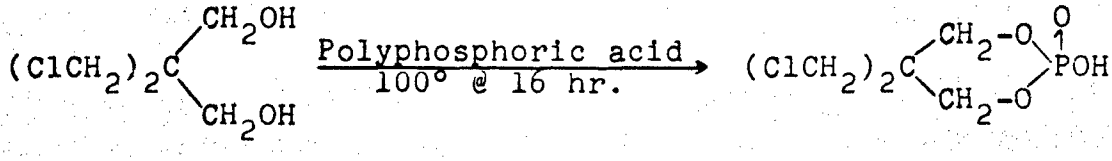


Three runs were made: without catalyst, with catalytic amounts of triethylamine and with catalytic amounts of water. Ethanol was obtained in yields >90% in each run suggesting that the reaction had

essentially gone to completion. However, during the distillation of each run, a vigorous reaction took place just prior to the boil ing point of the product, giving decomposition and a large residue

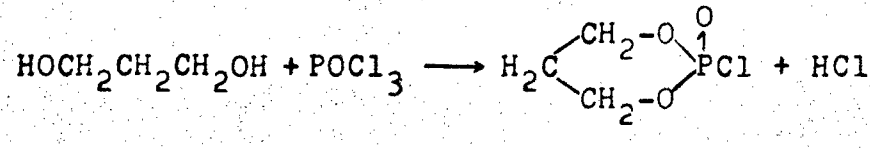
Preparations given in the literature [20,21] do not mention this secondary reaction. The physical constants of the product obtaine (b.p. 108°/0.13, m.p. 41°) do not agree with those given in the literature (b.p. 97-98°/2.5), however instrumental and analytical data support the proposed structure.

5,5-Bis(chloromethyl)-2-hydroxy-1,3,2-dioxaphosphorinane-2-oxide (32882; 32885) was prepared by heating 2,2-bis(chloromethyl)-1,3-propanediol (pentaerythritol dichlorohydrin) with polyphosphoric acid:



Three attempts to synthesize this acid from 2,2-bis(chloromethyl)-1,3-propanediol and phosphorus oxychloride, under varying conditior gave only polymeric materials (see Section C). Apparently the chlorine atoms in 2,2-bis(chloromethyl)-1,3-propanediol sterically interfere with the ring formation since the dioxaphosphorinane can be readily made from 2,2-dimethyl-1,3-propanediol [22].

Lanham in U.S. 2,892,862 [23] reports the preparation of 2-chloro-1,3,2-dioxaphosphorinane-2-oxide by the reaction,



which was subsequently distilled at 78°/0.2 mm. (m.p. 39°) using a falling film-type still. The product obtained on repetition of this procedure decomposed between 80-100° and could not be distille through a Vigreux column (34816). A second preparation decomposed at 70°/0.03 mm. but on pressing between filter paper it had a m.p.

of 42-44° in contrast with the 39° reported. NMR data supported the structure (34831).

c. Phosphorochloridates and phosphorodichloridates

This series of compounds was synthesized by two general methods:

(1) Reaction of an alcohol with phosphorus oxychloride,

$$ROH + POCl_3 \longrightarrow RO\overset{O}{\overset{\uparrow}{P}}Cl_2 + (RO)_2\overset{O}{\overset{\uparrow}{P}}Cl$$ and

(2) by chlorination of a dialkyl phosphite,

$$(RO)_2\overset{O}{\overset{\uparrow}{P}}H \xrightarrow{Cl_{2(g)}} (RO)_2\overset{O}{\overset{\uparrow}{P}}Cl$$

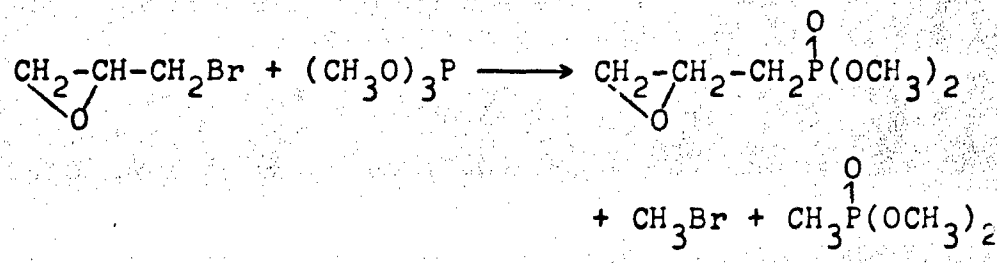
Method 1 was used for preparing aromatic phosphorochloridates $[(RO)_2\overset{O}{\overset{\uparrow}{P}}Cl]$ and aromatic or aliphatic phosphorodichloridates $(RO\overset{O}{\overset{\uparrow}{P}}Cl_2)$. Chlorination of a phosphite (method 2) was used in the preparation of aliphatic phosphorochloridates $[(RO)_2\overset{O}{\overset{\uparrow}{P}}Cl]$. The preparation of aliphatic phosphorochloridates by method 1 usually gives very low yields and/or inseparable mixtures as a result of disproportionation.

The value of using a Lewis acid-catalyst in the preparation of an aromatic phosphorochloridate or phosphorodichloridate is questionable since yields of the m-chlorophenyl derivatives were higher without a catalyst (23038). However, it appears that the catalyst does promote formation of the tertiary phosphate since the yield of tris(m-chlorophenyl) phosphate in the presence of a catalyst was twice that of the same size run without catalyst.

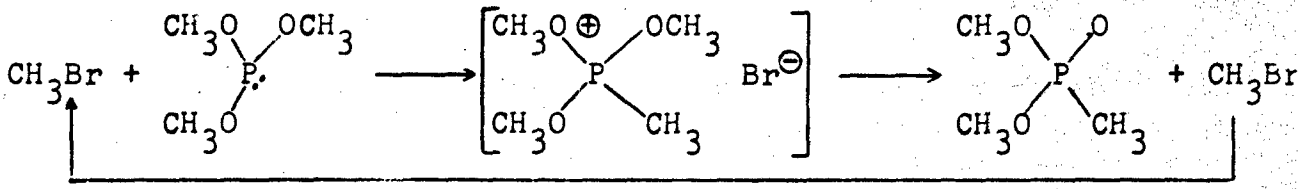
2. DERIVATIVES OF PHOSPHONIC ACID

a. Phosphonates

Dimethyl 2,3-epoxypropylphosphonate was prepared from epibromohydrin and trimethyl phosphite (30063):

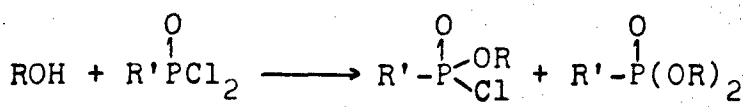


This reaction gave only moderate yields (30%) of the epoxypropylphosphonate. The main product (60%) was dimethyl methylphosphonate which was formed by an Arbuzov reaction of the by-product methyl bromide and trimethyl phosphite:



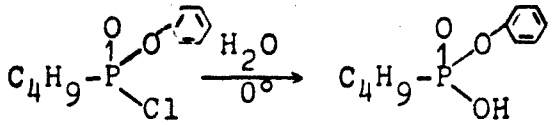
b. Phosphonochloridates

The phosphonochloridates were synthesized from a phosphon dichloride and an alcohol:



The yield of disubstituted phosphonates, which invariably accompanied the desired products, can be minimized by using an excess of phosphonic dichloride (24352; 32878). Catalytic amounts of aluminum chloride appear to promote formation of the undesired disubstituted phosphonates (21846).

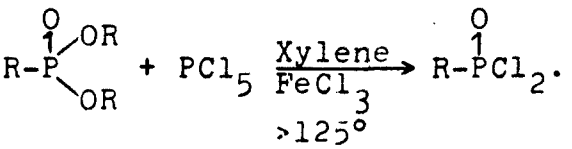
Phenyl hydrogen butylphosphonate was prepared by hydrolysis of phenyl butylphosphonochloridate in an ice/water/ether mixture:



Ether was added to solubilize the water-insoluble phosphonochloridate; ice was added to retard hydrolysis of the phenyl ester (24360). The potassium salt of this acid did not have the required solubility for use in this application.

c. Phosphonic dichlorides

Aliphatic phosphonic dichlorides were synthesized by the following method:

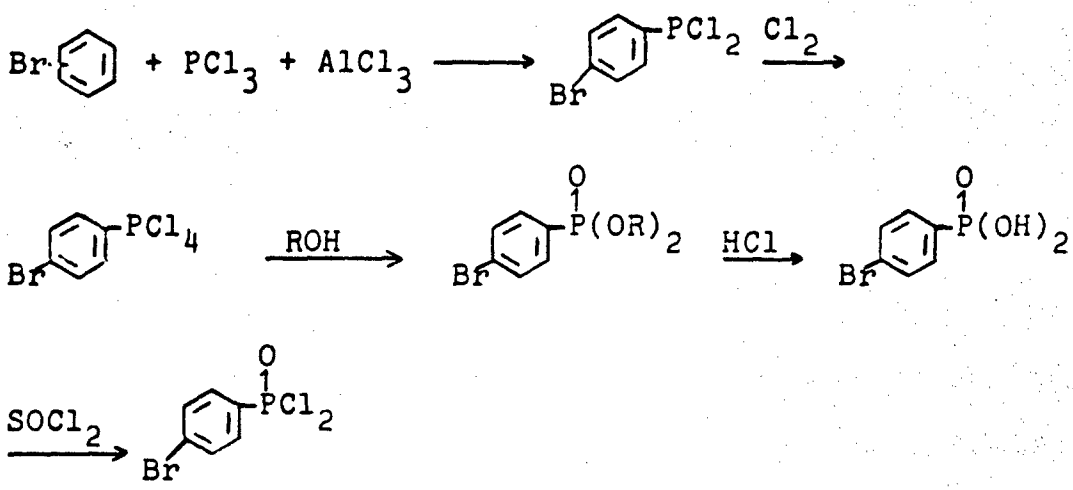


A successful reaction requires:

(1) catalytic amounts of ferric chloride to promote the reaction;
(2) a minimum temperature of 125° for continuous removal of by-products to prevent side reactions;
(3) dilution with an inert solvent in order to moderate the vigorous reaction.

Aliphatic pnosphonic dichlorides were formerly obtained by hydrolyzing dialkyl alkylphosphonates with concentrated hydrochloric acid, followed by careful evaporation to dryness, then treatment with phosphorus pentachloride. The present method has the advantage of being a single-step synthesis.

A bromoaromatic phosphonic dichloride was prepared as follows:



This method is ordinarily employed for the synthesis of substituted aryl phosphonates and is one of the few practical methods available for this class. Diethyl p-bromophenylphosphonate, the product desired, could not be separated from the reaction mixture. Conversion to the phosphonic dichloride gave a lower-boiling material which was separable by distillation (32853). It was also noted that considerable debromination took place during the reaction as evidenced by the formation of phenylphosphonic dichloride.

d. Alkylphosphonic acids

The alkylphosphonic acids were synthesized by hydrolysis of dialkyl alkylphosphonates:

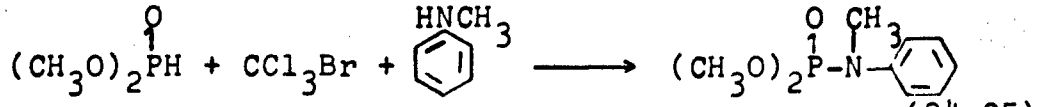
$$R\text{-}P(O)(OR)_2 \xrightarrow{\text{Concentrated HCl}} RP(O)(OH)_2$$

3. DERIVATIVES OF PHOSPHORAMIDIC ACID

a. Phosphoramidates

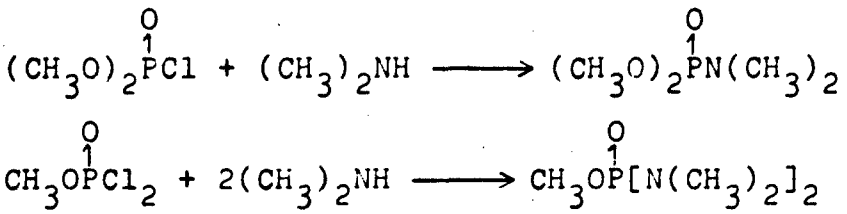
Dimethyl N-methyl-N-phenylphosphoramidate was synthesized by treating trimethyl phosphite with N-methylaniline in the presence

of a carbon tetrahalide:



Carbon tetrachloride is generally used in this reaction (24,25) with strong bases such as ammonia (34841), dimethylamine, etc., but it is not sufficiently reactive in the presence of weaker bases such as the aromatic amines. With weaker bases, bromotrichloromethane or bromoform are more reactive than carbon tetrachloride.

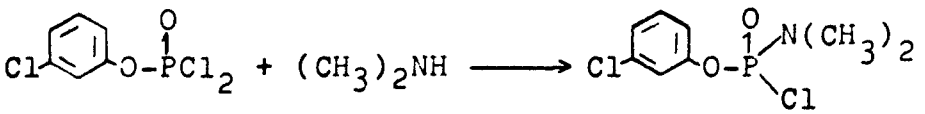
Tetramethyl phosphoramidate (27125) and methyl tetramethylphosphorodiamidate (27086) were synthesized from dimethylamine and the appropriate methyl phosphorochloridate:



Dimethylamine was strongly retained by both products and could be removed only with strong absorbents such as charcoal and Attapulgus clay. The products, when free of dimethylamine, had a pleasant, terpene-like odor.

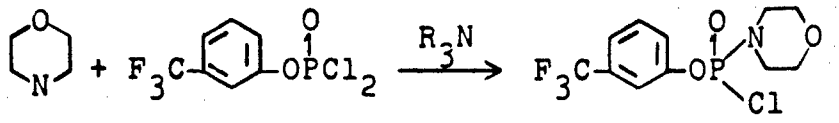
b. Phosphoramidochloridates

Reaction of dimethylamine with m-chlorophenyl phosphorodichloridate (27082) gave m-chlorophenyl dimethylphosphoramidochloridate:



Dimethylamine hydrochloride slowly separated from the phosphoramidochloridate on long standing indicating an inherent instability.

3-Trifluoromethylphenyl morpholinophosphorochloridate was synthesized as follows:



This material, on long standing, appeared more stable than the m-chloropnenyl dimethylphosphoramidochloridate.

Diethylphosphoramidic dichloride was synthesized by an adaptation of the method used for the dimethyl derivative [26]

$$2(C_2H_5)_2NH + POCl_3 \longrightarrow (C_2H_5)_2NP(O)Cl_2 + (C_2H_5)_2NH\cdot HCl$$

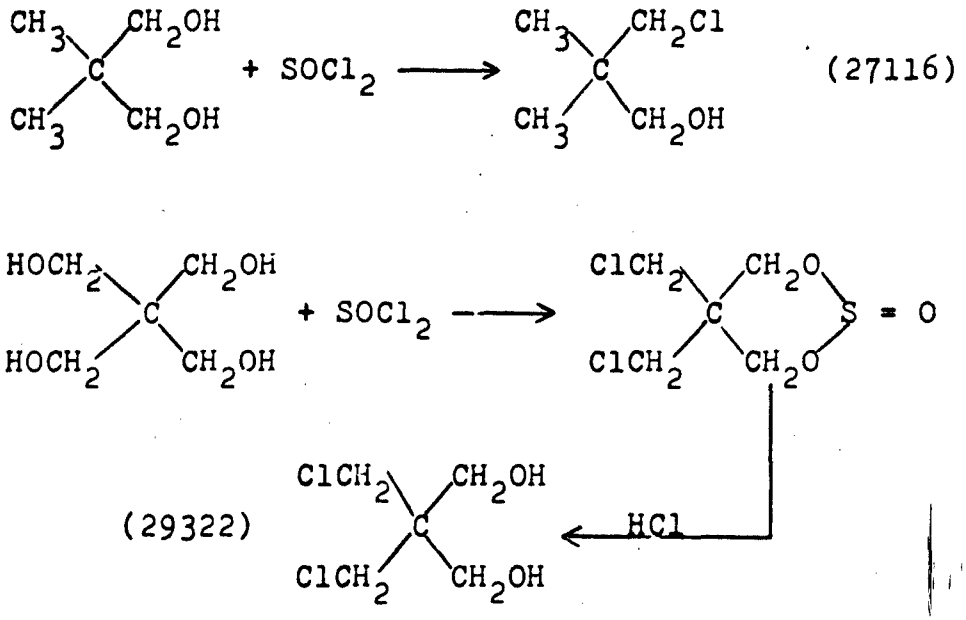
$$(C_2H_5)_2NH\cdot HCl + POCl_3 \longrightarrow (C_2H_5)_2NP(O)Cl_2 + 2HCl$$

This is a two-step reaction in which one-half of the diethylamine is immediately converted to the phosphoramidic dichloride; the other half of the amine forms the hydrochloride which reacts slowly with phosphorus oxychloride to produce a second mole of product. Amine hydrochlorides can be used with equal facility in this reaction. The product appeared stable on long standing.

4. ALCOHOLS

a. Chloroalkyl

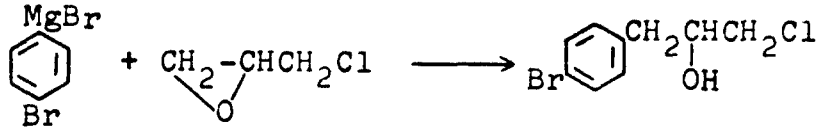
This class was synthesized by reaction of thionyl chloride on a multifunctional alcohol:



Higher-halogenated analogs, up to the per-halogenated derivatives, are also formed during the reaction but these can be held to a minimum by adjusting the stoichiometry and reaction conditions. For example, 2,2-bis-(chloromethyl)-1,3-propanediol can be prepared in much higher yields by the method of Pietsch[27] (80-95%) than by the method of Mooradian and Cloke[28] (40-60%). The method of Pietsch employs lower temperatures, higher ratios of reactants, longer reaction time and a different method of isolation than that of Mooradian and Cloke who obtained considerable amounts of higher-halogenated analogs.

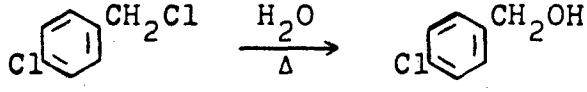
b. Aralkyl

A low yield (11%) of 3-bromophenyl-1-chloro-2-propanol (32864) was obtained by the following reaction:



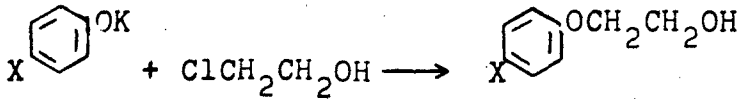
A mixture of compounds, varying from solids to viscous liquids, was obtained on distillation. This is in accordance with the literature [29], as a number of compounds, including $RCH_2CH(OH)CH_2Cl$, $XCH_2CH(OH)CH_2Cl$ and $CH_3C(R)=CHCHR$ have been isolated from similar reaction mixtures. These products apparently are not the result of a rearrangement but are due to statistical substitution [30]. It is evident that other compounds in this type of reaction are as yet unidentified, as the total yield of products is often less than 50% of theory.

p-Chlorobenzyl alcohol was prepared in an 87% yield by hydrolysis of the analogous benzyl chloride:



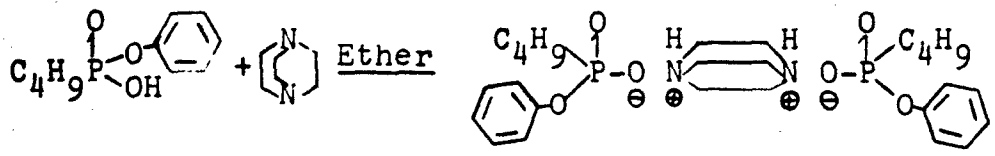
c. Aryloxyalkyl

Compounds in this class were prepared in high yield by the reaction of a substituted potassium phenoxide with an aliphatic chloroalcohol in alcoholic solution:



5. SALTS

1,4-Bis(butyl(phenoxy)phosphinyloxy)-1,4-dihydro-1,4-diazonia-bicyclo[2.2.2]octane was prepared by the neutralization of butyl hydrogen phenylphosphonate with 1,4-diazobicyclo[2.2.2]octane (Dabco):



This amine salt was prepared in an attempt to solubilize butyl hydrogen phenylphosphonate with a strong organic base (in contrast with KOH) but the salt did not have sufficient solubility in aqueous systems to be of further interest.

6. DIPHOSPHINE DISULFIDES

Tetramethyldiphosphine disulfide (27067) was synthesized according to the procedure of Reinhardt, et al.[31]

$$PSCl_3 + \underset{\text{(excess)}}{CH_3MgBr} \xrightarrow{\text{Ether}} (CH_3)_2\overset{S}{\overset{\|}{P}}-\overset{S}{\overset{\|}{P}}(CH_3)_2$$

This disulfide intermediate represents the only known, practical route to lower alkylphosphinic acids.

Thiophosphoryl chloride appears to be unique in its reaction with Grignard reagents in that it invariably gives the tetraalkyl dimer. In contrast, phosphorus oxychloride will substitute stepwise with Grignard reagents and give mixtures which consist mainly of trialkylphosphine oxides.

C. MISCELLANEOUS REACTIONS

This section includes preparations which were either unsuccessful or which produced other than the desired products. It can be divided into four classes of reactions:

(1) Reactions in which the desired product hydrolyzed during its formation (32883; 27072; 35140);

(2) Reactions in which polymeric materials and/or tars were produced (27121; 30053; 35137; 29328; 27091; 29312);

(3) Reactions which gave inseparable mixtures (29321; 29331; 27118; 35122; 29342);

(4) Reactions which gave mixtures from which a by-product could be isolated and identified (35109; 29314; 30057; 27075).

VI. EXPERIMENTAL

A. FINAL PRODUCTS

1. PHOSPHATES

Diethyl potassium phosphate (Cpd. 468) MRC 23022, 23026

Diethyl phosphorochloridate (172.6 g., 1 mole) was added dropwise at 10° to a vigorously stirred solution of potassium hydroxide (125 g., 2 moles @ 90%) in 500 ml. of water. The solution was adjusted to pH 8.2 by dilute potassium hydroxide, filtered and then concentrated in a boiling water bath using water pump vacuum until a quantity of potassium chloride separated. The solution was diluted with methanol and filtered. The filtrate was evaporated to dryness and the residue was dissolved in 250 ml. of methanol, cooled to 0 to 5° and filtered. The total insolubles, as potassium chloride, were 73 g. (theory 74.5 g.). Removal of the methanol and drying of the residue in a vacuum oven at 90°-110° for 18 hours yielded 164 g. (85%) of a white solid, an aqueous solution of which gave a pH of 6.9.

A second preparation in which the pH was adjusted to 9.8 gave the product in about 90% yield.

^{31}P magnetic resonance at -0.6 ppm. (quintet, J_{PH}= 6 cps.) is consistent with the structure $(C_2H_5O)P(O)OK$ in D_2O (solvent).

Proton magnetic resonance for the $POCH_2CH_3$ groups is observed as two general multiplets at 4.07 ppm. (two overlapping quartets), characterizing the presence of $PO\{CH_2\}CH_3$, and at 1.40 ppm. (triplet), indicating the $-CH_2\{CH_3\}$ group. The proton magnetic resonance pattern was referenced externally to TMS. Residual protons in D_2O (solvent) appeared at 4.8 ppm.

Diethyl potassium phosphate (Cpd. 468) MRC 23033, 23036

A mixture of triethyl phosphate (400 g., 2 moles), potassium hydroxid (120.4 g., 2 moles @ 90%), 1500 ml. of absolute alcohol and 70 ml. of water was refluxed for 20.5 hr. The solution was evaporated to dryness in a rotary evaporator in a boiling water bath. The solids were washed by decantation with ether to remove unreacted triethyl phosphate. The residue was redried at 10 mm. in a boiling water bath. The yield of white solid was 343 g. (89.2%).

A 40% aqueous solution had a pH of 10.36.

A second, identical run, refluxed for 32 hr., gave a 77.6% yield of product. It was oven-dried at 110°.

Dimethyl potassium phosphate (Cpd. 442) MRC 23027

Dimethyl phosphorochloridate (181 g., 1.25 moles) was added dropwise at 10°- 12° to a solution of potassium hydroxide (156 g., 2.5 moles @ 90%) in 600 ml. of water. The pH was adjusted to 9.4 and the product was obtained as on 23022. Yield of white solid was 182 g.(89%).

Dimethyl potassium phosphate (Cpd. 484) MRC 23034

A mixture of trimethyl phosphate (300 g., 2.14 moles), potassium hydroxide (120.4 g., 2 moles @90%), 1500 ml. of methanol and 70 ml. of water was refluxed for 12 hr. The reaction was worked up as in experiment 23036. The white, crystalline product weighed 298 g. (90.7% yield). A 40% aqueous solution had a pH of 3.6.

^{31}P chemical shift at -3.2 ppm. appears to be consistent with the proposed structure. Since ^{31}P in $(CH_3O)_3P(O)$ has a chemical shift of ~-0.5 ppm. and in $CH_3OP(O)(OK)_2$ the chemical shift is -5.4 ppm.,

it should follow that the chemical shift for $(CH_3O)_2P(O)OK$ should fall between these two structures (-3.2 ppm.).

Proton magnetic resonance for the $-POCH_3$ grouping is observed as a doublet (J_{PH}=11 cps) at 3.96 ppm. and the residual HDO in D_2O (solvent) at 5.02 ppm. Both resonances were referenced externally to tetramethylsilane. The spectral data are consistent with the $(CH_3O)_2P(O)OK$ structure.

Partially Hydrolyzed Tetraethylene Glycol-Phosphorus Oxychloride Reaction Product (Cpd. 672) MRC 32894

Phosphorus oxychloride (61.3 g., 0.4 mole) was added dropwise to a solution of the dipotassium salt of tetraethylene glycol in 500 ml. benzene, made by treating a benzene solution of tetraethylene glycol (116.5 g., 0.6 mole) with potassium metal (46.9 g., 1.2 atoms), while holding the temperature at 55° or above. The slurry was refluxed one hour and then filtered. The solids were freed of benzene and then dissolved in 2 liters of water containing an excess of potassium hydroxide (40 g.; 22.4 g. theory). The solution was refluxed overnight, adjusted to pH 9.4, and then evaporated to dryness on a steam bath. The residue was treated, first with benzene to remove tetraethylene glycol, and then with methanol to separate potassium chloride. The methanolic solution was filtered and evaporated to dryness leaving a viscous, dark brown mass. The yield was slightly over theory.

Reaction of diethylene glycol (3.0 moles) with phosphorus oxychloride (0.33 mole) and subsequent hydrolysis (Cpd. 668) MRC 28531

Sodium (23 g., 1 atom) was dissolved with stirring in diethylene glycol (318.4 g., 3.0 moles) at 65-100°. The stirred solution was cooled to 50° and the phosphorus oxychloride was added dropwise.

During the addition the temperature rose to 95° where it was held for 2 hr. To the cold solution was added methanol (450 ml.) and ether (900 ml.) followed by filtration to remove the sodium chloride (collected 50 g.; theory 58.5 g.).

The ether and methanol were removed under vacuum and replaced with ethanol (500 ml.) containing potassium hydroxide (20 g.) and water (70 ml.). The solution was refluxed for 16 hr. at which time the pH by meter was 11.75. In order to further lower the pH, triethyl phosphate (20 g.) was added, and refluxing was continued for 21 hr., at which time the pH was 9.8. The ethanol and the excess diethylene glycol were distilled to 120°/5 mm. The oily residue was dissolved in methanol and filtered from additional sodium chloride. Removal of the methanol yielded a residue of 114.6 g.

Reaction of methyl phosphorodichloridate (2 moles) with triethylene glycol (3 moles) MRC 31431

A benzene solution (180 ml.) of methyl phosphorodichloridate (65 g., 0.436 mole) was added dropwise with stirring below 10° to a solution of triethylene glycol (100 g., 0.666 mole) and triethylamine (90 g., 0.89 mole) in 420 ml. of benzene. The reaction was then warmed to reflux for 5 hr. followed by filtration to remove the amine hydrochloride. Evaporation of the benzene yielded a residue of 107 g., (theory 133 g.). This residue was subsequently hydrolyzed.

Hydrolysis of the products from the reaction of methyl phosphorodichloridate (2 moles) with triethylene glycol (3 moles) (Cpd. 679) MRC 31432

The reaction product (107 g.) from the previous experiment (31431) was hydrolyzed by refluxing in ethanol (500 ml.) containing potassium hydroxide (16 g.) and water (50 ml.). After 20 hr. of

refluxing the pH was 12.7. In an effort to lower the pH, additional triethyl phosphate (10 ml.) was added and refluxing was continued for 23 hr., after which the pH was 12. 3. The solution was topped in a rotating evaporator in a boiling water bath under water pump vacuum, yielding a residue of 106 g. and a N/1 solution gave a pH of 8.2

Potassium Salt of 5,5-Bis(chloromethyl)-2-hydroxy-1,3,2-dioxaphosphorinane-2-oxide (Cpd. 640) MRC 32887

Potassium hydroxide was added to a solution of 5,5-bis(chloromethyl)-2-hydroxy-1,3,2-dioxaphosphorinane-2-oxide (33.0 g., 0.14 mole) in 250 ml. water tc pH 8.75, which had been previously determined as the endpoint. The solution was evaporated to dryness and a methanolic solution of the solids was charcoaled, filtered and evaporated to dryness to give a 99.3% yield of the product.

Dipotassium ethyl phosphate (Cpd. 488) MRC 27114, 27140

Ethyl phosphorodichloridate (288 g., 1.77 moles) was added over a two-hour period to a stirred mixture of potassium hydroxide (440 g., 7.09 moles) in water (1000 ml.) at 14°. The pH of the solution was adjusted to 9.5 and concentrated to 400 ml. followed by cooling, which enabled filtration of most of the potassium chloride. The solution was evaporated to dryness in a rotatory vacuum evaporator. The solids were triturated with methanol to remove traces of potassium chloride. Evaporation of the methanol yielded 263 g. (75%) of dipotassium ethyl phosphate.

NMR (^{31}P) showed a chemical shift in ppm. at -4.2 (triplet).
NMR (^{1}H) showed chemical shifts in ppm. at 5.05 (residual OH in D_2O), 4.05 ($PO\{CH_2\{CH_3$; overlapping quartets) and 1.41 ($POCH_2\{CH_3\}$; triplet).

Dipotassium methyl phosphate (Cpd. 443) MRC 27110

To a stirred mixture of potassium hydroxide (44.8 g., 0.8 mole) in water (60 ml.) at 0-5°, was added methyl phosphorodichloridate (30 g., 0.201 mole). The pH was adjusted to 8.9 and the mixture was evaporated to dryness under vacuum on a water bath. The solids were triturated with methanol (150 ml.) and filtered at 0° to remove potassium chloride. Removal of the methanol under vacuum yielded 28 g. (74%) of product.

NMR (^{31}P) showed a chemical shift in ppm. at -4.2 (quartet; J_{PH}=11 cps.).

Potassium salt of 5,5-dimethyl-2-hydroxy-1,3,2-dioxaphosphorinane-2-oxide (Cpd. 493) MRC 27146

2,2-Dimethyl-3-chloropropyl phosphorodichloridate (10 g., 0.0418 mole) was added to a solution of potassium hydroxide (10.4 g., 0.1672 mole @ 90%) in water (30 ml.) at ice bath temperature. The pH was adjusted to 9.5 and the mixture was extracted with heptane to remove any 2,2-dimethyl-3-chloropropanol. The aqueous solution was evaporated to dryness at 90°C. Treatment with methanol, filtration, then removal of solvent to 90° yielded 2 g. (23.4%) of the product.

NMR (^{1}H) showed chemical shifts in ppm. at 5.17 (residual OH in D_2O), 4.45 ($PO\{CH_2\}CH_2$; doublet), 4.09 (small impurity) and 1.50 $\left(\begin{matrix} CH_3 \\ | \\ \{C\} \\ | \\ CH_3 \end{matrix}\right)$.

NMR (^{31}P) showed chemical shifts in ppm. at +3.3 ($KOP(O)(OR)_2$; quintet) and + 10.3 (small impurity).

Potassium salt of 2-hydroxy-1,3,2-dioxaphosphorinane-2-oxide
(Cpd. 727) MRC 34835

2-Chloro-1,3,2-dioxaphosphorinane-2-oxide (39.2 g., 0.25 mole) (34831) was added at 0 to -5° slowly with stirring to a water (500 ml.) solution of triethylamine (50.6 g., 0.5 mole). After stirring the solution for 0.75 hr. at -3°, it was treated with a water (50 ml.) solution of potassium hydroxide (31.1 g., 0.5 mole @ 90%) holding the temperature below 0°. At this point the solution had a pH of 11.7, and on treatment with 2.5 g. of 2-chloro-1,3,2-dioxaphosphorinane it dropped to 6.5. The pH of the solution was adjusted to 8.95 with dilute potassium hydroxide and evaporated to dryness in a boiling water bath in a rotating evaporator under water pump vacuum. The solids were dissolved in methanol (400 ml.) and filtered to remove potassium chloride (17.4 g.). The methanol was removed under vacuum and the solids were again dissolved in methanol (150 ml.) and filtered, yielding 2 g. of potassium chloride for a total of 19.4 g. (theory 19.8 g.). Final removal of the methanol yielded 43.4 g. of a white crystalline product (theory yield 44 g.).

Bis(m-chlorophenyl) Potassium Phosphate (Cpd. 591) MRC 29318

Bis(m-chlorophenyl) phosphorochloridate (100g., 0.30 mole) was added dropwise to a mixture of potassium hydroxide (37.9 g., 0.60 mole @ 88%), 250 ml. water and 50 ml. ether while holding the temperature at ~15°. The ether layer sank to the bottom after completion of addition, but rose to the top after stirring overnight at room temperature. The solution was evaporated to dryness in vacuo on a steam bath and the residue was dried at 90° in vacuo. The solids were treated first with methanol, then ethanol, to separate the potassium chloride. The ethanolic solution was passed through a column of caticnotropic aluminum oxide to remove m-chlorophenol and color, and then evaporated to dryness to give a 93% yield of product.

Some hydrolysis of the ester group took place as evidenced by a strong odor of m-chlorophenol.

Diphenyl Potassium Phosphate (Cpd. 771) MRC 35121

A suspension of diphenyl phosphorochloridate (200.4 g., 0.75 mole) in 450 ml. water was vigorously stirred at 96-98° for 3 hr. The water was removed in vacuo up to a temperature of 145°. The residue was resuspended in water (400 ml.) and the mixture was adjusted to pH 9.55 with potassium hydroxide. The solids dissolved at pH 2.5. The solution was evaporated to dryness at 90°/12 mm. and a methanolic solution of the residue was charcoaled, filtered, then evaporated to dryness giving a near theory yield of a white, amorphous solid.

Potassium di[β-(2-pyridyl)ethyl] phosphate (Cpd. 692) MRC 34807

An ethanol (300 ml.)-water (100 ml.) solution of tri[β-(2-pyridyl)-ethyl] phosphate (109 g., 0.262 mole) and potassium hydroxide (13.9 g., 0.222 mole) was refluxed with stirring for 26 hr. after which time the pH was 9.83. The hydrolyzate was filtered and evaporated to dryness in a boiling water bath under water pump vacuum in a rotating evaporator. The oily residue was dissolved in methanol (500 ml.), and treated twice with decolorizing charcoal. After evaporating the methanol, the oily residue was redissolved in water (100 ml.) and washed four times with 100 ml. of ether. Final evaporation of the water yielded 81.1 g. of a thick oil (theory 83.2 g.).

Potassium di(2-phenoxyethyl) phosphate (Cpd. 691) MRC 34808

Tri(2-phenoxyethyl) phosphate (125.3 g., 0.274 mole) was dissolved in ethanol (350 ml.), treated with a potassium hydroxide (14.6 g., 0.234 mole) solution in 100 ml. of water and refluxed for 26 hr.

The pH became constant at 10.97. The solution was evaporated to an oily residue, redissolved in 500 ml. of methanol, treated with decolorizing charcoal, filtered and the solvent removed at 95°/5 mm. A white crystalline residue was obtained on addition of 700 ml. of ether. The solid was separated by filtration and dried at 95°/10 mm., yield 73 g.

2. PHOSPHONATES

Ethyl potassium ethylphosphonate (Cpd. 486) MRC 23037

A mixture of diethyl ethylphosphonate (365 g., 2.2 moles), potassium hydroxide (120.4 g., 2 moles @ 90%), 1500 ml. of absolute alcohol and 70 ml. of water was refluxed for 76 hr. The pH was 9.4. Most of the alcohol was removed by distillation and the residual solution was treated with charcoal, filtered, and evaporated to dryness on a rotary evaporator in a boiling water bath under water pump vacuum. The dry salt was washed on a funnel with ether to remove unhydrolyzed phosphonate and redried in a rotary dryer at 9 mm. in a boiling water bath. The yield of white solid was 318 g. or 90.2%. A 40% aqueous solution of this material gave a pH of 10.1.

Methyl potassium methylphosphonate (Cpd. 485)

MRC 27071, 23040

A mixture of dimethyl methylphosphonate (273 g., 2.2 moles), potassium hydroxide (120.4 g., 2 moles), 1500 ml. of methanol and 70 ml. of water was refluxed for 17 hr. Approximately 1 liter of methanol was removed by distillation. The residual solution was treated with charcoal, filtered and evaporated to dryness. The residue was washed with ether to remove excess phosphonate and dried in a boiling water bath at 6 mm. Yield of white solid 267 g. (90%).

NMR (^1H) showed chemical shifts in ppm. at 4.85 (residual OH in D_2O); 3.67 (doublet; $PO\{CH_3\}$) and 1.38 (doublet; $P\{CH_3\}$). The relative number of protons was 2.9+:3.0; theory, 3.0:3.0.

Dipotassium ethylphosphonate (Cpd. 490) MRC 27132, 27145)

Pure ethylphosphonic acid (6.8 g., 0.06 mole) was titrated with 30% potassium hydroxide to pH 10.3 and evaporated to dryness in vacuo at 85°. The yield was theoretical.

Dipotassium methylphosphonate (Cpd. 489) MRC 27127, 27144

Methylphosphonic acid (10 g., 0.104 mole) was titrated with 30% potassium hydroxide to pH 10 and evaporated to dryness in a rotary evaporator. The yield was theoretical.

NMR (^1H) showed a chemical shift in ppm. at 1.16 (doublet; J_{PH}=15-16 cps.).

Potassium ethyl p-chlorophenylphosphonate (Cpd. 631) MRC 32390

Diethyl p-chlorophenylphosphonate (130.5 g., 0.525 mole) was hydrolyzed by refluxing for 6.5 hr. in ethanol (300 ml.) containing water (25 ml.) and potassium hydroxide (30.1 g., 0.5 mole @ 90%). The alcoholic solution was filtered and evaporated to dryness in a rotating evaporator under water pump vacuum in a boiling water bath. The solids were washed with ether to remove any chlorophenol and redried as before. Yield 102.6 g. (theory 113.7 g.). The pH of a 40% solution of this salt became constant at 9.38.

3. PHOSPHINE OXIDES

Tris(hydroxymethyl)phosphine oxide (Cpd. 438) MRC 23020

A mixture of tetrakis(hydroxymethyl)phosphonium chloride (238 g., 1 mole; 80%; Hooker), barium carbonate (197.4 g., 1 mole) and 400 ml. of water were heated at reflux with stirring for 10 hr.( ). Excess barium carbonate was removed by filtration and the soluble barium chloride was precipitated with dilute cold sulfuric acid. The solution was filtered and concentrated by distillation to remove formic acid and possibly some hydrogen chloride. The residue was diluted to about 1000 ml. with water, decolorized with charcoal and passed thru Amberlite IR-45 ion exchange resin until neutral. The water was removed until the amber-colored liquid residue weighed 179 g. (theory 140 g.).

Two phosphorus environments in a molar ratio of 90/10 are indicated by ^{31}P magnetic resonance at -49.2 ppm. (broad) and -26.4 ppm. (sharp). The former characterizes the presence of $(HOCH_2)_3P(O)$ as the major constituent, whereas the latter is indicative of an unidentified phosphorus environment containing no protons or dissimilar phosphorus in close proximity. Spectra were recorded for an undiluted sample.

4. PHOSPHINATES

Potassium Bis(hydroxymethyl)phosphinate MRC 23019

An attempt was made to prepare this compound in general accordance with Hoffman's method[19], but substituting potassium hydroxide for the barium hydroxide. Tetrakis(hydroxymethyl)phosphonium chloride (238.2 g., 1 mole; 80%; Hooker) was treated gradually with a water (250 ml.) solution of potassium hydroxide (120.4 g., 2 moles

@ 90%). A vigorous evolution of hydrogen took place and the solution was finally refluxed until no more hydrogen was evolved. The solution was treated with decolorizing carbon, filtered and 130 ml. of water was distilled; filtration yielded 46 g. of solids as potassium chloride. An additional 100 ml. of water was removed, 250 ml. of methanol added, and the solution was filtered again to separate the potassium chloride (26 g.). The total potassium chloride collected was 72 g. (theory 74.6 g.). The methanol solution was decolorized with charcoal and filtered thru Attapulgus clay. Removal of the methanol in a boiling water bath (90°/10 mm.) yielded 176 g. of product (theory, 164 g.).

A 40% solution of this residue had a pH of 6.0 and crystallized at -15°C. A 50% solution had a pH of 6.5 and crystallized at -22°C.

NMR (^{31}P) chemical shift and assignment is as follows,

Peak	Chemical shift ppm.	Assignment	Relative Area
1	-46.6	$R_3P(O)$	1.04
2	-34.4	$R_2P(O)OK$	1.00

This suggests the sample is a 1 to 1 mixture of $(HOCH_2)_3P(O)$ and $(HOCH_2)_2P(O)OK$. Our reference file lists the chemical shifts in ppm. as $(HOCH_2)_4PCl$ (-25.2), $(HOCH_2)_3P(O)$ (-45 to -49), $(ClCH_2)_2P(O)OH$ (-32.0) and $HOCH_2P(O)(OH)_2$ (-23.5).

Dimethylphosphinic acid (Cpd. 749) MRC 37355

Hydrogen peroxide (30%; 179 g., 1.58 moles) was added dropwise with stirring to a refluxing mixture of carbon tetrachloride (330 ml.) and tetramethyldiphosphine disulfide (98 g., 0.53 mole) over a period of 3.5 hr. and refluxing was continued for 18.5 hr. Starch-iodide paper confirmed the absence of peroxides at this point.

The reaction mixture was filtered and the water layer evaporated to dryness first under aspirator vacuum, then under a vacuum pump with a rotary flash evaporator in a boiling water bath. The yield was 83.2 g. (83.4%), m.p. 87-88°C. Literature[31,17] m.p. 88.5-90.5° and 85-87°.

5. PHOSPHORAMIDATES

Methyl Potassium N-Methyl-N-Phenylphosphoramidate (Cpd. 766)

MRC 31447

Dimethyl N-Methyl-N-Phenylphosphoramidate (112 g., 0.53 mole) was dissolved in methanol (500 ml.) containing potassium hydroxide (31.1 g., 0.5 mole @ 90%) and 100 ml. of water. The solution was refluxed for 24 hr. after which the pH was 6.8. The solution was adjusted to a pH of 7.2, filtered, and the methanol was removed under vacuum in a rotating evaporator. The residue was dissolved in water and extracted with ether to remove an oily substance. Evaporation of the water gave 91 g. of solids which were purified by dissolving first in methanol, then in ethanol, followed by cooling to -40° and filtering. The product was obtained by evaporating the ethanolic solution to dryness in a rotary evaporator.

m-Chlorophenyl potassium dimethylphosphoramidate (Cpd. 481)

MRC 27092

m-Chlorophenyl dimethylphosphoramidochloridate (50.8 g., 0.2 mole) was added in one portion, without cooling, to a solution of potassium bicarbonate, made by adding dilute hydrochloric acid (3N) to a solution of potassium carbonate (55.2 g., 0.4 mole) in 100 ml. water until the phenolphthalein endpoint was reached (pH 8.7). The mixture became homogeneous after stirring 48 hr. at room temperature; pH 8.7. The solution was evaporated to dryness in vacuo on a steam bath. The residue was dried at 90°/15 mm. and it was first treated with methanol to separate potassium chloride,

then with ethanol to separate unreacted potassium bicarbonate. An 82% yield of product was obtained on evaporation of the ethanol solution.

NMR (^1H) showed chemical shifts in ppm. at 7.67 (aromatic) and 3.03 (doublet: $PN\{CH_3\}$). The relative number of protons was 4.0:6.0; theory 4.0:6.0.

A second run, employing a benzene/aqueous potassium bicarbonate mixture at benzene reflux, resulted in nearly complete hydrolysis of the product.

6. PHOSPHOROTHIONATES

Diethyl Potassium Phosphorothionate (Cpd. 502) MRC 27147

Potassium (19.5 g., 0.5 atom) was dissolved under nitrogen at 20°-40° in a stirred mixture of diethyl phosphite (69 g., 0.5 mole) and 1,2-dimethoxyethane (250 ml.). Sulfur (16 g., 0.5 atom) was added slowly under nitrogen with cooling. The reaction mixture was heated to 60° then stirred overnight at room temperature. Ethanol was added slowly to destroy excess potassium. The solution was filtered, diluted with ether and the resulting precipitate was dried at 50° in vacuo. The crude product was recrystallized from ethanol to yield 66.5 g. (64%) of product.

NMR (^{31}P) in D_2O showed chemical shift at -54.8 ppm (quintuplet; J_{PH}=7-9 cps.) which is consistent with $NaOP(S)(OC_2H_5)_2$.

NMR (^1H) in D_2O gave no indication of OH or labile protons.

3. INTERMEDIATES

1. DERIVATIVES OF PHOSPHORIC ACID

a. Phosphates

Tris[2-(p-bromophenoxy)ethyl] Phosphate (Cpd. 680) MRC 35119

Phosphorus oxychloride (30.7 g., 0.2 mole) in 200 ml. benzene was added dropwise in 0.75 hr. to a solution of 2-(p-bromophenoxy)-ethanol (141.1 g., 0.65 mole) and triethylamine (65.8 g., 0.65 mole) in 500 ml. benzene while holding the temperature at 5°-10°. The mixture was refluxed 10 hr. The solids were removed by filtration and the solution was evaporated to dryness. The residue was dissolved in methanol and, after filtration of a small amount of solids, the methanol was evaporated to dryness leaving a viscous residue which slowly crystallized.

Recrystallization from ethanol gave an 86.5% yield of product, m.p. 70.5-71.2°.

Tris(3-pyridyl) Phosphate (Cpd. 677) MRC 33841

Phosphorus oxychloride (24.5 g., 0.16 mole) was added dropwise at 15° to a well-stirred mixture of 3-pyridinol (52 g., 0.55 mole), triethylamine (70 g., 0.7 mole), benzene (400 ml.) and pyridine (100 ml.), and the mixture was held at 84° for 5 hr. The reaction was cooled, filtered, and the solvents were stripped to a pot temperature of 100°/2.0 mm. Treatment with charcoal and recrystallization of the solid from ether gave 48 g. (91%) of tris(3-pyridyl) phosphate, m.p. 49°.

Anal. Calcd. for $C_{15}H_{12}N_3O_4P$: N, 12.77; P, 9.42; Mol. Wt. 329.
Found: N, 12.64; P, 9.44; Mol. Wt. 335 (benzene).

NMR (^{31}P) showed chemical shifts in ppm. at +10.3 (single peak; D_2O) and +17.5 (single peak; acetone).

NMR (^{1}H) showed that all protons were aromatic in character.

The data appear to be consistent with the proposed structure.

Hydrolysis of tris(3-pyridyl) phosphate MRC 31436

Tris(3-pyridyl) phosphate (10.5 g., 0.032 mole), dissolved in water (10 ml.), was heated with stirring at reflux for 16 hr. Upon initial solution in water, considerable heat was generated which appeared in excess of heat of solution. Filtration of the hydrolyzate yielded 2.5 g. of white crystalline solid, m.p. 127-127; identified by mixed melting point as 3-pyridinol. Theory yield for one equivalent of 3-pyridinol is 3.34 g. The water was evaporated until the residue weighed 15.5 g. From the NMR data it appeared that the hydrolysis had progressed much further than the removal of one equivalent of 3-pyridinol.

^{31}P magnetic resonance at -1.1 ppm. suggests the orthophosphoric acid or salt of orthophosphoric acid as the major component. The minor resonance (approximately 8 mole %) at +11.0 ppm is probably due to either tripyridyl orthophosphate or dipyridyl orthophosphate.

Tris(2-phenoxyethyl) phosphate (Cpd. 678) MRC 34804

Phosphorus oxychloride (51.1 g., 0.333 mole) was added dropwise to a solution of 2-phenoxyethanol (145 g., 1.05 moles), and triethylamine (105 g., 1.04 moles) in benzene (50 ml.) at 5-10°.

The reaction mixture was then heated to reflux for 8 hr., cooled and filtered to remove the amine hydrochloride. The benzene was removed and the oily residue was dissolved in methanol and again filtered from precipitated solids. Removal of the solvent to 95°/5 mm. yielded 149.5 g., of oily residue, n_D^{25} 1.5504 (theory 152.8 g.). An attempt to distill this material resulted in decomposition.

Tris[β-(2-pyridyl)ethyl] phosphate (Cpd. 676) MRC 34805

Phosphorus oxychloride (51.1 g., 0.33 mole) in benzene (250 ml.) was added dropwise at 5-10° to a stirred benzene (500 ml.) solution of β-(2-pyridyl)ethanol (129.3 g., 1.05 moles) and triethylamine (118 g., 1.16 moles). The reaction was heated to reflux for 8 hr., cooled and filtered to remove the amine hydrochloride. Removal of the benzene under water pump vacuum yielded 136.2 g. of amber oil (theory 138.8 g.). The n_D^{25} was 1.5462 after treatment with decolorizing charcoal and filtering through supercel.

b. Alicyclic Phosphates

4-Ethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane MRC 29327

A mixture of 2-ethyl-2-hydroxymethyl-1,3-propanediol (268.4 g., 2.0 moles), triethyl phosphite (332.3 g., 2 moles) and 6 drops of triethylamine was slowly heated (1 hr.) to 104°, at which point ethanol (n_D^{25} 1.3591) began to distill. The reaction was allowed to run overnight (100°). The temperature was then slowly increased to 130° and the heat was removed. Distillation of the product on a odd 42" Vigreux column gave a 96.5% yield of product, b.p. 128-9°/21 mm., m.p. 56.5-57°; literature [32] m.p. 55-56°.

An attempt was made to prepare this compound according to the procedure given in U.S. 3,152,164 [21], and in two preparations in which triethylamine and water were used respectively as catalysts. A mixture of freshly distilled 1,3-propanediol (80 g., 1.05 moles) and diethyl phosphite (138 g., 1 mole) were heated at 140-150° for 1.5 hr. Vacuum (120 mm.) was then applied to the reaction until 84 grams of distillate was collected as ethanol (n_D^{25} 1.3612; theory 92 g.). The residue weighed 128.5 g. (theory 126 g.). On vacuum distillation through a 10" Vigreux column, the product appeared to undergo a violent reaction with some decomposition prior to distillation. Distillation results were as follows:

Fraction	Bp/mm	Gms.	n_D^{25}
1	-115/0.35	5	1.4315
2	115-118/0.35	8	1.4528
3	116-120/0.35-0.13	48	-
4	120/0.25-0.13	17	-
Residue		46	

Fractions 2, 3 and 4 were mushy solids.

A second run (31442) was made using freshly distilled 1,3-propanediol (51 g., 0.67 mole), diethyl phosphite (84 g., 0.608 mole) and six drops of triethylamine. The mixture was heated up to 145° and no alcohol distilled. Vacuum (140-150 mm.) was applied for 10 hr. at 130-140° and 49 grams of distillate (n_D^{25} 1.3617) was collected as ethanol (theory 55.9 g.). This product was vacuum distilled through a 10" Vigreux column and appeared to undergo violent reaction at 100°. Fractions collected were:

Fraction	Bp/mm	Gms.
1	-118/0.30	2
2	118-123/0.30-0.18	54
Residue		20

third run (31443) was made using freshly distilled 1,3-propanediol 86 g., 1.13 moles), diethyl phosphite (138.1 g., 1 mole) and water 1 ml.). The mixture was heated under nitrogen to 135° and 69 g. f distillate was collected as alcohol (n_D^{25} 1.3604). Vacuum (140 n.) was then applied at 135-140° for 4 hr. and an additional 9 g. f distillate was collected. The product was then distilled under 10" Vigreux column. As before, a violent reaction set in at 10-140° after which some distillate was collected:

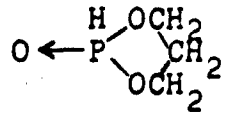
Fraction	Bp/mm	Gms.
1	-120/0.22	5
2	118-120/0.15-0.20	49
Residue		80

ractions 2, 3 and 4 (31441), 2, (31442) and 2(31443) were combined id redistilled through a Todd 42" Vigreux column. The following ractions were collected:

raction	Bp/mm	n_D^{25}	Gms.	
1	104-114/0.14	1.4359-1.4511	21.8	Solid-liquid
2	111/0.13	1.4525-1.4528	13.7	Solid
3	111/0.13-109/0.09	1.4533-1.4543	64.9	"
4	108/0.13	-	8.6	m.p. 41°
5	108/0.1	1.4548	38.9	"

ie molecular weight of Fraction 4 was determined by Galbraith Lab- ratories to be 133 and 135. The molecular weight of 1,3,2-dioxa- iosphorinane-2-oxide is 122.

The ^{31}P magnetic resonance data (Fraction 4), -27.7 ppm. (quintet) and +16.1 ppm. (quintet), and the spin-spin coupling constants, J_{PH_1}=710 cps. and J_{PH_2}=15 cps., are consistent with the



structure. Spectral data were recorded with an undiluted sample.

The infrared absorption is consistent with the proposed structure although it shows a small impurity absorbing at 3400 cm^{-1} which is either water or alcoholic hydroxyl.

5,5-Bis(chloromethyl)-2-hydroxy-1,3,2-dioxaphosphorinane-2-oxide MRC 32882

2,2-Bis(chloromethyl)-1,3-propanediol (73 g., 0.42 mole) and 740 g. polyphosphoric acid were heated on a steam bath with occasional swirling until homogeneous, then the solution was heated 16 hr. The reaction mass was poured slowly into 1.5 liters of 80:20 ice-water mixture. The aqueous solution was exhaustively extracted with ether in a liquid-liquid extractor to give a 34% yield of product, m.p. 146-147°; literature [33] m.p. 147-148°.

2-Chloro-1,3,2-dioxaphosphorinane-2-oxide MRC 34816

This preparation was carried out essentially according to U.S. 2,892,862 [23].

1,3-Propanediol (190 g., 2.5 moles) was added dropwise to phosphorus oxychloride (38.3 g., 2.5 moles) at 15-25° over a period of 1.5 hr. while maintaining the absolute pressure at 500 mm. The reaction was then stirred for 1 hr. at 500 mm., 1 hr. at 350 mm., and another hour at 50°/5 mm. Attempts to distill this product

howed decomposition at 80°-100°C., yet the patent reports distilling he product at 78°/0.2 mm. and a melting point of 39°. Preparation f this compound is repeated in 34831.

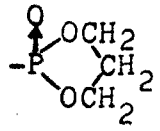
2-Chloro-1,3,2-dioxaphosphorinane-2-oxide MRC 34831

1,3-Propanediol (76.1 g., 1 mole) was added dropwise with stirring over a period of 0.5 hr. to phosphorus oxychloride (153.4 g., mole) maintaining the absolute pressure at 240 mm. and the temerature at 18-23°. When all had been added, stirring was contined for 0.5 hr. at 15-20/240 mm., 0.3 hr. at 25°/240 mm., and inally 1 hr. at 50-55°/14 mm.

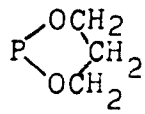
stillation was again attempted thru a 10" Vigreux column using a nall portion of the material. Decomposition was again evident at)°/0.03 mm. and increased at higher temperature. U.S. 2,892,862 ported distillation of the product at 78°/0.2 mm. (m.p. 39°) ing a falling-film type still.

e crude reaction product solidified on chilling, and after pressg between filter paper it melted at 42-44°. This product was ed directly for hydrolysis (34835).

P magnetic resonance at +1.8 ppm. (multiplet due to P,H spin-spin upling) is consistent with the proposed structure,



(no solvent).

oton magnetic resonance for the  grouping is observed

two complex multiplets ca. 5.0-4.0 ppm. and ca. 2.2-1.7 ppm., ving a relative peak area of 4.1 and 2.0, respectively. The specal data are consistent with the proposed structure.

c. Phosphorochloridates and Phosphorodichloridates

Bis(m-chlorophenyl) Phosphorochloridate

MRC 23038, 28379, 28507

A mixture of m-chlorophenol (514.3 g., 4.00 moles), phosphorus oxychloride (358 g., 2.33 moles) and titanium tetrachloride (1.6 ml.) was heated to reflux (110°) for 4 hr. The mixture was distilled on a 10" Vigreux column:

1. b.p. 108-109°/0.65-0.35 mm., 77.1 g., n_D^{25} 1.5401;
2. b.p. 130-227°/0.35-0.40 mm., 163.2 g., n_D^{25} 1.5670;
3. b.p. 227-224°/0.35-0.15 mm., 314.6 g., n_D^{25} 1.5784.

A second run was made with exact proportions of the first run except that the catalyst was omitted. Distillation on a Todd 42" Vigreux column gave the following fractions:

4. b.p. 126-142°/0.8-0.3 mm., 146.4 g., n_D^{25} 1.5381-1.5408;
5. b.p. 174-192°/0.48-0.18 mm., 201.7 g., n_D^{25} 1.5611-1.5670;
6. b.p. 220-245°/1.75-0.30 mm., 160.5 g., n_D^{25} 1.5784.

Fractions 1 and 4 were combined, then distilled to give 128.8 g., m-chlorophenyl phosphorodichloridate, b.p. 101-102°/0.025 mm., n_D^{25} 1.5372.

Fractions 2 and 5 were combined, then distilled to give 236.0 g., bis(m-chlorophenyl) phosphorochloridate, b.p. 158-165°/0.08-0.25 mm., n_D^{25} 1.5650. Fractions 3 and 6 were saved as tris(m-chlorophenyl) phosphate but were not redistilled.

Diethyl phosphorochloridate (34)

MRC 23021

Chlorine was passed into diethyl phosphite (414.3 g., 3 moles) below 5° until a yellow color developed. The hydrogen chloride

and excess chlorine were removed under water pump vacuum and the residue was distilled through a Todd 42" Vigreux column giving 455 g. (88% yield) of product, b.p. 86°/10 mm., n_D^{25} 1.4150.

Dimethyl phosphorochloridate MRC 23023

Dimethyl phosphite (550.3 g., 5 moles) was chlorinated as in experiment 23021. The product (348 g.; 53% yield) distilled at 81-82°/20 mm., n_D^{25} 1.4008.

Bis(β-chloroethyl) phosphorochloridate MRC 27122

2-Chloroethanol (161 g., 2.0 moles) was added dropwise over a two-hour period to a stirred mixture of phosphorus oxychloride (153.3 g., 1.0 mole) and heptane (200 ml.) at reflux (83°). Hydrogen chloride was removed by a nitrogen sweep. The mixture was distilled through a 12" x 1" Vigreux column to yield 45 g., (19%) of a material with b.p. 129-32°/1.3 mm., n_D^{25} 1.4705. Voshkus and Herweh [35] give b.p. 137-9°/5 mm., n_D^{25} 1.4742.

The product was originally intended for conversion to potassium bis(β-chloroethyl) phosphate but this conversion was not carried out because alkali α- and β-halogenated alkyl phosphates are unstable at elevated temperatures.

2,2-Dimethyl-3-chloropropyl phosphorodichloridate MRC 27128, 27143

2,2-Dimethyl-3-chloropropanol (207 g., 1.69 moles) was added under nitrogen over a two-hour period to a stirred mixture of phosphorus oxychloride (259 g., 1.69 moles) and hexane (200 ml.) at 75°. The product was distilled through a 12" x 1" Vigreux column to yield 10 g. (2%) of product, b.p. 55-8°/0.07 mm., n_D^{25} 1.4662.

NMR (^{31}P) showed chemical shifts in ppm. at -4.5 (triplet) and +3.8 (minor impurity).

ß-Chloroethyl phosphorodichloridate MRC 27123, 27124

2-Chloroethanol (80.5 g., 1.0 mole) was added dropwise over a two-hour period to a stirred mixture of phosphorus oxychloride (153.3 g., 1.0 mole) in hexane (200 ml.) at 60°. After 2 hr. additional reflux, distillation through a 12" Vigreux column gave 271.8 g. (69%) of product, b.p. 106°/14.0 mm., n_D^{25} 1.4682. Rossiiskaya and Kabachnik [36,37] give b.p. 71.5°/2.0 mm. and n_D^{20} 1.4960.

NMR (^{31}P) showed a chemical shift in ppm. at -6.2 (triplet).

NMR (^{1}H) showed chemical shifts in ppm. at 4.60 ($PO\{CH_2\{CH_2Cl$; multiplet) and 3.88 ($POCH_2\{CH_2\{Cl$; multiplet).

Ethyl phosphorodichloridate MRC 27109

Ethanol (138 g., 3.0 moles) was added over 0.75 hr. to a stirred mixture of phosphorus oxychloride (484 g., 3.15 moles) and ethyl ether (300 ml.) at 0° under a nitrogen purge. After stirring an additional 2 hr., the hydrogen chloride and excess phosphorus oxychloride were removed under water-aspirator vacuum at 0-10°. The product was distilled through a Todd Vigreux column to yield 371.4 g. (73%) of product, b.p. 56.5°/13.0 mm., n_D^{25} 1.4323. Grunze and Thilo [38] give b.p. 58°/13.0 mm.

Methyl phosphorodichloridate MRC 27108

Methanol (96 g., 3.0 moles) was added during 1 hr. to a stirred mixture of phosphorus oxychloride (460.5 g., 3.0 moles) and ethyl ether (300 ml.) at 0°, then stirred an additional 2 hr. Hydrogen

:hloride and excess phosphorus oxychloride were removed by water-
ıspirator vacuum at 0-10°. The product was distilled through a
:odd Vigreux column to yield 321 g. (72%) of product, b.p.
17.5°/13.0 mm., n_D^{25} 1.4332. Grunze and T..ilo [38] give b.p.
19°/13 mm.

IMR (^{31}P) showed a chemical shift in ppm. at -6.5 (quartet).

ın attempt to hydrolyze the dichloridate with water at 30°C.
esulted in hydrolysis of the CH_3-O-P linkage.

m-Chlorophenyl Phosphorodichloridate MRC 28353

Molten m-chlorophenol (514.2 g., 4.00 moles) was added dropwise
ver a period of 1.5 hr. to a stirred mixture of phosphorus oxy-
hloride (1226.8 g., 8.04 moles) and aluminum chloride (5.3 g.) while
olding the temperature at 95°-100°. The mixture was filtered,
hen distilled on a Todd 42" Vigreux column to give two fractions:

1. B.p. 100°/0.60 mm. - 98°/0.25 mm., 127.7 g., n_D^{25} 1.5371-1.5383;
2. B.p. 92°/0.05-0.07 mm., 454.5 g., n_D^{25} 1.5373.

he residue (167.1 g.) was considered to be mainly bis(m-chloro-
henyl) phosphorochloridate.

raction 1 was redistilled to give 93.5 g. product, b.p. 88°/0.11
m., n_D^{25} 1.5370. This material and Fraction 2 above were combined
epresenting a 59.9% yield of desired product.

2. DERIVATIVES OF PHOSPHONIC ACID

a. Phosphonates

Diethyl p-chlorobenzenephosphonate MRC 32387

This preparation was essentially according to Kosolapoff and Huber [39]. A mixture of phosphorus trichloride (412 g., 3.0 moles), aluminum chloride (133.3 g., 1 mole), and chlorobenzene (112.6 g., 1 mole) was heated at reflux with stirring for 8 hr. The excess phosphorus trichloride was removed up to 70° under a 10" Vigreux column at water pump vacuum (ca. 10 to 12 mm.). The Friedel-Crafts reaction was then diluted with tetrachloroethane (250 ml.) and chlorine was bubbled in at 20-25° until 59 g., had been absorbed. Ethanol (200 ml.) was then added dropwise to the stirred reaction mass held during the addition under water pump vacuum at 15-20° to remove the ethyl chloride and hydrogen chloride as it was formed. The reaction was then held under vacuum for 1.5 hr. at ambient temperature after which it was poured onto crushed ice (500 g.) containing concentrated hydrochloric acid (60 ml.). The organic layer was washed with water, dried over magnesium sulfate and distilled through a Todd 42" Vigreux column. The following fractions were collected:

Fraction	Bp/mm	n_D^{25}
1	117/0.45	1.5022
2	117-120/0.45	1.5017
3	118/0.45	1.5030
4	117/0.45	1.5022
5	117-114/0.45	1.5022-42

Fractions 2 through 5 were combined as product, yield 154 g., (theory 248.6 g.).

Dimethyl 2,3-epoxypropylphosphonate MRC 30063, 30068

Epibromohydrin (100 g., 0.73 mole) and trimethyl phosphite 31 g., 1.46 moles) were heated to reflux (~145°) for 3 hr. hyl bromide (26.5 g., 0.279 mole) was recovered in a dry-ice ap. Distillation yielded 46.5 g. unreacted bromohydrin, 133 g. ethyl methylphosphonate and 38.4 g. (32%) dimethyl 2,3-epoxy-opylphosphonate, b.p. 82°/0.07 mm., n_D^{25} 1.4450. Coover [40] es b.p. 85-7°/1.4 mm.

t (^1H) showed chemical shifts in ppm. at 3.71 ($PO\{CH_3\}$; doublet) l 3.3-1.3 (indefinite).

b. Phosphonochloridates

m-Trifluoromethylphenyl ethylphosphonochloridate MRC 32878-9

α,α,α-Trifluoromethyl-m-cresol (129.7 g., 0.80 mole) was added pwise over a period of 4.5 hr. to ethylphosphonic dichloride 8.2 g., 2.4 moles) at 150°-187°. The reaction mixture was purged n dry nitrogen for 1 hr. to remove excess hydrogen chloride and n distilled through a Todd 42" Vigreux column to give a 67% yield m-trifluoromethylphenyl ethylphosphonochloridate, b.p. 95%0.2 mm., 1.4658 and a 21.7% yield of bis(m-trifluoromethylphenyl) ethyl-sphonate, b.p. 125-126°/0.15 mm., n_D^{25} 1.4668.

Phenyl Butylphosphonochloridate MRC 24352

Phenol (47 g., 0.5 mole) was added dropwise with stirring over riod of 4.25 hr. to butylphosphonic dichloride (262.5 g., 1.5 s) while holding the temperature at 180-190°. The solution purged with a slow stream of dry nitrogen for an additional to remove traces of hydrogen chloride. Distillation on a Todd

42" Vigreux column gave two products:

1. Phenyl butylphosphonochloridate, b.p. 100°/0.05 mm., n_D^{25} 1.5095, 58% yield;
2. Diphenyl butylphosphonate, b.p. 143°/0.06 mm., n_D^{25} 1.5350, 14.5% yield.

NMR (^{31}P) showed chemical shifts in ppm. at -40.8 (1) and -25.2 (2).

NMR (^{1}H) showed chemical shifts (2) in ppm. at 7.19 (aromatic), 2.2-1.15 (multiplet; $P\{CH_2CH_2CH_2\{CH_3$) and 0.92 (triplet; $-CH_2\{CH_3\}$). The aromatic-aliphatic ratio was 10.0:9.2; theory, 10.0:9.0.

In a second experiment (21846) diphenyl butylphosphonate was obtained almost exclusively in the presence of catalytic amounts of aluminum chloride.

Phenyl Hydrogen Butylphosphonate MRC 24360, 24362

A mixture of phenyl butylphosphonochloridate (57.2 g., 0.24 mole), 50 g. ice, 50 g. water and 150 ml. ether was agitated in a sealed bottle for 18 hr. The ether layer was separated and the water layer extracted three times with small portions of ether. The ether layers were combined, dried, treated with charcoal and filtered through Attapulgus clay. Evaporation of the ether and low boilers up to 100°/0.06 mm. gave a 95.5% yield of a viscous, light yellow product.

NMR (^{31}P) showed a chemical shift at -27.8 ppm.

Attempts to distill a portion of this material on an 11" heated Vigreux column yielded phenol and a glassy residue, the physical and chemical properties of which closely resembled the anhydrides reported by Cherbuliez [42], i.e., $R(O)P<^{O}_{O}>P(O)R$, where $R=C_4H_9$.

c. Phosphonic Dichlorides

Ethylphosphonic Dichloride — MRC 28524

Over a period of 1.5 hr. phosphorus pentachloride (1729 g., 3 moles) was added portionwise through a powder funnel to a xylene lution (1700 ml.) of diethyl ethylphosphonate (683 g., 4.12 moles) i ferric chloride (9.1 g.). The temperature during the addition s maintained at 110°-120°; phosphorus oxychloride and ethyl loride came over at a head temperature of 105° using a short dis- .lation head. After all the phosphorus pentachloride had been led, the temperature of the reaction was raised until the head perature reached 127° at which point the distillation was contin- l under a Todd 42" Vigreux column.

following fractions were collected:

Fraction	Bp/mm	G.	n_D^{25}
1	107-109/99	103	1.4751-1.4649
2	109/99	359	1.4645

ction 2 represents a theoretical yield of 59%.

Butylphosphonic Dichloride — MRC 21836, 21840

Finely ground phosphorus pentachloride (1395 g., 6.68 moles) added portionwise (1 hr.) to a stirred mixture of dibutyl ylphosphonate (835 g., 3.35 moles), anhydrous ferric chloride 4 g.) and xylene (1 liter), while holding the temperature at -135°. Butyl chloride and phosphorus oxychloride began to till upon addition of ~1/5 of the phosphorus pentachloride. It necessary to occasionally interrupt the addition in order to ntain a minimum pot temperature of 125°. Distillation was con- ued, upon completion of addition, until the temperature of the

distillate reached 140°. The mixture was then distilled on a Todd 42" Vigreux column and the fraction boiling at 120°-124°/50 mm., n_D^{25} 1.4675-1.4649, was collected. Redistillation of this fraction gave 316 g. (54% yield) butylphosphonic dichloride, b.p. 124°/50 mm., n_D^{25} 1.4648.

NMR (^{31}P) showed a chemical shift in ppm. at -50.6.

The NMR (^{1}H) pattern was consistent with the proposed structure but overlapping environments prevented accurate integration and assignments.

p-Bromophenylphosphonic Dichloride MRC 32853

A mixture of bromobenzene (392.5 g., 2.5 moles), phorphorus trichloride (1027.5 g., 7.5 moles) and aluminum chloride (333.8 g., 2.5 moles) was refluxed for 8 hr. The excess phosphorus trichloride was removed up to 70°/10 mm. Freshly distilled 1,1,2,2-tetrachloroethane (625 ml.) was added as a solvent and 119 g. (1.7 moles) chlorine gas was introduced by weight difference (2 hr.) while holding the temperature at 22-23°. Absolute ethanol (230 g., 5 moles) was then added over a period of 1 hr. while maintaining nearly full aspirator vacuum on the system. The mixture was stirred at 25°/10 mm. for 2 hr. to remove excess hydrogen chloride and ethyl chloride. The mass was slowly poured into a mixture of 1500 g. ice and 150 ml. concentrated hydrochloric acid. A solid resulted, whereas the desired ester, diethyl p-bromophenylphosphonate, is a liquid. The solid-ester mixture was converted to p-bromophenylphosphonic dichloride, in order to get a greater separation of boiling points, as follows:

The solvents were removed up to a temperature of 140°/10 mm. and the residue was extracted three times with refluxing (overnight) concentrated hydrochloric acid. The hydrochloric acid was removed

· spontaneous evaporation. Thionyl chloride (650 g., 5.45 moles) ıs added to a suspension of the dry solids in benzene (500 ml.) at ;° and the mixture was refluxed 8 hr. The solution was filtered ıd then distilled through a Todd 42" Vigreux column to give two ·oducts: a 5.6% yield of phenylphosphonic dichloride, b.p. 7°/16 mm., n_D^{25} 1.5581; literature [42] b.p. 137-8°/15 mm., ^{5} 1.5581; and a 10.6% yield of p-bromophenylphosphonic dichloride, p. 169-172°/16 mm., n_D^{25} 1.5979; literature [43] b.p. 165°/16 mm.

d. Alkylphosphonic Acids

Ethylphosphonic acid (Cpd. 476) MRC 27129, 27138

Diethyl ethylphosphonate (166 g., 1.0 mole) and concentrated drochloric acid (450 ml.) were refluxed for 43 hr. The mixture s concentrated to dryness under water-aspirator vacuum and the lids were dried at 70° under vacuum. Recrystallization from her/heptane yielded 99 g. (90%) of product, m.p. 58-60°. solapoff [44] gives m.p. 44°, 30-5°, 61-2.5°.

R (^{1}H) showed chemical shifts in ppm. at 5.01 (residual OH in O), 1.93-1.20 (PCH_2CH_3; multiplet), and 1.20-0.54 (PCH_2CH_3; ltiplet).

Methylphosphonic acid (Cpd. 487) MRC 27112, 27139

Dimethyl methylphosphonate (420 g., 3.39 moles) and concen- ated hydrochloric acid (1400 ml.) were refluxed for 44 hr. The xture was concentrated under water-aspirator vacuum and the re- lting solids dried at 70° under vacuum. The yield of product s 303 g. (91%), m.p. 95°. A portion was recrystallized from ıer/acetone to give pure methylphosphonic acid, m.p. 102-3°. solapoff [45] gives m.p. 104-5°.

NMR (^1H) showed chemical shifts in ppm. at 5.68 (residual OH in D_2O) and 1.30 ($P\{CH_3\}$; doublet).

3. DERIVATIVES OF PHOSPHORAMIDIC ACID

a. Phosphoramidates

Dimethyl N-methyl-N-phenylphosphoramidate MRC 31446

N-methylaniline (219 g., 2.02 moles) was added dropwise to a solution of dimethyl phosphite (110.1 g., 1 mole) in 200 g. of carbon tetrachloride. There was no apparent reaction on heating to 40°. A mixture of bromotrichloromethane (143 g., 0.72 mole) and bromoform (70 g., 0.28 mole) was then added dropwise while holding the temperature at 20-30° with an ice bath. After stirring for 2 hr. and standing overnight, the reaction mixture was diluted with ether, cooled to 0° and filtered. Evaporation of the ether yielded 216 g. of a dark amber oil (theory 215 g.).

Dimethyl phosphoramidate (Cpd. 739) MRC 34841

This preparation was adapted from that of E. N. Walsh [24]. Ammonia gas was passed into a stirred solution of dimethyl phosphite (55 g., 0.5 mole) in carbon tetrachloride (100 g.) at 20-30° until the exothermic reaction ceased. The ammonium chloride was removed by filtration (25.4 g., theory 26.2 g.). The carbon tetrachloride was removed under water pump vacuum and the oily residue was dissolved in methanol (50 ml.), filtered cold, and precipitated from the very cold solution with ether (700 ml.). Yield Crop 1, 20.6 g., m.p. 40-41. Stepwise dilution with more ether yielded additional crops of crystals; Crop 2, 7.7 g., m.p. 39-40°; Crop 3, 17.8 g., m.p. 38-40°.

Tetramethyl phosphoramidate (Cpd. 460) MRC 27125

Dimethylamine (104 g., 2.3 moles) was metered into a well-tirred mixture of dimethyl phosphorochloridate (162.3 g., 1.12 oles) and ether (500 ml.) at 7° over 2 hr. The filtered mixture as chromatographed through Amberlite 1R-45(OH) resin to remove ast traces of chloride ions. Distillation through a Todd Vigreux olumn gave 131.3 g. (77%) of product, b.p. 81°/14.0 mm., n_D^{25} 1.4168. Kamai and Kharrasova [46] give b.p. 72-2.5°/11 mm., n_D^{20} 1.4175.

reatment of the distillate with Attapulgus clay removed traces of ntrained dimethylamine. The final product had a distinct terpene-ike odor.

Methyl Tetramethylphosphorodiamidate (Cpd. 462) MRC 27086

A solution of dimethylamine (180.4 g., 4 moles) in 400 ml. enzene was added over 2.5 hr. to a solution of methyl phosphoro-ichloridate (149 g., 1 mole) in 400 ml. benzene at 5-10°. The ixture was heated to 45° for 2 hr., cooled, then filtered. The olids were washed with dry benzene and the combined filtrates were istilled on a Todd 42" Vigreux column to give an 82% yield of prod-ct boiling at 99°/17 mm., n_D^{25} 1.4364. The distilled material was reated with amberlite IR-112(H), then with charcoal at 80° and iltered through an Attapulgus clay/charcoal/Hyflo Supercel mat remove traces of amine odor.

IR (^{1}H) showed chemical shifts in ppm. at 3.60 ($PO\{CH_3\}$) and 2.62 ($N\{CH_3\}$). The relative number of protons was 3.0:12.0; theory, 0:12.0.

b. Phosphoramidochloridates

m-Chlorophenyl dimethylphosphoramidochloridate

MRC 27082, 28368

A solution of dimethylamine (51.0 g., 1.13 moles) in 200 ml. benzene was added over a period of 2 hr. to a solution of m-chlorophenyl phosphorodichloridate (138.8 g., 0.57 mole) in 200 ml. benzene while holding the temperature below 10°. The slurry was then heated to 55° for 1 hr., cooled, and filtered. The filter cake was washed with benzene and the combined filtrates were distilled on a Todd 42" Vigreux column to give a 71% yield of product boiling at 124°/0.10 mm., n_D^{25} 1.5254.

NMR (^1H) showed chemical shifts in ppm. at 7.25 (aromatic) and 2.79 (doublet; $PN(CH_3)$). The relative number of protons was 4.0:6.2, theory, 4.0:6.0.

A second, larger run (0.71 mole) gave a 65% yield of desired product. Optimum yields appear to be obtained from 0.5-0.6 mole runs.

3-Trifluoromethylphenyl morpholinophosphorochloridate

MRC 32886

A mixture of morpholine (26.1 g., 0.3 mole) and triethylamine (30.4 g., 0.3 mole) was added dropwise over a period of 2 hr. to a solution of 3-trifluoromethylphenyl phosphorochloridate (83.7 g., 0.3 mole) in 250 ml. ether at 5°. The slurry was allowed to warm to room temperature and then refluxed 1.5 hr. The solids were removed by filtration, washed with ether and the combined ether filtrates were distilled to give a 32.5% yield of product boiling at 138-140°/0.3 mm., n_D^{25} 1.4862.

NMR (^1H) areas were integrated directly giving the relative number of protons as 8.0:4.0; theory, 8.0:4.0.

Diethylphosphoramidic Dichloride MRC 21842

Diethylamine (215 g., 2.94 moles) was added to phosphorus oxychloride (1806.3 g., 11.75 moles) with stirring over a period of .25 hr. while holding the temperature below 50°. The mixture was ıen stirred at reflux (115°) until it cleared (36 hr.). Dis-illation on a Todd 42" Vigreux column gave 488 g. of product 37% yield) boiling at 106-107°/18 mm., n_D^{25} 1.4622.

ALCOHOLS

a. Chloroalkyl

2,2-Dimethyl-3-chloropropanol MRC 27116.

Thionyl chloride (292 g., 2.45 moles) was added dropwise over period of 1.5 hr. to a refluxing mixture of 2,2-dimethyl-1,3-opanediol (256 g., 2.45 moles) and pyridine (218.6 g., 2.77 moles). ıe evolution of hydrogen chloride and sulfur dioxide was rapid. ıe mixture was diluted with ether, then washed with water, dilute drochloric acid and water. Distillation gave 207 g. (69%) of oduct, b.p. 71°/14.0 mm., n_D^{25} 1.4442. Mooradian [47] gives b.p. -6°/32 mm.

2,2-Bis(chloromethyl)-1,3-propanediol

MRC 29322, 29348, 32861, 32870

Thionyl chloride (1180 g., 10 moles) was added dropwise to a xture of pyridine (80 g., 1 mole) and pentaerythritol (408 g., moles) at 20° at such a rate that the white fumes in the reaction ask did not rise into the condenser. The rate of addition was creased to a small stream when the temperature began to drop and e white fumes disappeared. The mixture was stirred at 20° for

2 hr. and then allowed to warm to room temperature, whereupon it became solid. The solid was cautiously warmed to 60° (1 hr.), heated at 60-65° for 1 hr. followed by an hour at 90-95°. Distillation on a Todd Vigreux column gave an 81.5% yield of the cyclic sulfite, b.p. 147°/16 mm., N_D^{25} 1.5060.

A mixture of the cyclic sulfite (349 g., 1.67 moles) and 700 ml. 6 N hydrochloric acid was evaporated to dryness on a steam bath. A copious evolution of sulfur dioxide took place at 83° and the solution became homogeneous. Recrystallization of the residue from benzene gave a 97% yield of product, m.p. 82-82.5°; literature [27] m.p. 83°.

b. Aralkyl

3-Bromophenyl-1-chloro-2-propanol MRC 32864-8, 32871

Epichlorohydrin (306 g., 3.30 moles) was added to an ether (1400 ml.) suspension of the half Grignard of p-dibromobenzene, made from p-dibromobenzene (390 g., 1.65 moles) and magnesium (41.3 g., 1.70 moles) according to the directions of Bergmann and von Christiani [48], at such a rate that gentle reflux was maintained. The addition required 3.3 hr. The reaction mass was stirred for 2 hr. at reflux and then placed in an ice-salt bath. A solution of 102 g. ammonium chloride in 600 ml. water was added at a rapid dropwise rate while holding the temperature below 10°. Concentrated hydrochloric acid was then added until the emulsion broke and two distinct layers were formed. The ether layer was separated, filtered to remove a small amount of solids, and washed to neutrality with water. It was then distilled on a Todd 42" Vigreux column and the material boiling at 138-122°/16-0.13 mm. was saved. Refractionation gave a 10.7% yield of product, b.p. 120°/0.10 mm., n_D^{25} 1.5752.

IR (^{1}H) demonstrated the presence of a p-substituted benzene ring id the relative number of protons was 4.1:2.0:2.0:1.1:1.0; theory 0:2.0:2.0:1.0:1.0.

p-Chlorobenzyl alcohol MRC 27142

α,p-Dichlorotoluene (60 g., 0.37 mole) and water (4 l.) were fluxed to homogeneity (3.5 hr.). Crystals of product separated cooling. Four such runs were made using the same liquors, elding a total of 185.5 g., (87%) of product, m.p. 69-70°. ckson and Field [49] give m.p. 70.5°.

c. Aryloxyalkyl

3-(2,4-Dibromophenoxy)-1,2-propanediol (Cpd. 497) MRC 23039

2,4-Dibromophenol (208 g., 0.824 mole) was dissolved in 1000 .. of absolute alcohol containing potassium hydroxide (49.6 g., 82 mole). 3-chloro-1,2-propanediol (95 g., 0.86 mole) was then ided dropwise to the refluxing alcohol solution and reflux was con- nued for 8 hr. Potassium chloride (56 g.; theory 61.4 g.) was moved by filtration. Removal of the alcohol under a water pump cuum in a boiling water bath yielded 266 g., of a dark reddish l (theory 269 g.). The oily residue solidified on treatment th ether and was twice recrystallized from toluene, m.p. 91-92°.

Anal. Calcd. for $C_9H_{10}O_3Br_2$: C, 33.15; H, 3.09.
Found: C, 32.36; H, 2.98.

2-(p-Bromophenoxy)ethanol MRC 32874

2-Chloroethanol (150 g., 1.86 moles) was added dropwise at 25° an ethanol (1000 ml.) solution of potassium p-bromophenoxide, ide by azeotropic distillation of a mixture of p-bromophenol (292.3

g., 1.69 moles), potassium hydroxide (115.5 g., 1.81 moles @ 88%) and 35 ml. toluene. The mixture was refluxed overnight and filtered. The filtrate was distilled on a Todd 42" Vigreux column to give an 86.5% yield of product, b.p. 117-18°/0.13 mm., m.p. 49-55°. The material was recrystallized from cyclohexane/benzene (3:1), m.p. 56.5-57°, literature [50] m.p. 55°.

5. SALTS

1,4-Bis(butyl(phenoxy)phosphinyloxy)-1,4-dihydro-1,4-diazonia-bicyclo[2.2.2]octane — MRC 24364

Butyl hydrogen phenylphosphonate (4.28 g., 0.02 mole) in 10 ml. ether was added in one portion to 1,4-diazabicyclo[2.2.2]octane (1.12 g., 0.01 mole) in 25 ml. ether. The solution became cloudy, warmed slightly and then cleared. An oily layer, which would redissolve on warming, separated upon standing in the cold. Ether and low boilers were removed up to 100°/0.06 mm. giving a viscous light brown oil in theory yield.

NMR (^{31}P) showed a chemical shift at -22.8 ppm.

NMR (^{1}H) showed chemical shifts in ppm. at 13.87 ($\oplus NH$), 7.23 (aromatic), 2.92 (NCH_2CH_2N), 1.58 (multiplet; $PCH_2CH_2CH_2CH_3$), and 0.88 (triplet; $-CH_2CH_3$). The relative number of protons was 1.9:10.0:12.0:18.1; theory, 2.0:10.0:12.0:18.0.

6. DIPHOSPHINE DISULFIDES

Tetramethyldiphosphine Disulfide — MRC 27067

Thiophosphoryl chloride (234.0 g., 1.38 moles) was added to methyl magnesium bromide (4.5 moles) in ether (1800 ml.) at such a rate that the reaction temperature did not exceed 5° with a bath tempera-

ıre of -15° to -20°. The Grignard reagent was made from methyl romide (427 g., 4.5 moles) and magnesium (109.2 g., 4.5 moles) in ther (1800 ml.). A nitrogen atmosphere was maintained during the eaction. The bath was allowed to warm to -8° to -10° near the ıd of the addition in order to maintain stirring. The mixture ıs stirred for 2 hr. at room temperature, cooled to 10°., and then ıidified to pH 2 with cold, 10% sulfuric acid. The solids were ltered, washed with water and dried. A 76% yield of product, .p. 227-228°, was obtained after recrystallization from toluene/ hanol (3:1). Literature [31] m.p. 225-226°.

. MISCELLANEOUS REACTIONS

MRC 32883

-Trifluoromethylphenol was formed in the attempted synthesis of otassium 3-trifluoromethyl ethylphosphonate by hydrolysis of 3-ifluoromethylphenyl ethylphosphonochloridate with potassium bi-ırbonate.

MRC 27072

tbasic potassium phosphate and potassium chloride were the major roducts formed in the attempted synthesis of dipotassium N,N-ethylphosphoramidate by alkaline hydrolysis of diethylphosphor-midic dichloride.

MRC 35140-2

ıe attempt to synthesize potassium diethyl phosphate by oxidation f diethyl phosphite with 30% hydrogen peroxide in the presence of otassium carbonate gave mixtures which apparently resulted from ydrolysis.

MRC 27121

ıe attempt to synthesize bis(β-chloroethyl)phosphorochloridate rom 2-chloroethanol and phosphorus oxychloride in the presence of riethylamine resulted in formation of tars and polymers.

A similar attempt to prepare β-chloroethyl phosphorodichloridate also failed to give expected product.

MRC 30053

Polymeric materials were formed in the attempted synthesis of bis(p-chlorobenzyl) phosphorochloridate from p-chlorobenzyl alcohol and phosphorus oxychloride.

MRC 35137

Polymers and other condensation products resulted in the attempt to synthesize bis(2-hydroxyethyl) phosphite by ester-interchange between diethyl phosphite and ethylene glycol.

MRC 29328, 29333, 32873

Three attempts to prepare 5,5-bis(chloromethyl)-2-chloro-1,3,2-dioxaphosphorinane-2-oxide from 2,2-bis(chloromethyl)-1,3-propanediol and phosphorus oxychloride by adaptation of the methods of Agfa A.-G. [51] and McConnell and Coover [22] resulted in inseparable mixtures. The product appeared to be polymeric.

MRC 27091, 28370, 28371

Attempts to synthesize either ethyl or methyl phenylphosphonochloridate from phenylphosphonic dichloride and the respective alcohol by the methods of Ramaswami and Kirch [52] and Hudson and Keay [53] resulted in a polymeric material with concomitant evolution of a low-boiling gas.

MRC 29312

Tars resulted in an attempt to synthesize 2-(bromomethyl)-2-ethyl-1,3-propanediol from 2-ethyl-2-hydroxymethyl-1,3-propanediol using the sulfuric acid-hydrobromic acid method of Kamm and Marvel [54].

MRC 27118

Apparently dehydrohalogenation, instead of partial saponification, took place in the attempted synthesis of β-Chloroethyl potassium

nylphosphonate from bis(β-chloroethyl) vinylphosphonate and
otassium hydroxide.

MRC 35122, 35124

xtures were formed in the attempted synthesis of diethyl 2-(p-
omophenoxy)ethyl phosphate from diethyl phosphorochloridate and
(p-bromophenoxy)ethanol in presence of triethylamine.

MRC 29342

separable mixtures resulted in the attempt to prepare the
potassium salt of 3,9-dihydroxy-2,4,8,10-tetroxa-3,9-diphospha-
iro[5.5]undecane-3,9-dioxide from the 3,9-dichloro derivative
d aqueous potassium hydroxide.

MRC 35109

thyl chloride was eliminated at 90-100° in the attempted dis-
llation of 2-(p-bromophenoxy)ethyl methyl phosphorochloridate
sulting in the formation of glassy polymers.

MRC 29331, 29336

o attempts were made to prepare 5-chloromethyl-5-ethyl-1,3,2-
oxaphosphorinane-2-oxide from 4-ethyl-2,6,7-trioxa-1-phospha-
cyclo[2.2.2]octane. Treatment of the latter compound with
lorine gas according to the method of Wadsworth and Emmons (32)
sulted in an explosion followed by a fire. A second attempt
ng sulfuryl chloride in adaptation of the method of Poshkus
Herweh (35) resulted in inseparable mixtures as shown by NMR.

MRC 30060

attempted synthesis of 3,9-dichloro-2,4,8,10-tetroxa-3,9-
hosphaspiro[5.5]undecane-3,9-dioxide from phosphorus oxychloride
pentaerythritol by literature methods (51,55) resulted in the
mation of a mixture of products which absorbed phosphorus oxy-
oride so avidly that it could not be removed at 100° in vacuo.

MRC 29321, 32882

3,9-Dihydroxy-2,4,8,10-tetroxa-3,9-diphosphaspiro[5.5]undecane-3,9-dioxide, made from pentaerythritol (50 g., 0.37 mole) and polyphosphoric acid (500 g.), according to a modification of the procedure of Meston [33], could not be isolated from aqueous solution. An attempt to extract the product with ether in a liquid-liquid extractor failed because it caused the ether to dissolve in the water layer.

MRC 29314, 29317

Mixtures resulted in two attempts to synthesize 5-chloromethyl-5-ethyl-2-oxo-1,3,2-dioxathiane from 2-ethyl-2-hydroxymethyl-1,3-propanediol, thionyl chloride and pyridine by adaptation of the methods of Pietsch [27] and Mooradian and Cloke [28] who used pentaerythritol.

A major component of these mixtures was identified as 2,2-bis-(chloromethyl)-1-chlorobutane, m.p. 41-2° (methanol); literature [56] m.p. 43-4°.

NMR (^{1}H) showed chemical shifts in ppm. at 3.52 (single; $-C(CH_2Cl)_3$), 3.60 (quartet; $C\underline{H_2}CH_3$) and 0.92 (triplet; $-CH_2\underline{CH_3}$).

The relative number of protons was 6.0:2.0:2.9; theory, 6.0:2.0:3.0.

MRC 30057

s(m-chlorobenzyl) ether was the major product formed in the at-
mpted synthesis of bis(m-chlorobenzyl) phosphorochloridate from
osphorus oxychloride and 3-chlorobenzyl alcohol.

MRC 27075

attempt to synthesize bis(ß-chloroethyl) potassium phosphate
om bis(ß-chloroethyl) phosphorochloridite and potassium hydroxide
sulted, instead, in a near theory yield of ß-chloroethyl potassium
osphite:

$$(ClCH_2CH_2O)_2PCl + KOH \not\rightarrow (ClCH_2CH_2O)_2POK \xrightarrow{H_2O_2} (ClCH_2CH_2O)_2P(O)OK$$
$$\longrightarrow ClCH_2CH_2OP(O)(H)OK$$

r (^{31}P) showed chemical shifts in ppm. at -26.4 (triplet) and
3.0 (triplet) which is typical of a -P(O)H system.

r (^{1}H) showed chemical shifts in ppm. at 12.8 (1/2-PH doublet),
-4.0 (Complex multiplet; $ClCH_2CH_2OP$) and 1.86 (1/2-PH doublet).
relative number of protons was 0.5:4.0:0.5; theory for

$H_2CH_2OP(O)(H)OK$, 0.5:4.0:0.5.

confirmed the presence of P-H, P-OH, P-O, and P-O-R.

bility of Chloromethylphosphonic acid MRC 27133

analytical sample of chloromethylphosphonic acid was dissolved
water and titrated electrometrically with standard potassium
roxide. Two equivalents of alkali were required; the pH was
6 and the test for chloride ion was negative. On heating an
eous solution of dipotassium chloromethylphosphonate to boiling
pH dropped to 7.85 and a strong positive test for chloride ion
obtained which demonstrates tne hydrolytic instability of this
t in boiling water.

VII. EVALUATION TEST METHODS

A. POUR POINT

Pour points were measured by the ASTM D 97-57 procedure. A small pour point tube, Model J-2436 supplied by Scientific Glass Apparatus Company, was substituted for the larger tube prescribed in the ASTM D 97-57 procedure in order to conserve material.

B. VISCOSITY

Kinematic viscosity was determined by the ASTM D 445-T 1961 procedure, using Cannon-Manning Semi-Micro viscometers, calibrated and supplied by the Scientific Development Corporation, State College, Pennsylvania.

C. ASTM SLOPE

Values were determined by plotting 100° and 210°F. measured viscosities on viscosity-temperature charts (ASTM D 341-39).

D. AUTOGENOUS IGNITION TEMPERATURE (AIT)

AIT was measured by the procedure recommended by ASTM D-60T, "Tentative Method of Test for Autoignition Temperatures of Liquid Petroleum Products." This procedure and apparatus was developed and is described in detail by Zabetakis et al[57].

Our apparatus is constructed to duplicate as closely as practicable that of Zabetakis. The 200-ml. borosilicate Erlenmeyer flask, used as the combustion chamber, is heated in a Hoskins Model FD104 Electric Furnace provided with auxiliary heaters at the top and bottom of the heating chamber to eliminate temperature gradients within the furnace. The temperature within the furnace is recorded on a Honeywell Brown Electronik recorder Model 153X72PG-X-26A1 with a range of 400-1400°F. through three iron-constantan thermocouples:

touching the bottom center of the flask; (2) touching the side the flask halfway up; (3) touching the flask near the top. The ciliary heaters and the main furnace heater are adjusted with ; amp. and 15 amp. variable transformers, respectively, so that temperature is the same at all three thermocouples. Constant nperature is maintained with a Wheelco Capacitrol Model 243 it operates through the main furnace heater and uses a fourth rmocouple halfway up the inner wall of the furnace as the sens- element. A Redmond Company Model 3981 Type L Air Blower is d for sweeping fumes from the flask.

procedure for obtaining the minimum autoignition temperature essentially that of Zabetakis. Results are reported as minimum and ignition delay, the time lag between introduction of the mple and the ignition flash.

h this apparatus and procedure, we have obtained satisfactory reement with Zabetakis in the temperature range 400-1100°F.

MICRO FLASH AND FIRE POINTS

flash and fire points of the experimental fluids were determined a method based on ASTM D 92-57.

ASTM-approved Cleveland Open Cup heating apparatus was modified accept a 1 ml. test cup. The temperature was measured by an n-constantan thermocouple immersed in the test fluid. As an in adjusting and controlling the rate of temperature rise, a rmometer well was drilled directly below the test chamber into metal body of the test cup. A thermometer was placed here to mit a constant approximate check on the temperature. The proce- e, i.e., rate of temperature rise, use of test flame application ice, etc., was the same as with the macroscale Cleveland Open test (ASTM D 92-57).

F. FLUID-PAINT COMPATIBILITY EVALUATION

The test procedure for the evaluation of the compatibility of experimental fluids with paint was as follows. Sheets of a mild steel, 4 in. by 12 in., were sandblasted to a satin finish using 220-mesh alumina (or equivalent). The prepared surfaces were either painted immediately or covered with a protective grease coating. (Prior to painting the surfaces were subjected to vapor degreasing.) Paint was applied by a doctor blade in a 2 mil wet coat thickness, and dried for 24 hr. at 80°F. and 50% relative humidity before application of a second coat of paint or treatment with test fluids. The paint surface used was a Formula 20 L over Formula 116.

Four portions (ca. 0.05-ml. each) of the test fluid were placed on the paint surface, covered by watch glasses, sealed with petroleum wax to prevent evaporation, and kept at ambient temperature. One portion of each test fluid was examined after 1, 3, 7 and 10 days. The composite evaluation was then made on each fluid and the fluids rated against one another.

G. FLUID-ELASTOMER COMPATIBILITY EVALUATION

The "O" rings tested were obtained from Precision Rubber Products, Dayton, Ohio. They are identified as AN 6227 to MIL-P-5516B; the rings tested have 1-inch I.D.

Tests were run on ten "O" rings with the values reported being the average of ten determinations and the average deviation.

The "O" rings were measured (weight, volume, Shore "A" hardness) then suspended on glass "I-tubing" such that they could not touch the bottom of the container or float to the surface of the liquid. The rings were then immersed in the test fluid contained in a tightly-capped, 70 ml., ground-glass weighing bottle (40 mm. I.D.

30 mm. high) and placed in a forced air craft oven capable of intaining temperatures of ±2°F. After aging for 168±1 hr. at 3±2°F. the rings were removed and evaluated, together with ten :reated rings, using the following test methods:

Federal Test Method	Evaluated Property
ieral Test Method No. 601; Method 4111	Ultimate tensile
ieral Test Method No. 601; Method 4121	Ultimate elongation
ieral Test Method No. 601; Method 6211	Volumetric change
ieral Test Method No. 601; Method 3021	Hardness, Shore A

: weight change was determined by weighing the ring before and :er testing.

ısile and elongation measurements were made on an Instron tester.

"COKE" BOTTLE HYDROLYSIS TEST

homogeneous hydrolytic stability of candidate materials was ermined using a modification of method 4.4.3 of MIL-Spec-19457A. olution of 40 g. of the test compound and 60 g. of water, in- ad of the specified heterogeneous mixture of 75 g. and 25 g. pectively, was adjusted to approximately ph8 and heated under specified test conditions. The pH at the end of the test was djusted to its original value as a measure of change. If the rose, acid was used to back-titrate and it was reported accord- ly.

CORROSION TEST

rosion was measured by a modification of method 4.4.4.1 of -H-19457A (Ships). A metal specimen, 1/4" x 1" x 0.032", was ced into about 1/2" - 3/4" (0.75 ml.) of the test solution in a x 75 mm. test tube, allowing approximately 1/2" to remain above liquid. The tube was sealed, and heated in an oven at 199-201°F. -94°C.) for the desired length of time, usually 2 to 5 weeks. A

visual observation of the vapor phase and liquid phase corrosion could thus be obtained and where desired, the weight change of the specimen could be determined.

J. SONIC SHEAR TEST

Sonic shear was measured by the procedure recommended in the Raytheon Instruction Manual, number 7-410, 27 Dec. 1960, using a Raytheon 250-watt, 10-kilocycle, "Magnetostrictive" Oscillator, model DF-101. The instrument was placed under full power and the "match" and "tune" circuits were adjusted to get maximum "frying noise".

The test conditions were as follows:

Initial amount of sample - 50 ml.
Amount of sample taken at each sampling interval - 5 ml.
Temperature of cooling water - 100°F., ±5°
Amount of cooling water circulating through unit - 1 qt. per minute
Total irradiation time - 2 hrs.
Sampling intervals - as shown in the chart.

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