AD610674

BIMONTHLY REPORT NO. 5

DEVELOPMENT OF FIRE-RESISTANT WATER BASE HYDRAULIC FLUID

Contract NObs 90270
1 December 1964 - 31 January 1965

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

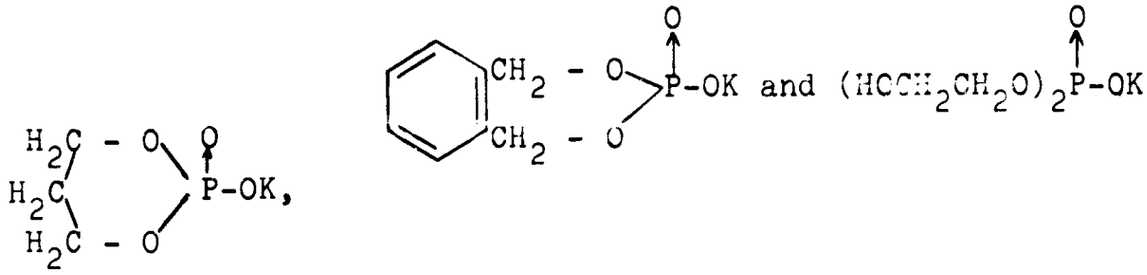
The alkali alkyl phosphates continue to afford the optimum properties as pour point depressant candidates. Introduction of a phenyl moiety into the ethyl group raised the AIT to 900°F.

Of the commercially available thickener's tested, Cellosize hydroxyethyl cellulose (WP4400) and WSR 205 were of interest as thickeners. The low percentages suggest that from a shear stability standpoint they may be suspect.

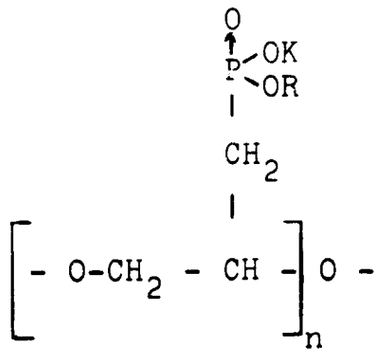
The AIT of phosphates appears unaffected by large amounts of water.

III. GENERAL DISCUSSION

Efforts to improve the AIT of the alkali dialkyl phosphate depressants are continuing by the synthesis of three final compounds:



Should these compounds show no significant improvement in AIT over the alkali dialkyl phosphates, emphasis will be shifted to thickeners containing phosphorus. The synthesis of one such polymer is underway:



It seems appropriate here to raise the question of how significant the AIT is in a hygroscopic depressant such as $(CH_3O)_2POOK$. A 40% solution of this compound is a low 7.3% organic. The hygroscopicity of this material makes it unlikely that it would dry out in a stagnant hydraulic line to create a fire hazard.

IV. PHYSICAL TESTING

A. FLAMMABILITY PROPERTIES

If the nonaqueous phase of a water-base hydraulic fluid is to have a minimum AIT of 900°F, then either a fire-resistant pour point depressant possessing sufficient AIT to compensate for the lowering by additives and/or a fire-resistant thickener must be used. Pending the synthesis of three additional depressants, the latter approach seemed the most fruitful since the maximum AIT of the $(alkyl\text{-}O)_2\overset{O}{\overset{\|}{P}}OK$ type, the molecule which meets the pour point depressant specifications, appears to be less than 900°F.

Flammability data on potential thickeners, blends and molecularly modified pour point depressants are listed in Table I.

From these data it can be concluded that:

1. The AIT of an $(alkyl\text{-}O)_2\overset{O}{\overset{\|}{P}}OK$ depressant is unaffected by large amounts of water (compare compounds 468 and 468A), although the lag time was increased six-fold probably due to the exclusion of air by water vapor.

2. Incorporation of an aromatic moiety into the potassium diethyl phosphate raised the AIT to about 900°F. (Compare cpds. 682, with 678, 691, and 674.)

3. Incorporation of stabilized aliphatic halogen improved only slightly the AIT of the potassium dialkyl phosphates. (Compare cpds. 640 and 493.)

4. Tris(tetrahydrofurfuryl) phosphate (Cpd. 637) is 240°F lower in AIT than is triethyl phosphate (840°F) and therefore is of no value.

5. Attempts to synthesize thickeners by the reaction of $POCl_3$ with polyethylene oxides and subsequently partially hydrolyzing the reaction products are not encouraging based on the low AIT's of compounds 679, 672, and 668.

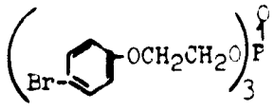
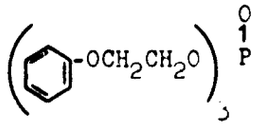
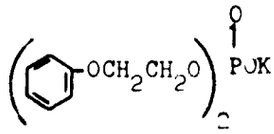
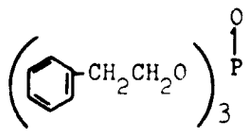
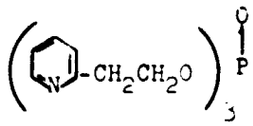
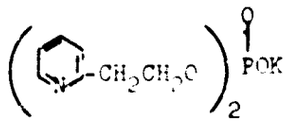
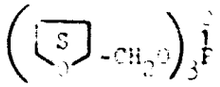
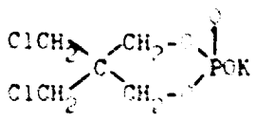
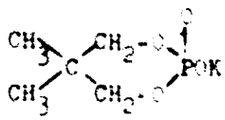
6. Hydrolysis of a trialkyl phosphate to the monopotassium salt essentially maintains the AIT of the unhydrolyzed product. (Compare cpds. 678 and 691; 676 and 692.)

Table 1

FLAMMABILITY PROPERTIES

MRC No.	Mixture, Compound or Blend	Parts by Weight, g.	Composition, %	AIT °F.	AIT Time Lag, Sec.
468	$(C_2H_5O)_2\overset{O}{\overset{\uparrow}{P}}OK$	----	----	850	7
468A	$(C_2H_5O)_2\overset{O}{\overset{\uparrow}{P}}OK$ H_2O	---- ----	40 60	850	40
650	$(HOCH_2CH_2OCH_2CH_2)_2O$	----	----	690	5
679	Partially hydrolyzed (KOH) $2\ CH_3O\overset{O}{\overset{\uparrow}{P}}Cl_2/3(HOCH_2CH_2OCH_2)_2$ reaction product	----	unknown	675	24
672	Partially hydrolyzed (KOH) $3(HOCH_2CH_2OCH_2CH_2)_2O/2\ POCl_3$ reaction product	----	unknown	750	44
668	Partially hydrolyzed (KOH) excess $HOCH_2CH_2OCH_2CH_2OH/POCl_3$ reaction product	----	unknown	730	12
66[illegible]	$(C_2H_5O)_2\overset{O}{\overset{\uparrow}{P}}OK$ H_2O Carbowax 600	3.30 1.25 3.75	39.9 15.1 45.3	[illegible]	[illegible]
689	$(C_2H_5O)_2\overset{O}{\overset{\uparrow}{P}}OK$ H_2O WSR-205	4.00 [illegible] 0.25	39.0 [illegible] 2.44	845	[illegible]
682	$(C_2H_5O)_2\overset{O}{\overset{\uparrow}{P}}OK$ H_2O WP-[illegible]	2.500 3.[illegible] 0.031	40.[illegible] [illegible] [illegible]	[illegible]	[illegible]
675	$(C_2H_5O)_2\overset{O}{\overset{\uparrow}{P}}OK$ H_2O WSR-205 $Co(O\text{-}\underset{\underset{O}{\uparrow}}{C}\text{-}CH_3)_2$	2.000 3.[illegible] [illegible] 0.155	37.2 [illegible] 2.[illegible] 2.88	[illegible]	[illegible]

Table I, Continued

MRC No.	Mixture, Compound or Blend	Parts by Weight, g.	Composition, %	AIT °F.	AIT Time Lag, Sec.
680		----	----	785 (1)	10
678		----	----	920	4
691		----	----	900	22
674		----	----	890	10
676		----	----	850	7
692		----	----	855	21
[illegible]		----	----	600	[illegible]
640		----	----	845	[illegible]
623		----	----	800	10
626	$C(CH_2Cl)_4$	----	----	1045	[illegible]

(1) The low AIT may be due to impurity

7. A cobaltous salt added to a phosphate depressant did not improve the AIT. (Compare cpds. 682 and 675.)

8. Low concentration of flammable thickeners must be employed if the AIT of the potassium dialkyl phosphate is to remain unchanged. (Compare cpds. 666, 689 and 682.)

B. VISCOSITY STUDIES

Preliminary viscosity data were obtained on blends of several commercial thickeners as shown in Table 2. WP-4400 (Cellosize hydroxyethyl cellulose; formulation 682) approximated the specifications. The solution remained clear in presence of high electrolyte concentrations; the viscosities and ASTM slope essentially met the viscosity requirements; the AIT of the pour point depressant was unaffected. The shear stability of this thickener is suspect as judged by the low concentration required.

The Gelvatols (polyvinyl alcohol/polyvinyl acetate polymers; formulations 657, 658, 662 and 663) were eleiminated on the basis of their tendency to gel in presence of high concentrations of electrolytes; cooling hastened the gelling process.

The low and medium molecular weight carbowax's (polyethylene glycols; formulations 664, 665, 666, 667, 694, 695 and 696) in the high concentration required for thickening remained clear in the presence of high concentrations of salts. They were tentatively shelved as potential candidate thickeners because of the low AIT value of the thickened solution. Carbowax 6000 gelled before a viscosity >800 cs. at 28°F was obtained; the maximum concentration which would remain in solution being about 28% (formulations 694, 695 and 696).

The Ucar Polyox resins (high molecular weight polyethylene glycols; formulations 697, 698 and 699) are of some interest. The polymer solutions were cloudy in the presence of high concentrations of salts, and the viscosity decreased on standing due to precipitation of polymer. A clear solution with interesting viscosity could be obtained by filtration. These solutions will be checked again for viscosity stability.

Low concentrations of Acrysols (polyacrylic acids; formulations 686, 700 and 701) do not appear to be compatible with high concentrations of salts. Acrysol GS will salt out at low temperatures but will redissolve on warming; Acrysol ASE-60 will slowly salt out at room temperature. The latter polymer has a propensity for foaming.

Table 2

VISCOSITY DATA

MRC No.	Compound or Blend	Parts by Weight, g.	Composition, %	Viscosity, cs, °F. 28	100	150(1)	210	Remarks
682	$(C_2H_5O)_2\overset{O}{\overset{\|}{P}}OK$ H_2O WP-4400	2.500 3.619 0.031	40.6 58.8 0.51	827	76.0	23.5	8.96	
657	Gelvatol 20-30 H_2O	18.2 81.8	18.2 81.8	1390	-	-	-	
658	$(C_2H_5O)_2\overset{O}{\overset{\|}{P}}OK$ H_2O Gelvatol 20-30	48 62 10	40 51.7 8.35	1740	-	-	-	Pour point ~-40°F.; cooled solution gelled on warming and standing
662	658 H_2O	9 1	7.5 36.0 56.5	738	-	-	-	Pour point +15°F.; cooled sample gelled on standing
663	$(C_2H_5O)_2\overset{O}{\overset{\|}{P}}OK$ H_2O Gelvatol 1-30	3.60 5.65 0.75	36.0 56.5 7.5	Gelled in tube	-	-	-	
664	$(C_2H_5O)_2\overset{O}{\overset{\|}{P}}OK$ H_2O Carbowax 600	3.30 0.25 4.75	39.6 3.0 57.3	-	-	-	-	Gelled at room temperature
665	$(C_2H_5O)\ \overset{O}{\overset{\|}{P}}OK$ H_2O Carbowax 600	3.30 0.50 4.50	39.8 6.0 54.2	Gelled in tube	-	-	-	
666	$(C_2H_5O)_2\overset{O}{\overset{\|}{P}}OK$ H_2O Carbowax 600	3.30 1.25 3.75	39.8 15.1 45.3	820	48.7	18.5	8.15	Pour point -30°F.
667	$(C_2H_5O)_2\overset{O}{\overset{\|}{P}}OK$ H_2O Carbowax 600	3.30 0.83 4.75	37.[illegible] 9.4 53.5	2640	-	-	-	
694	$(C_2H_5O)_2\overset{O}{\overset{\|}{P}}OK$ H_2O Carbowax 6000	2.50 5.00 2.50	37.5 37.5 25.0	177	-	-	-	

Table 2 (cont'd)

MRC No.	Compound or Blend	Parts by Weight, g.	Composition, %	Viscosity, cs., °F. 28	100	150(1)	210	Remarks
695	$(C_2H_5O)_2\overset{O}{\overset{\uparrow}{P}}OK$ H_2O Carbowax 6000	2.40 3.86 3.32	25.1 40.3 34.6	Gelled in tube	-	-	-	Crystallized on standing; diluted to 33%, gelled at 28°F.
696	$(C_2H_5O)_2\overset{O}{\overset{\uparrow}{P}}OK$ H_2O Carbowax 6000	1.75 1.75 1.50	35.0 35.0 30.0	Gelled in tube	-	-	-	Cleared at room temperature
697	$(C_2H_5O)_2\overset{O}{\overset{\uparrow}{P}}OK$ H_2O WSR-35	7.06 10.55 0.40	39.2 58.6 2.22	460	-	-	-	Solution cloudy; polymer settled out on standing
689	$(C_2H_5O)_2\overset{O}{\overset{\uparrow}{P}}OK$ H_2O WSR-205	4.0 6.0 0.25	39.0 58.5 2.44	733	-	-	-	Cloudy solution; viscosity 670 cs. at 28°F. after standing several days
698	$(C_2H_5O)_2\overset{O}{\overset{\uparrow}{P}}OK$ H_2O WSR-205	4.00 6.00 0.275	38.9 58.4 2.68	674	-	-	-	Cloudy solution; viscosity 607 cs. at 28°F. after standing several days
686	$(C_2H_5O)_2\overset{O}{\overset{\uparrow}{P}}OK$ H_2O Acrysol GS	2.342 4.562 0.260	32.7 63.7 0.36	Layered in tube (extrapolated 230)	66.7	-	19.5	Acrysol salted out at 28°F.
700	Acrysol ASE-60 H_2O	0.004 28.015	0.01 99.99	65	-	-	-	Made basic with KOH
701	Acrysol ASE-60 H_2O	0.287 24.754	1.15 98.85	-	-	-	-	Viscosity >>> 850 cs. at 28°F. as observed by cooling to 28°F.

(1) Data extrapolated from a plot of the 100°-210°F values.

C. COMPATIBILITY

1. Paint

Paint compatibility tests were carried out as described in the second bimonthly Progress Report (NObs-90270 - 3 August 1964), on five general classes of phosphorus compounds in order to further check paint compatibility. The data are shown in Table 3.

The order of compounds closely approximates that described in the second bimonthly Progress Report. Diethyl potassium phosphate (compound 468) appeared slightly more compatible than methyl potassium methylphosphonate (compound 485) and is a compound of choice along with the methyl homolog. Both compounds, 486 and 485, were vastly superior to the aromatic derivatives.

D. CORROSION STUDIES

1. Aluminum

The corrosion test was carried out on compounds 468 and 485 as described in the second bimonthly Progress Report (NObs-90270 - 3 August 1964) using sheet stock 2024 aluminum, QQ-A-355, which is identical in composition to alloy QQ-A-268, specified by BuShips. Diethyl potassium phosphate (compound 468) showed no visible signs of attack on aluminum after 336 hr. at 93-94.5°C. (199.5-201.5°F.), while methyl potassium methylphosphonate (compound 485) showed definite attack on aluminum after 72 hrs. The affect of pH on compound 485 will be reassessed.

TABLE 3

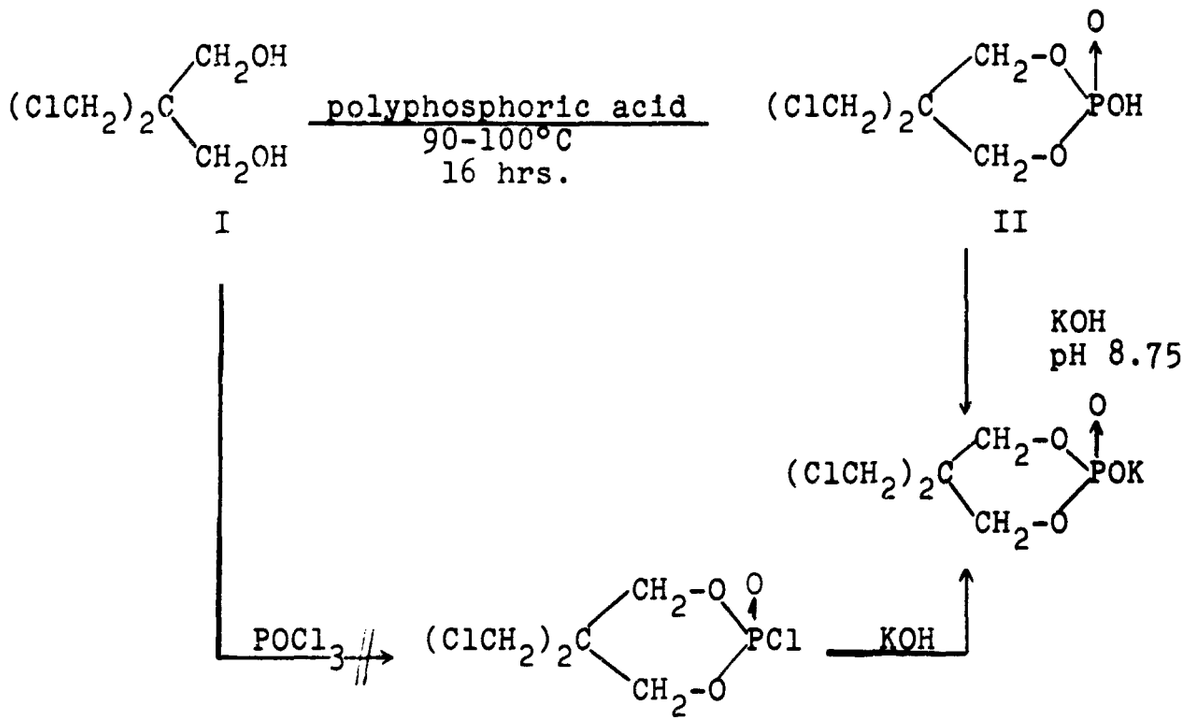
EFFECT OF PHOSPHORUS COMPOUNDS ON PAINT
(Formula 20L over Formula 116)

MRC No.	Compound[a]	% Concentration Water Solution	Effect
468	$(C_2H_5O)_2\overset{O}{\overset{\|}{P}}OK$	40.0	No detectable damage
485	$CH_3\overset{O}{\overset{\|}{P}}(CCH_3)_3(OK)$	40.0	Slight effect
634	$C_6H_5O\overset{O}{\overset{\|}{P}}(ONa)_2$	40.0	Paint softened; light to moderate damage
631	$ClC_6H_4\overset{O}{\overset{\|}{P}}(OC_2H_5)(OK)$	40.0	Moderate damage; paint could be removed with fingernail
591	$(ClC_6H_4O)_2\overset{O}{\overset{\|}{P}}OK$	40.0	Severe damage; some permanent damage; paint grainy and swelled

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

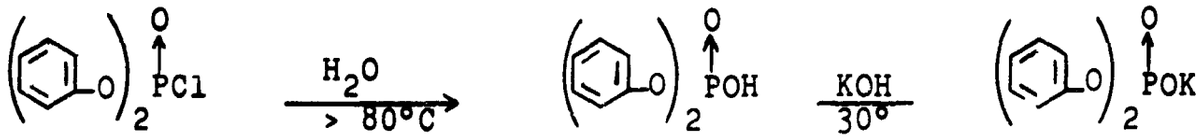
V. SYNTHESIS

The potassium salt of 5,5-bis(chloromethyl)-2-hydroxy-2-oxo-1,3,2-dioxaphosphorinane (IV) was successfully synthesized (34% yield) from the acid (II), which was prepared by the method of A. M. Meston (J. Chem. Soc., 1963, 6059-60):



Attempts to prepare the intermediate phosphorochloridate (III) from $POCl_3$ and the diol (I) resulted in polymeric mixtures. Apparently there is sufficient steric hindrance from the chlorine atoms in III to prevent cyclic ester formation with $POCl_3$. This is substantiated by molecular models and by the fact that the 5,5-dimethyl analog of III (substitution of $-CH_3$ for $-CH_2Cl$) can be prepared in good yield from dimethylpropanediol and $POCl_3$ (R. L. McConnell and H. W. Coover, Jr., J. Org. Chem., 24, 630-635 1959).

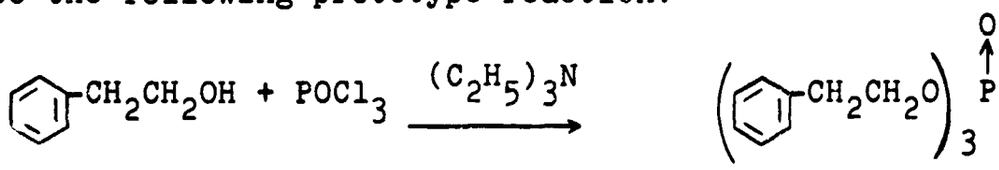
Diphenyl potassium phosphate (V) was prepared as follows:



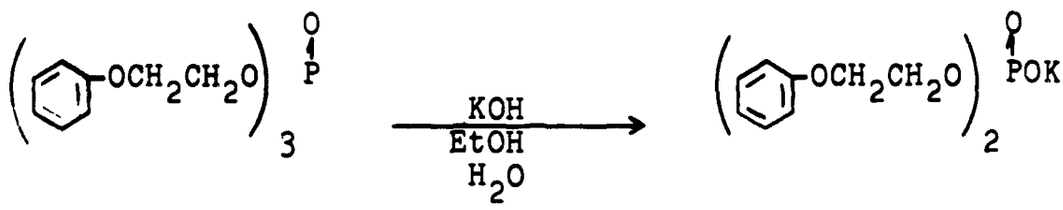
V

The compound was prepared in order to determine the hydrolytic stability of an alkali diphenyl phosphate but it was not sufficiently soluble to warrant further study.

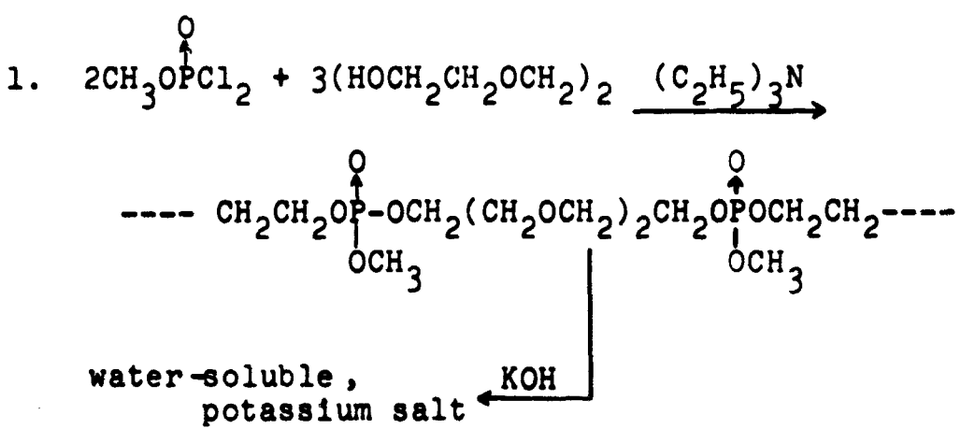
Tris(p-bromophenoxyethyl), tris(phenethyl), tris-2-(α-pyridyl-ethyl) and tris(phenoxyethyl) phosphates were prepared according to the following prototype reaction:



The tris(phenoxyethyl) and tris-2-(α-pyridyethyl) phosphates were converted to a monopotassium salt:



Three polyethylene oxide phosphates were prepared and partially hydrolyzed (crude) with one equivalent of potassium hydroxide to each phosphorus atom.



2. $POCl_3$ + 3Na(metal) + excess $(HOCH_2CH_2)_2O$ ⟶

$$\overset{O}{\uparrow}P(OCH_2CH_2OCH_2CH_2OH)_3$$

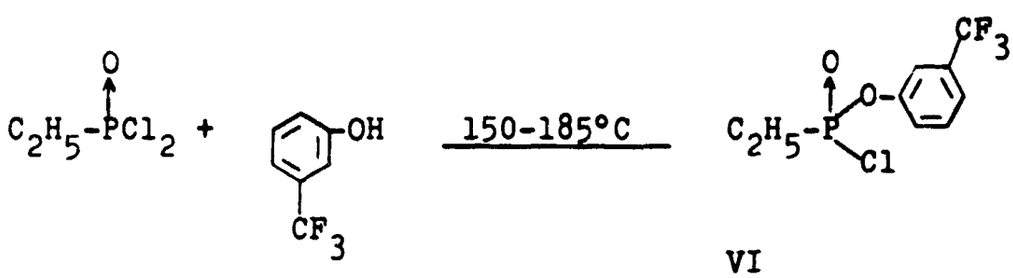
$$KO\overset{O}{\uparrow}P(OCH_2CH_2OCH_2CH_2OH)_2 \xleftarrow{KOH}$$

3. $2POCl_3$ + 6K(metal) + $3(HOCH_2CH_2OCH_2CH_2)_2O$ ⟶

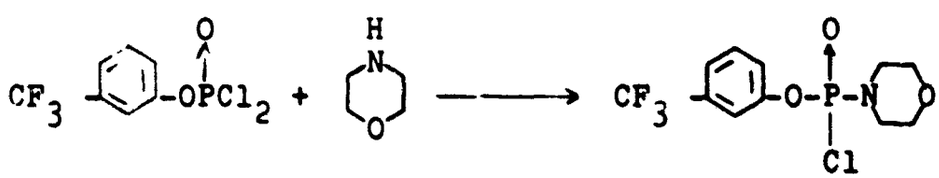
insoluble polymeric product

water-soluble, potassium salt ← KOH

<u>3-Trifluoromethylphenyl ethylphosphonochloridate (VI)</u> and <u>3-trifluoromethylphenyl morpholinophosphonochloridate (VIII)</u> were prepared as intermediates:



VI

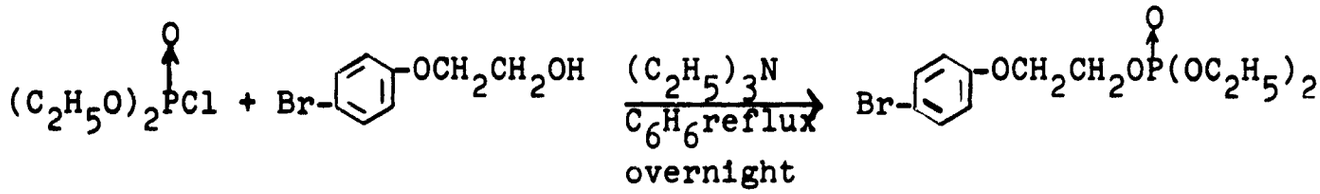


VII

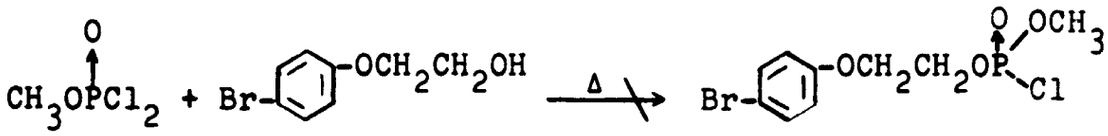
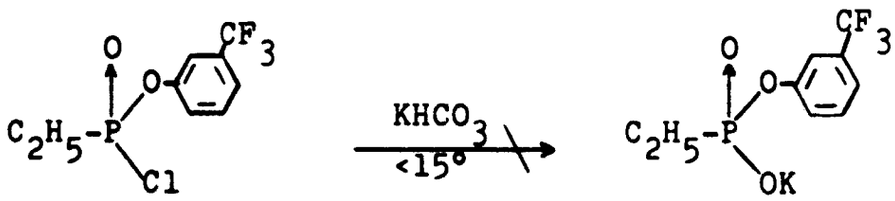
The trifluoromethyl-group was added for increased paint compatibility (VI and VII) and the morpholino-group was added to improve hydrolytic stability of the aromatic group and to improve the AIT

over the dialkylamino-group.

Mixtures were formed in the synthesis of <u>diethyl 2-(p-bromophenoxy)-ethyl phosphate</u>:



Methyl chloride was formed when the synthesis of <u>methyl 2-(p-bromophenoxy)ethyl phosphorochloridate</u> was attempted as follows:



<u>3-Trifluoromethylphenol</u> resulted in an attempt to synthesize <u>potassium 3-trifluoromethylphenyl ethylphosphonate</u>: