BIMONTHLY REPORT NO. 2

DEVELOPMENT OF FIRE-RESISTANT WATER BASE HYDRAULIC FLUID

Contract NObs 90270
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To
Bureau of Ships
Department of the Navy
Washington 25, D.C.

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WATER BASE HYDRAULIC FLUID

I. INTRODUCTION

The broad objective of this contract is the development of a usable, fire-resistant water-base hydraulic fluid for shipboard use, in which the nonaqueous phase is fire-resistant. The contract effort is restricted to water solutions as contrasted with emulsions and/or suspensions.

Fire resistance in the nonaqueous phase is important in hydraulic systems operating at 5000 psi, where the aqueous phase in certain segments of the system may, under special circumstances, evaporate, thereby leaving a hazardous explosive residue, and where spray leaks develop there may be flammable residues exposed to ignition sources.

The suggested, desirable, and tentative specifications for a fire-resistant, water-base hydraulic fluid, which we are repeating here for convenient reference, are:

1.	Autogenous Ignition Temperature	(AIT) >900°F (nonaqueous phase)
2.	Flash Point	(AIT) >450°F (nonaqueous phase)
3.	Fire Point	(AIT) >550°F (nonaqueous phase)
4.	Viscosity cs.	850 (max) at 25°F and 25-31 at 150°F
5.	Pour Point	0°F (max)
6.	Shear Stability	±10% change at 150°F
7.	Specific Gravity 60/60°F	1.0-1.2 (1.6 max)
8.	Lubrication	Shipboard screw and variable stroke piston pumps at 5000 psi
9.	Compatibility	
	(a) Metals	Steel, copper, copper-nickel, nickel-copper-bronze, phosphorus-bronze, and anodized aluminum (see metal specifications)
	(b) Elastomers	Buna N
	(c) Sea Water	Functional with 10%

10.	Stability	
	(a) Storage	-20 to +110°F
	(b) Use	+25 to 180°F
	(c) Filterable	5 Micron filter
11.	Foaming	No stable foam
12.	Toxicity	Non-hazardous
13.	Fluid Residues	Water soluble

Our approach to this problem will be divided into four major phases:

(1) Selection, by synthesis and evaluation, of one or two fire-resistant pour point depressants.

(2) Selection of a water-soluble polymeric thickener compatible with the pour point depressant.

(3) Inhibition of the specified metals against corrosion in the liquid and vapor phases by the water solution of the pour point depressant and thickener.

(4) Compounding the finished fire-resistant, water-base hydraulic fluid.

II. SUMMARY

The alkali alkyl phosphates and alkali alkylphosphonates continue to hold promise as candidates for fire-resistant, pour point depressants.

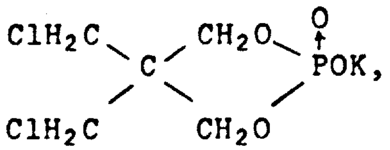
The former appear somewhat more compatible with metals, while the latter have higher AIT's.

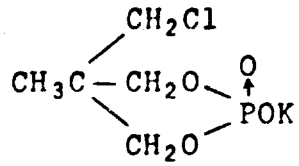
Phosphoramidates and alkali alkyl thiolphosphates, in general, are of no further interest.

III. GENERAL DISCUSSION

A large number of preliminary exploratory tests were conducted, concomitant with a synthesis program, in an effort to establish more firmly which type of water-soluble phosphorus compounds would be the best choice as fire-resistant, pour point depressants. Phosphoramidates, neutral phosphorus esters, both aryl and alkyl, and alkali alkyl thiolphosphates have essentially been eliminated as candidate classes because of hydrolytic instability and/or low AIT. Presently, the dialkali phosphates and phosphonates are of questionable utility.

Improvement in the AIT of the alkali alkyl phosphates would be desirable, and we are attempting to accomplish this by the synthesis of the following type compounds:





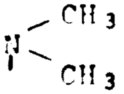
IV. PHYSICAL TESTING

A. FLAMMABILITY PROPERTIES

Of the several phosphorus classes tested, and as reported in the first bimonthly Progress Report (NObs-90270 - 1 June 1964), alkali alkyl phosphates and alkali alkylphosphonates appear the most suitable as fire-resistant, pour point depressants. The flammability properties of these two types were investigated more thoroughly during the present contractual period. An aryl alkylphosphoramidate and a thiolphosphate are also included for comparison. The data are presented in Table 1.

Some broad conclusions can be drawn from these data:

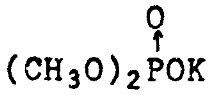
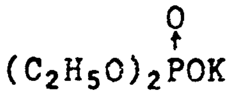
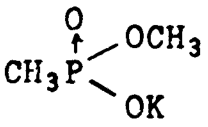
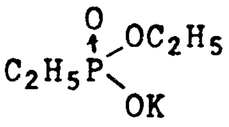
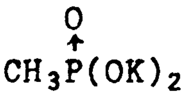
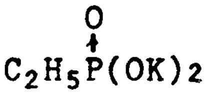
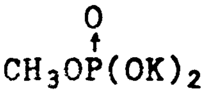
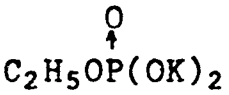
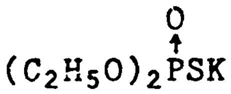
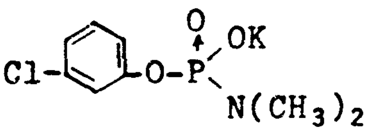
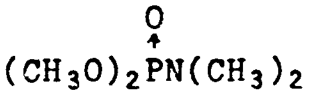
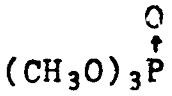
(1) The N,N-dialkyl group in a phosphoramidate appears to lower the AIT appreciably from closely analogous oxygen compounds (compare cpds. 455, 460, and 484). In compound 481, the



$N{<}^{CH_3}_{CH_3}$ group is required to stabilize the molecule hydrolytically but the chlorophenyl group does not raise the AIT above that of the alkali alkyl phosphates (compare cpds. 481, 484, and 468), which renders the compound of little interest.

Table 1

FLAMMABILITY PROPERTIES

MRC No.	Compound	AIT °F	AIT Time Lag, sec.	Micro Flash, °F	Micro Fire, °F	
484	 $(CH_3O)_2\overset{\overset{O}{\uparrow}}{P}OK$	845	25	522	No fire	752
468	 $(C_2H_5O)_2\overset{\overset{O}{\uparrow}}{P}OK$	850	7	547		676
485		890	15	707	No fire	752
486		860	14	590	No fire	752
489	 $CH_3\overset{\overset{O}{\uparrow}}{P}(OK)_2$	1180	17	No flash	No fire	752
490	 $C_2H_5\overset{\overset{O}{\uparrow}}{P}(OK)_2$	1040	19	No flash	No fire	752
443*	 $CH_3O\overset{\overset{O}{\uparrow}}{P}(OK)_2$	925	18	-	-	-
488	 $C_2H_5O\overset{\overset{O}{\uparrow}}{P}(OK)_2$	880	24	No flash	No fire	752
502	 $(C_2H_5O)_2\overset{\overset{O}{\uparrow}}{P}SK$	535	47	-	-	-
481		820	22	-	-	-
460*	 $(CH_3O)_2\overset{\overset{O}{\uparrow}}{P}N(CH_3)_2$	500	10	-	-	-
455*	 $(CH_3O)_3\overset{\overset{O}{\uparrow}}{P}$	725	13	-	-	-

*Reported previously but included for comparison

(2) Substitution of a thiol sulfur for an analogous oxygen in an alkali alkyl phosphate lowers the AIT approximately 300°F (compare compounds 502 and 468), which removes the class from further consideration.

(3) The alkali alkyl phosphates and alkali alkylphosphonates continue to show promise as candidates for fire-resistant, pour point depressants based on flammability properties (see cpds. 484, 468, 485, 486, 489, 490, 443 and 488).

B. HYDROLYTIC STABILITY

The hydrolytic stability of alkali alkyl phosphates and alkali alkylphosphonates was further investigated. Results are shown in Table 2.

These data were obtained by a modification of MIL-H-19457A (standard "coke" bottle) test procedure. A solution of 40 g. of the test compound and 60 g. of water, instead of the specified heterogeneous mixture of 75 g. and 25 g. respectively, was adjusted to approximately pH 8 and heated under the specified test conditions. The pH at the end of the test was readjusted to its original value as a measure of change. Since the pH rose in compounds 485 and 486, acid was used to back-titrate and it is reported accordingly.

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, 484, 485, and 486) do not appear to be especially corrosive to copper, even without an inhibitor. However, the dipotassium alkylphosphonates (cpds. 488, 489 and 490) have questionable utility because of severe copper corrosion.

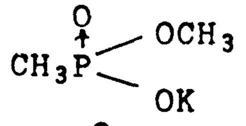
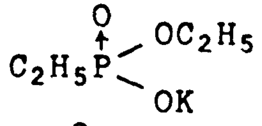
C. FREEZING POINT AND STORAGE STABILITY

Tentative specifications require a pour point of 0°F (max) and stability at -20°F under storage conditions. It is evident from the freezing point and storage stability data in Table 3 that the required low temperature properties are no problem with aqueous solutions of these salts. For example, the

Table 2

HYDROLYSIS OF ALKYL METAL PHOSPHATES AND METAL ALKYLPHOSPHONATES

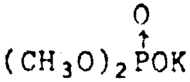
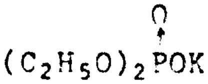
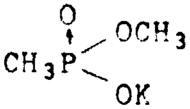
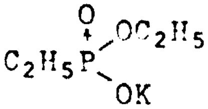
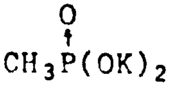
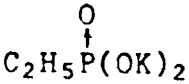
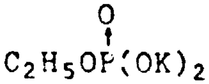
(Coke Bottle Test MIL Spec MIL-H-19457A)(1)

MRC No.	Compound	Initial pH	Final pH	Total Acidity,(2) mg KOH/g	Copper Strip		Residue in Solution
					Weight Change(4) mg/cm^2	Corrosion	
484	$(CH_3O)_2\overset{\overset{O}{\uparrow}}{P}OK$	7.91	7.43	0.06	0.041	Stained	None
468	$(C_2H_5O)_2\overset{\overset{O}{\uparrow}}{P}OK$	8.24	7.32	0.10	+1.1	Film on copper	None
485		8.03	8.30	0.09(3)	0.083	Corroded	Very small
486		7.99	9.45	0.18(3)	1.45	Corroded	None
489	$CH_3\overset{\overset{O}{\uparrow}}{P}(OK)_2$	8.00	8.00	0	10.1	Heavy film on copper	Moderate
490	$C_2H_5\overset{\overset{O}{\uparrow}}{P}(OK)_2$	7.95	7.87	0	13.6	Corroded	Moderate to heavy
488	$C_2H_5O\overset{\overset{O}{\uparrow}}{P}(OK)_2$	8.08	8.15	0	9.7	Stained	Very heavy

(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

Table 3

FREEZING POINTS AND STORAGE STABILITY OF AQUEOUS PHOSPHORUS ACID SALTS

MRC No.	Compound	% Conc. in H_2O Solution	Freezing Point (°F)	Melting Point (°F)	Solution Cleared (°F)	Storage Stability -20°F	
						Time	Appearance
484	 $(CH_3O)_2\overset{\overset{O}{\uparrow}}{P}OK$	40.0	-24	-16	-6	5 days	clear
468	 $(C_2H_5O)_2\overset{\overset{O}{\uparrow}}{P}OK$	40.0	-18	-18	-8	5 days	clear
		50.0	-50	-	-30		
		40.7 (pH 7.95)	-20	-14	-		
		40.7 (pH 9.12)	-20	-14	-		
485		39.9	-34	-	-20	5 days	clear
486		40.0	-36	-	-20	5 days	clear
489	 $CH_3\overset{\overset{O}{\uparrow}}{P}(OK)_2$	40.0	-25	-16	-10	5 days	clear
490	 $C_2H_5\overset{\overset{O}{\uparrow}}{P}(OK)_2$	40.0	-28	-18	-12	5 days	clear
		30.0	-15	-	- 4		
488	 $C_2H_5O\overset{\overset{O}{\uparrow}}{P}(OK)_2$	39.9	-30	-	-16	5 days	clear

freezing point of aqueous diethyl potassium phosphate (cpd. 468) was lowered from -18° to -50° by a 10% increase in concentration.

D. COMPATIBILITY

1. Sea Water

An investigation was made of the compatibility of the potassium salts of the alkyl phosphates and alkylphosphonates with natural sea water, obtained offshore at Marblehead, Massachusetts. The data are listed in Table 4.

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.

2. Paint

We assumed that paint and elastomer compatibility are closely related, therefore we carried out some preliminary evaluation on paint.

An alkyd base paint, formula 20L applied over formula 116 was used. The data of Table 5 represent preliminary screening data.

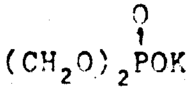
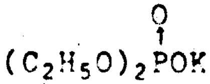
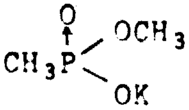
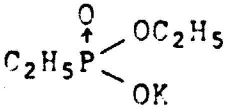
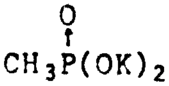
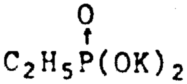
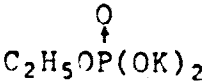
The order of increasing compatibility with paint appeared to be: aromatic-O-P(OH)$_2$<aromatic-O-P(aliphatic)OH<aliphatic-P(OH)$_2$< (aromatic)$_2$P-O-alkali<aromatic-O-P(O alkali)$_2$$\cong$ aromatic-P(O alkali)$_2$ <alkyl-P(O alkali)$_2$. Phosphorus compound with free acid groups attacked the paint severely. Aromatic groups in general showed greater attack on paint than alkyl groups.

These data suggest that alkali alkyl phosphates should be compatible with paint, borne out by the data presented in Table 6. The difference, in paint compatibility, between compound 273, a fluorinated organic phosphorus compound, and compound 486, a potassium salt of an alkylphosphonate alkyl ester, was so minor that it was difficult to rate the intermediate compounds of Table 6.

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 is permanently softened.

Table 4

COMPATIBILITY WITH SEA WATER

MRC No.	Compound	% Conc. in H_2O Solution	pH of H_2O Solution	% Concentration Sea Water(3)	Precipitation No Heat(1)	Precipitation Boil(2)
484	 $(CH_2O)_2\overset{O \uparrow}{P}OK$	40.0	8.01	10.3	No	No
468	 $(C_2H_5O)_2\overset{O \uparrow}{P}OK$	40.0	7.95	10.2	-	-
485		39.9	8.00	10.0	-	-
486		40.0	7.96	9.99	-	-
489	 $CH_3\overset{O \uparrow}{P}(OK)_2$	40.0	7.98	10.2	-	-
490	 $C_2H_5\overset{O \uparrow}{P}(OK)_2$	40.0	7.90	9.99	-	Very small amount
488	 $C_2H_5O\overset{O \uparrow}{P}(OK)_2$	39.9	8.01	10.4	-	No

(1) Allowed to stand three days.
(2) Boiled solutions vigorously and allowed to stand two days.
(3) Sea water pH 8.10.

Table 5

PRELIMINARY PAINT TEST EVALUATIONS

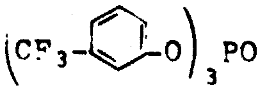
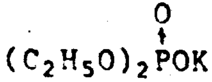
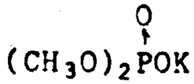
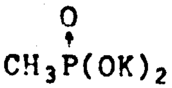
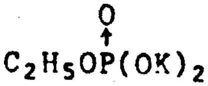
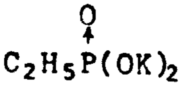
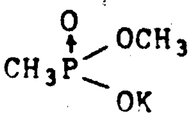
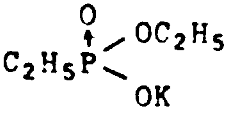
MRC No.	Compound(a)	% Concentration Water Solution	Effect
271	2110-H (Hydrocarbon hydraulic fluid)(b)	-	No apparent effect
508	$C_2H_5\overset{O}{\overset{\uparrow}{P}}(ONa)_2$	40.0	
92	MIL-H-19457	-	Very slight effect
509	$C_6H_5\overset{O}{\overset{\uparrow}{P}}(ONa)_2$	40.0	
510	$C_6H_5O\overset{O}{\overset{\uparrow}{P}}(ONa)_2$	46.0	Paint softened; greater damage than above
511	$(C_6H_5)_2\overset{O}{\overset{\uparrow}{P}}ONa$	39.0	Paint very soft; easily scratched
339	$C_2H_5\overset{O}{\overset{\uparrow}{P}}(OH)_2$	40.0	Greater damage than above; pieces of paint easily removed
466	$C_4H_9\overset{O}{\overset{\uparrow}{P}}<^{OC_6H_5}_{OH}$	(water insoluble)	
433	$C_6H_5O\overset{O}{\overset{\uparrow}{P}}(OH)_2$	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 straight, not a solution.

Table 6

EFFECT OF ALKYL (ALKALI) PHOSPHATES AND ALKALI ALKYLPHOSPHONATES ON PAINT

(Formula 20L Over Formula 116)

MRC No.	Compound[(a)]	% Concentration Water Solution	Effect
273		-	Very slight effect, if any
468	 $(C_2H_5O)_2\overset{O}{\overset{\uparrow}{P}}OK$	40.0	
484	 $(CH_3O)_2\overset{O}{\overset{\uparrow}{P}}OK$	40.0	Slightly more damage than above
489	 $CH_3\overset{O}{\overset{\uparrow}{P}}(OK)_2$	40.0	
488	 $C_2H_5O\overset{O}{\overset{\uparrow}{P}}(OK)_2$	39.9	
490	 $C_2H_5\overset{O}{\overset{\uparrow}{P}}(OK)_2$	40.0	Slightly more damage than above
485	 $CH_3\overset{O}{\overset{\uparrow}{P}}\genfrac{}{}{0pt}{}{OCH_3}{OK}$	39.9	
486	 $C_2H_5\overset{O}{\overset{\uparrow}{P}}\genfrac{}{}{0pt}{}{OC_2H_5}{OK}$	40.0	
92	MIL-H-19457	-	Worst of compounds tested

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

E. CORROSION STUDIES

Using steel, aluminum, and copper, some rapid preliminary screening corrosion tests were conducted, essentially on a microscale basis in order to conserve the compound.

1. Steel (52-100)

Into about 1" (1.5 ml) of the test solution in a 10 x 75 mm test tube was placed a piece of 24-gauge, 52-100 steel, 3/16" x 1-1/2", allowing approximately 1/2" to remain above the liquid. The tube was sealed, and heated in an oven at 199-201°F (93-94°C). A crude but rapid reading on vapor phase and liquid phase corrosion could thus be obtained simultaneously.

The preliminary corrosion experiments on 52-100 steel are listed in Tables 7 and 8. This type of steel was chosen as an expediency, although it may have been a poor choice because of its high susceptibility to corrosion, in spite of which the actual weight change, even on the poorest samples, was not serious on the basis of penetration. For example, calculated on a weight loss basis at 200°F, compounds 486 and 490 showed a penetration of 2-3% of that reported for carbon steel immersed in natural sea water at oceanside temperatures in a subtropical climate.

From the data in Table 7, it would appear that solutions of dipotassium alkylphosphonates (cpds. 489 and 487), adjusted to pH 7, could be used in the presence of 52-100 steel, whereas potassium alkyl phosphates (cpds. 441 and 468) could be used at any pH from 7 to 9.

It can be seen in Table 8 that all potassium alkyl phosphorus compounds, except one (cpd. 485 in water/10% sea water), produced a precipitate upon heating in the presence of 52-100 steel in distilled water and distilled water/sea water mixtures at pH 7.5-8.4. Compound 489 did not corrode 52-100 steel in the liquid phase.

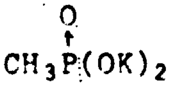
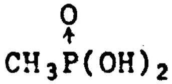
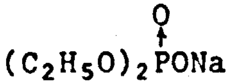
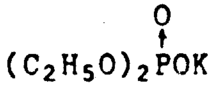
Dipotassium ethyl phosphate (cpd. 488) was generally the most corrosive to 52-100 steel, and dipotassium methylphosphonate (cpd. 489) appeared to be the least corrosive, to have the smallest pH change, and the least amount of precipitate of all compounds tested.

2. Aluminum (303)

Some preliminary corrosion studies of phosphonates on aluminum were carried out, as shown in Table 9. In these tests, an aluminum strip (sheet stock, 3/16" x 1-1/2" x 16 gauge) was

Table 7

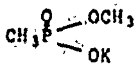
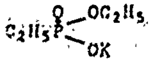
CORROSION EFFECTS OF PHOSPHORUS COMPOUNDS AT VARIOUS pH LEVELS ON 52-100 STEEL

MRC No.	Compound	% Conc. Water Solution	pH Before Heating	pH After Heating[a]	Metal Weight Change (%)	Remarks
489	 $CH_3\overset{O}{\overset{\uparrow}{P}}(OK)_2$	40.0	9.0	8.7	0.36	Metal coated; precipitate present
			8.0	8.1	0.17	Metal rusted; precipitate present
			7.0	(spilled)	0.04	Solution and metal clean
-	K_2HPO_4	30.0	8.0	7.9	0.32	Crystalline precipitate on metal and in liquid phase
487	 $CH_3\overset{O}{\overset{\uparrow}{P}}(OH)_2$	50.0	9.0 8.1 7.0	8.9 8.1 6.7	0.30 0.12 0.09	Similar to 489 at various pH levels
441	 $(C_2H_5O)_2\overset{O}{\overset{\uparrow}{P}}ONa$	50.0	9.0 8.0 7.0	8.4 8.1 7.9	0.00 +0.04 +0.04	
468	 $(C_2H_5O)_2\overset{O}{\overset{\uparrow}{P}}OK$	50.0	9.1	7.9		Compared pH change to that of the sodium salt (441)

(a) Small-scale samples heated 4 days at 200°F

Table 8

CORROSION EFFECTS OF PHOSPHORUS SALTS ON 52-100 STEEL IN THE PRESENCE OF SEA WATER

MRC No.	Compound	Solvent	% Concentration Water Solution	pH Before Heating	pH After Heating	Metal Weight Change, %	Penetration,$^{(c)}$ mils/month	Remarks
484	$(CH_3O)_2\overset{O}{P}OK$	Water$^{(a)}$	40.0	8.26	7.73	+0.15		Moderate amount grey precipitate
		Water$^{(a)}$ 10.3% Sea Water	-	8.37	7.25	+0.30		Moderate amount grey precipitate
		"	-	7.55	8.35$^{(b)}$	+0.21		Steel severely rusted - heavy precipitate
468	$(C_2H_5O)_2\overset{O}{P}OK$	Water$^{(a)}$	40.0	8.28	7.42	+0.02		Moderate amount black precipitate
		Water$^{(a)}$ 10.2% Sea Water	-	8.18	7.10	+0.05		Small amount grey precipitate
		"	-	7.49	6.68$^{(b)}$	+0.11		Metal coated - small white precipitate
485	 $CH_3\overset{O}{P}(OCH_3)(OK)$	Water$^{(a)}$	39.9	8.22	8.23	+0.11		Small amount green-black precipitate
		Water$^{(a)}$ 10.0% Sea Water	-	8.30	7.65	+0.23		No precipitate
		"	-	7.50	6.74$^{(b)}$	+0.13		Metal coated - moderate brown precipitate
486	 $C_2H_5\overset{O}{P}(OC_2H_5)(OK)$	Water$^{(a)}$	40.0	8.12	9.70	0.77	0.54	Heavy black precipitate - two layers
		Water$^{(a)}$ 9.9% Sea Water	-	7.96	7.48	0.00		Small amount white precipitate
		"	-	7.48	6.50$^{(b)}$	0.64		Metal coated - very small precipitate
489	$CH_3\overset{O}{P}(OK)_2$	Water$^{(a)}$	40.0	7.92	7.54	0.01		Precipitate on metal above solution - solution clear
		Water$^{(a)}$ 10.2% Sea Water	-	7.81	7.50	0.06		Small amount crystalline precipitate
		"	-	7.54	6.92$^{(b)}$	0.02		Metal coated-very small precipitate
490	$C_2H_5\overset{O}{P}(OK)_2$	Water$^{(a)}$	40.0	7.88	7.80	0.15		Very small amount white precipitate
		Water$^{(a)}$ 9.9% Sea Water	-	7.78	7.39	1.00	0.76	Heavy white precipitate
		"	-	7.54	7.02$^{(b)}$	0.07		Metal coated - moderate white precipitate
488	$C_2H_5O\overset{O}{P}(OK)_2$	Water$^{(a)}$	39.9	8.01	8.24	0.68		Extremely heavy precipitate - two layers
		Water$^{(a)}$ 10.4% Sea Water	-	7.83	7.67	0.41		Extremely heavy precipitate - iron coated
		"	-	7.54	7.68$^{(b)}$	+2.0		Heavy white precipitate - metal heavily coated

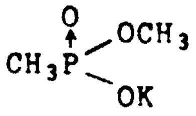
(a) Triply distilled water

(b) Heated one month at 200°F; all others heated one week

(c) Carbon steel penetration is reported to be 0.025"/month in sea water

Table 9

PRELIMINARY CORROSION STUDIES OF PHOSPHONATES ON ALUMINUM

MRC No.	Compound	Solvent	pH Before Heating	pH After Heating[(a)]	Metal Weight Change %	Remarks
485	 $CH_3\overset{O\uparrow}{P}(OCH_3)(OK)$	distilled water 10% sea water	8.70	-	-	Tube shattered - sample lost
489	$CH_3\overset{O\uparrow}{P}(OK)_2$	distilled water	7.95	-	-	Tube shattered - sample lost
490	$C_2H_5\overset{O\uparrow}{P}(OK)_2$	distilled water	7.89	-	-	Tube shattered - sample lost
		distilled water 10% sea water	7.54	-	-	Tube shattered - sample lost
-	$(HOC_2H_4)_3N$	distilled water	10.9	-	0.39	Solution turned solid
487	$CH_3\overset{O\uparrow}{P}(OH)_2$	distilled water	0.60	-	0.87	Tube shattered
-	$(HOC_2H_4)_3N\cdot CH_3\overset{O\uparrow}{P}(OH)_2$	distilled water	7.96	-	1.60	Tube shattered
-	-	sea water	7.97	7.92	+0.02	Sample and solution clear

(a) Heated at 200°F.

sealed in a tube as described above for the 52-100 steel test method. All of the tubes containing the phosphonates shattered within 2-3 hours, indicating that excessive hydrogen gas pressure had been generated. The effect of inhibitors on the phosphonates has not been investigated, as yet.

A second series of corrosion tests was conducted using alkali alkyl phosphate solutions with and without known aluminum inhibitors, as shown in Table 10. Potassium dichromate was soluble 1%, but other common aluminum inhibitors, Na_2SiO_3, Na_2CrO_4, $Na_2Cr_2O_7$, and Na_2SiF_6, were not soluble to the extent of 1% in 40% aqueous alkali alkylphosphonates.

This series of experiments suggests that:

(1) $K_2Cr_2O_7$ is a partially effective corrosion inhibitor for aluminum in the presence of dipotassium alkyl phosphate, and Na_2SiO_3 is not an effective corrosion inhibitor in this system.

(2) Potassium dialkyl phosphates may not require inhibition in the presence of aluminum

3. Copper

These results are listed under Section IV-B, Hydrolytic Stability. The dialkali salts of phosphorus compounds caused severe corrosion of copper, whereas the monoalkali salts affected it very little. Dimethyl potassium phosphate (cpd. 484) and methyl potassium methylphosphonate (cpd. 485) had a very slight, if any, corrosive effect on copper. In contrast, the copper weight change with dipotassium methylphosphonate (cpd. 489) was 330 times that of dimethyl potassium phosphate (cpd. 484). (See Table 2.)

Table 10

COMPARATIVE CORROSION OF ALUMINUM BY MONO- AND DIPOTASSIUM PHOSPHATES

MRC No.	Compound(a)	Inhibitor	% Concentration Inhibitor	Metal Weight Change %	Remarks
468	$(C_2H_5O)_2\overset{O}{\overset{\uparrow}{P}}OK$	-	-	0.00	No change after 3.5 weeks
488	$C_2H_5O\overset{O}{\overset{\uparrow}{P}}(OK)_2$	-	-	-	Tube shattered after 3 hr
468	$(C_2H_5O)_2\overset{O}{\overset{\uparrow}{P}}OK$	$K_2Cr_2O_7$	0.99	+0.06	Solution slightly hazy after 3.5 weeks
488	$C_2H_5O\overset{O}{\overset{\uparrow}{P}}(OK)_2$	$K_2Cr_2O_7$	0.99 (did not dissolve)	-	Heavy green precipitate after 24 hr. Tube intact after 1 week.
468	$(C_2H_5O)_2\overset{O}{\overset{\uparrow}{P}}OK$	Na_2SiO_3	0.14	0.00	No change after 3.5 weeks
488	$C_2H_5O\overset{O}{\overset{\uparrow}{P}}(OK)_2$	Na_2SiO_3	0.097 (did not dissolve)	-	Tube shattered after 3 hr
468	$(C_2H_5O)_2\overset{O}{\overset{\uparrow}{P}}OK$	Na_2SiO_3	1.10	0.04	Small amount white precipitate. Exceeded solubility of Na_2SiO_3.

(a) All solutions heated at 199-201°F.

V. SYNTHESIS

The following syntheses and/or synthetic attempts were carried out in support of this program.

m-Chlorophenyl Potassium Dimethylphosphoramidate (Cpd. 481) was prepared in 82% yield by the following method:

NMR(^{1}H) confirmed the theoretical structure.

Dipotassium Ethylphosphonate (Cpd. 490) was prepared by adding KOH pellets to aqueous ethylphosphonic acid until a pH of 9.8 (electrometrically) was reached. Evaporation of the solvent in a vacuum evaporator at 90°C gave the product:

$$C_2H_5\overset{\overset{O}{\uparrow}}{P}(OH)_2 + 2KOH \longrightarrow C_2H_5\overset{\overset{O}{\uparrow}}{P}(OK)_2 + 2H_2O$$

Ethylphosphonic Acid (Cpd. 482) was prepared by hydrolysis of diethyl ethylphosphonate:

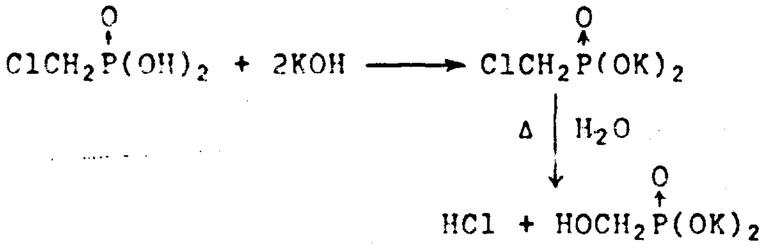
$$C_2H_5\overset{\overset{O}{\uparrow}}{P}(OC_2H_5)_2 + 2HOH \xrightarrow[\Delta\ (92\%)]{\text{Conc. HCl}} C_2H_5\overset{\overset{O}{\uparrow}}{P}(OH)_2$$

(m.p. 58-60°C)

The product was recrystallized from an ether/acetone/heptane mixture in the form of white crystals. The structure was confirmed by NMR.

Potassium 5,5-Dimethyl-2-oxo-1,3,2-dioxophosphorane-2-oxide (Cpd. 493) was prepared by the following sequence of reactions in an attempt to synthesize dipotassium 2,2-dimethyl-3-chloropropyl phosphate (III):

Stability of Chloromethylphosphonic Acid   This compound was titrated to pH 9.46 with aqueous potassium hydroxide at room temperature. Chloride ion was absent as determined by the silver nitrate test. However, upon heating to boiling (100°C), a strong chloride test was obtained and pH dropped to 7.85. Thus the dipotassium chloromethylphosphonate is hydrolytically unstable at a basic pH.



$$\mathrm{ClCH_2\overset{\overset{O}{\uparrow}}{P}(OH)_2 + 2KOH \longrightarrow ClCH_2\overset{\overset{O}{\uparrow}}{P}(OK)_2}$$

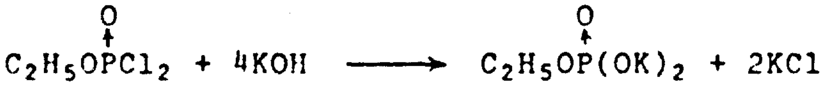
$$\Big\downarrow \Delta \; \mathrm{H_2O}$$

$$\mathrm{HCl + HOCH_2\overset{\overset{O}{\uparrow}}{P}(OK)_2}$$

Dipotassium Methylphosphonate (Cpd. 489)   An aqueous sample of methylphosphonic acid (Cpd. 487) was titrated with KOH pellets to its end point (electrometrically) of pH 9.68. Solids were isolated by vacuum evaporation of the solvent. NMR supported the theoretical structure:

$$\mathrm{CH_3\overset{\overset{O}{\uparrow}}{P}(OH)_2 + 2KOH \longrightarrow CH_3\overset{\overset{O}{\uparrow}}{P}(OK)_2 + 2H_2O}$$

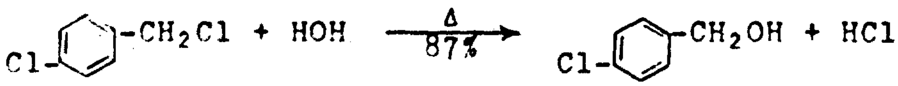
Dipotassium Ethyl Phosphate (Cpd. 488) was prepared as follows:



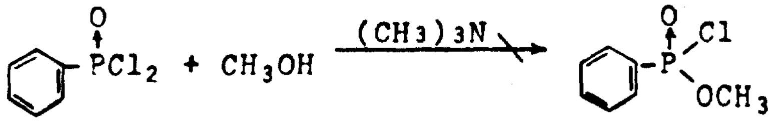
$$\mathrm{C_2H_5O\overset{\overset{O}{\uparrow}}{P}Cl_2 + 4KOH \longrightarrow C_2H_5O\overset{\overset{O}{\uparrow}}{P}(OK)_2 + 2KCl}$$

The KCl was separated from the product by fractional crystallization from methanol. The product was obtained by evaporating the methanol solution to dryness in a rotary evaporator.

P-Chlorobenzyl Alcohol was prepared as a possible intermediate by hydrolysis of the chloride:

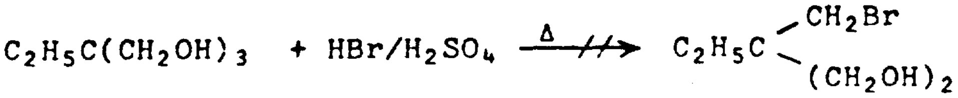


An attempted synthesis of Methyl Phenylphosphonochloridate in accordance with the equation,



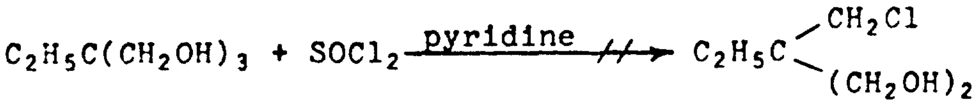
at 0-15°C resulted in a yellow-brown, polymeric material, which formed with concomitant evolution of a low-boiling gas.

Tars resulted in an attempt to synthesize 2-(Bromomethyl)-2-ethyl-1,3-propanediol using a sulfuric acid-hydrobromic acid mixture:



$$C_2H_5C(CH_2OH)_3 + HBr/H_2SO_4 \xrightarrow{\Delta} \hspace{-1em}/\!/\; C_2H_5C\begin{matrix} CH_2Br \\ (CH_2OH)_2 \end{matrix}$$

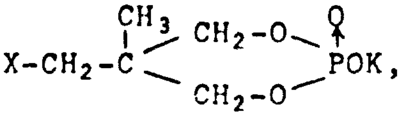
Inseparable mixtures resulted in two attempts to synthesize 2-(Chloromethyl)-2-ethyl-1,3-propanediol from trimethylolpropane, thionyl chloride and pyridine:



$$C_2H_5C(CH_2OH)_3 + SOCl_2 \xrightarrow{\text{pyridine}} \hspace{-1em}/\!/\; C_2H_5C\begin{matrix} CH_2Cl \\ (CH_2OH)_2 \end{matrix}$$

VI. FUTURE PLANS

To improve the AIT of the potassium alkyl phosphates by compounds such as



which incorporate stabilized aliphatic halogen.