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APPLICATION OF ALIPHATIC PHOSPHORUS DERIVATIVES

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1 Introduction

(p.9)

Remarkable advances have recently been achieved in the study of organophosphorus compounds and a number of interesting results have been obtained for the application of these compounds to various fields. With the exception of a few; *i.e.*, some aromatic phosphorus derivatives that have earned a great deal of fame as pesticides because of their merit as well as toxicity and some aliphatic derivatives especially those which possess such substitution groups as CN and F and which were at one time subjected to extensive studies as dangerous nerve gases1), these compounds are used effectively in a variety of fields, though in a somewhat inconspicuous manner, depending on their characteristics. Among phosphorus derivatives having alkyl chains, there are many compounds of

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interest which are characterized by dissolubility in such organic materials as mineral oil and synthetic resins or by surface active properties when dissolved in water, and their use also extends over a wide area.

Since it is of course impossible to cover all the areas of application of these compounds, in this paper recent progress in the application of aliphatic phosphorus derivatives mainly as flame retardants, surfactants, antistatic agents, lubricant additives, and anticorrosives will be outlined*.

2 Flame Retardants

There are some difficult points in flameproofing plastics and textiles, since this ends in two conflicting results - prevention of disasters and waste disposal problems. However, from a safety viewpoint such operation is strongly demanded, and numerous products have already been in practical use, the detailed account of which is given in special works of Konishi and Hirao2). Flame retardation by phosphorus compounds is believed to be effected by exclusion of oxygen due to formation of nonvolatile membranes on the surface of an object by polyphosphoric acid produced as a pyrolyzate and at the same time by progression of such changes catalyzed by the polyphosphoric acid as dehydration, decarbonation and carbonization, leading to the formation of carbon films on

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*Throughout this paper compounds possessing the structure of $O:PH(OR)_2$ are called phosphonate diester, whereas those with the structure of $P(OH)(OR)_2$ phosphite diester.

the surface.

2.1 Flame retardants for textiles

Flameproofing textiles is developed in response to social demand for saving lives and extends over a wide area ranging from industrial and military uses to general public's use as exemplified by curtains and garments3).

Arney and Kuryla4) have carried out some fundamental examination with 11 aliphatic and aromatic esters of phosphite, phosphate and phosphonate on the relation between their chemical sturcture and flameproofing effect on cotton fabrics. In this examination the flameproofing effect is expressed as oxygen indices** 5). Hence it is obvious that compounds with larger oxygen indices are less inflammable. Oxygen indices of the 11 phosphorus derivatives used are shown in Table 1. The cotton fabrics showed an oxygen index of 18.5. Judging from Table 1, the oxygen indices of these derivatives themselves are not so large, but they represent values in the air phase, whereas the index for the fabrics is the value for solid-phase pyrolysis, the combustion conditions being entirely different between the two. Fig. 1 demonstrates a few examples of the relation between the oxygen index of the treated cotton and the phosphorus content of the derivatives. Of the aliphatic

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[**] The index is obtained from the minimal concentration of oxygen required for the flaming of an object under various atmospheric O_2/N_2 ratios by using an equation

$$\text{oxygen index} = \frac{O_2}{N_2 + O_2} \times 100$$

Table 1 Oxygen indices of various phosphorus derivatives4)

Derivative	Oxygen index
Trimethyl phosphite	19.2
Triethyl phosphite	18.0
Isopropyl phosphite	18.0
Phenyl neobenzyl phosphite	23.0
Didecyl phosphite	19.0
Dimethyl methanephosphonate	22.0
Diethyl ethanephosphonate	22.0
Diethyl benzenephosphonate	24.0
Trimethyl phosphate	26.0
Triethyl phosphate	19.0
Tributyl phosphate	19.0

PHOSPHORUS derivatives, phosphate esters have the greatest flame-resisting effect, followed in decreasing order by phosphonate esters and phosphite esters. However, the aromatic derivatives show the opposite pattern. This difference may be effected by the dissimilar pyrolysis mechanism between alkyl and allyl esters.

For flameproofing fabrics, flame retardants must be selected also in consideration of tensile strength, washing durability, air-holding ability, weather resistance, and toxicity. Hence, although a number of flame retardants have been introduced, only a few are in practical use. Those

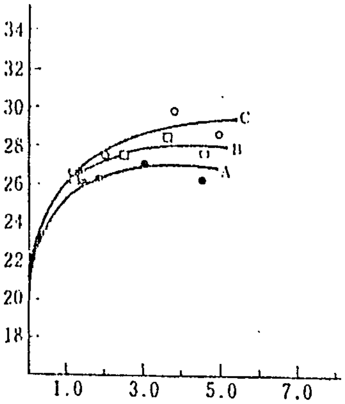


Fig. 1 Oxygen indices and phosphorus contents of cotton fabrics treated with phosphorus derivatives4)

Ordinate: Oxygen index

Abscissa: Phosphorus content (%) (fabric plus treating agent)

A: Triethyl phosphite

B: Diethyl ethanephosphonate

C: Triethyl phosphate

(p.10)

recognized as semipermanent, flameproofing reactants are tetrachis (hydroxymethyl) phosphonium chloride (THPC), $(HOCH_2)_4PCl$; tris (1-aziridinyl) phosphine oxide (APO), $(CH_2CH_2NH)_3PO$; and N-methylol-3-(dimethylphosphono) propionate amide (Pyrovatex CP), $(CH_3O)_2P(O)CH_2CH_2CONHCH_2OH$.

THPC is synthesized from phosphine, formaldehyde and hydrochloric acid as follows:

$$PH_3 + 4\ CH_2O + HCl = (HOCH_2)_4PCl$$

and there are a variety of flameproofing procedures for textiles using this compound. Nishino6) has compared each of these procedures. On the other hand, Goynes _et al._7) have observed the surface of cotton fibers treated with THPC-NH_3 with scanning and transmission electron microscopes to examine the flame resistance mechanism.

Cotton and polyester blends (Tetron) are recently in very wide use and therefore a proper means of flameproofing these products is earnestly being sought. A few available methods have been discussed by Tesoro _et al._8). For example, when the flame-resisting effect is compared between THPC-NH_3 and Pyrovatex CP as each is used to treat a pure cotton product and a cotton blend (Fig. 2), the effect is less in the blend than in the pure product with the same amount of phosphorus, indicating that the former product is more inflammable than the latter. When fibers preimpregnated with N-methyl-3-(diallylphosphono) propionamide8,9) having unsaturated bonds are brominated in chloroform solution at room temperature, the results are as shown in Table 2. Without

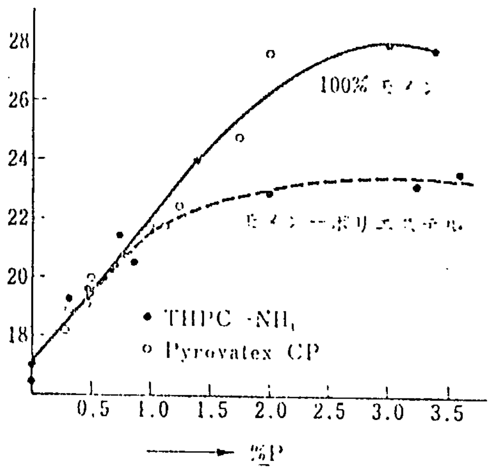


Fig. 2 Flame-resisting effect in products of pure cotton and of cotton blend8)

Ordinate: Oxygen index
Abscissa: Per cent phosphorus

Solid line: 100% cotton,
Interrupted line: cotton-polyester

Table 2 Treatment of fibers with N-methylol-3-(diallylphosphono) propionate amide and bromine8)

	I 100% もめん				II 50/50もめん－ポリエステル			
	酸素指数*	P%	N%	Br%	酸素指数*	P%	N%	Br%
A 処理前	18.2	-	-	-	16.9	--	-	-
B 処理後	27.8	1.1	0.7	5.8	25.8	1.1	0.5	5.2
C 5回洗タク後	27.8	1.1	0.6	--	25.4	0.9	--	5.2
D 25回洗タク後	26.8	1.1	0.6	5.1	25.0	0.9	0.1	3.9
E 溶剤抽出後	27.8				25.4	--	--	--

I 100% cotton
II 50/50 cotton-polyester
* Oxygen index

A Before treatment
B After treatment
C After washing 5 times
D After washing 20 times
E After solvent extraction

using bromination the oxygen index of the fibers is 22.0.

It is said that the production of APO is now suspended because of safety and cost.

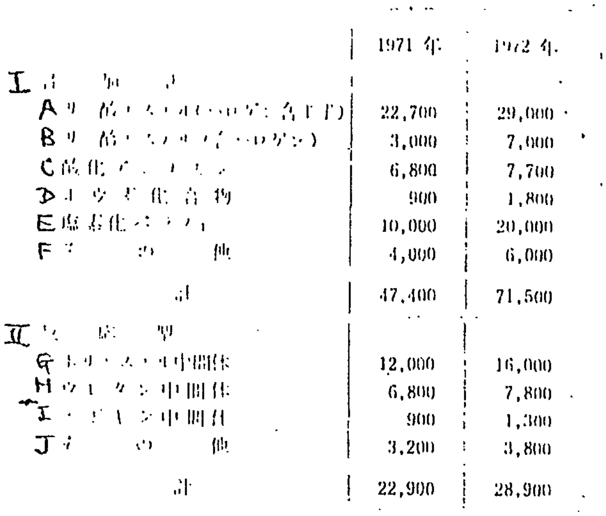
N-methylol compounds of dialkyl phosphonocarbonate amide such as Pyrovatex CP were developed by Ciba, and properties of 15 different compounds of this series as flame retardants have been examined by Aenishänslin _et al._10). Of these, dimethyl and diethyl esters of N-methylol phosphonopropionate amide show good quality. Pyrovatex CP, as compared with APO and THPC, has very low toxicity (LD_{50} = 69/kg), and products treated with this compound are superior in softness and durability to washing and cleaning.

2.2 Flame retardants for plastics

With increasing consumption of plastics especially as building materials, the flameproofing of these materials is increasingly in demand. However, in the development of flameproofing agents suppression of smoke production will also have to be considered. Available flameproofing agents for plastics are discussed in detail in the aforementioned book of Konishi and Hirao2) and a few others11). Methods of flameproofing plastics are generally divided into two; in one of which plastics themselves are made flameproof, whereas in the other flameproofing agents are added to plastics. The former concerns the formation of polymers containing phosphorus elements within their molecules; i.e., the field of high polymer synthesis, an outline of which is given for example in a treatise of Yokoyama12), whereas the latter is generally in more wide use. For example, in Table 3 the amount of flameproofing agents used for plastics in the U.S.A.13) is listed. In this table the amount of those used as additives shows a 1.5-fold annual increase. Since phosphorus derivatives has advantage of not producing any irritating poisonous gas on heating, they are in use in large quantities as flameproofing additives and flameproof plasticizers14).

Since urethane foam either in form of soft foam as bedding materials or in form of hard foam as heat-insulating materials has been in such a great demand that flameproof foam is in great demand. For this class of products phos- (p.11)
phorus derivatives are used either as reactants (e.g., phosphorus-containing polyols) or as additives. When the relation between the phosphorus content in the foam and the burning

Table 3 Amount of flameproofing agents used for plastics in the U.S.A. (ref.-13)



	1971年	1972年
I 添加型		
A リン酸エステル（ハロゲン含まず）	22,700	29,000
B リン酸エステル（ハロゲン）	3,000	7,000
C 酸化アンチモン	6,800	7,700
D ホウ素化合物	900	1,800
E 塩素化パラフィン	10,000	20,000
F その他	4,000	6,000
計	47,400	71,500
II 反応型		
G ポリエステル中間体	12,000	16,000
H ウレタン中間体	6,800	7,800
I エポキシ中間体	900	1,300
J その他	3,200	3,800
計	22,900	28,900

I As additives
  A Phosphate esters (containing no halogen)
  B Phosphate esters (containing halogens)
  C Antimony oxide
  D Boron compounds
  E Chlorinated paraffin
  F Others
II As reaction products
  G Polyester intermediates
  H Urethane intermediates
  I Epoxy intermediates
  J Others

Papa and Proops[15] synthesized soft urethane foam products using three commercial polyol preparations; i.e., phosphate-containing polyol (phosphate ester type), diethyl ester of N,N-bis(2-oxyethyl)-aminomethane phosphonate

distance (ASTM-D 1692-59T) as a parameter of self fire-extinguishability[11] is shown (Fig. 3), it is clear that flameproofing effect occurs within certain limits of phosphorus contents[11]. In other words, flameproofing effect is not expected to rise beyond a certain phosphorus content.

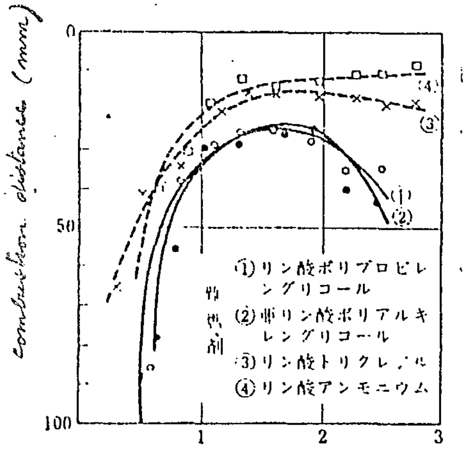


Fig. 3 Relation between phosphorus content and burning distance[11]

Ordinate: Burning distance (mm)
Abscissa: Phosphorus content (%)

Flameproofing agents: 1) Polypropyleneglycol phosphate, 2) Polyalkyleneglycol phosphite, 3) Tricrezyl phosphate, 4) Ammonium phosphate (phosphonate ester type), and tris (dipropyleneglycol) phosphite (phosphite ester type), and have examined the relation between chemical structure and flame-retarding ability for each type of the phosphorus reactants and also the existence of synergism for the flameproofing effect between phosphorus and halogens. Fig. 4 shows the relation between the phosphorus content and the oxygen index of the forms prepared with the three types of polyols. For the phosphate ester type, the flameproofing effect is greatly affected by the phosphorus content and it is inferior to that with the phosphonate or phosphite ester type at P contents of below 0.4% but increases with increasing phosphorus concentration above 0.4%. On the other hand, the effects with the phosphonate and phosphite ester types become nearly constant at P contents over 0.3%.

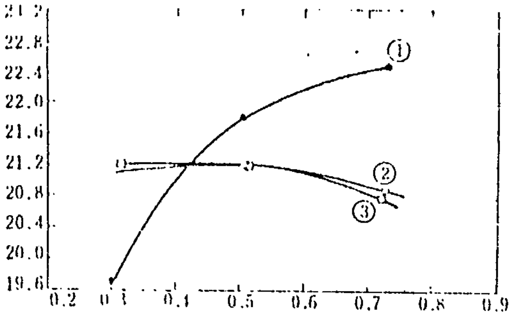


Fig. 4. Relation between phosphorus content and oxygen index of foam15)

Ordinate: Oxygen index
Abscissa: Phosphorus content

1) Phosphate ester
2) Phosphonate ester
3) Phosphite ester

Other methods of manufacturing self fire-extinguishable hard foam are treatment of polyols with addition compounds of amino group-containing phosphonate ethylene oxide; e.g., $CH_3N[CH_2PO(OH)_2]_2$ 16), use of an addition compound of phosphorus-containing glucose-propylene oxide as a polyol17), and use of a 1:1 reaction product between pentaerythrite and phosphoryl chloride as a part of polyols 18). Phosphorus-containing compounds as flameproofing additives for urethane foam are often used in combination with bromine or chlorine-containing flameproofing agents rather than by themselves. Generally aromatic esters such as tricrezyl phosphate and triphenyl phosphite are used for the flameproofing of both soft and hard types of urethane foam, whereas aliphatic derivatives are employed mostly for soft foam. The use of a reaction mixture of diethyl phosphite and hexamethylene tetramine is also effective in the preparation of self fire-extinguishable foam 19), and addition of dialkyl beta-[N(acetamide methyl)-carbamoyl] ethane phosphonate results in flame-retarding products 20).

Chlorinated plastics such as polyvinyl chloride are less inflammable than the other plastics. However, a demand for flameproofing is great for soft polyvinyl chloride that requires large quantities of inflammable plasticizers for its manufacturing. Flame-resistant plasticizers must be selected in consideration of plasticizability, cold resistance and other physical properties. Aromatic phosphorus compounds such as tricrezyl phosphate and crezyl diphenyl phosphate are good flame retardants but have such defects as an offensive odor and low cold resistance.

Table 4 compares the results of experiments in which di long-chain alkyl phosphoroamidates and tricrezyl phosphite were used as plasticizers of polyvinyl chloride 21). The

Table 4 Polyvinyl chloride prepared with dialkyl phosphoryl amidates $(RO)_2PONH_2$ as plasticizer[21)]

R	A 本品 部	A DOP 部	B 引張り強さ (kg/cm²)	C 伸び (%)	D 脆化温度 (°C)	E 表面固有抵抗 (Ω)	F 難燃性 (sec)
C_2H_5	20	30	187	349	−50	2×10^9	0
C_5H_{11}	20	30	179	347	−54	2×10^9	0.2
C_6H_{13}	20	30	186	368	−51	3×10^9	0.4
C_8H_{17}	20	30	179	328	52	4×10^9	2.9
TCP	20	30	194	281	−27	$>10^{12}$	0
C_8H_{17}	5	45	177	308	−42	1×10^{11}	3.8
TCP	5	45	183	292	−37	$>10^{12}$	3.5
なし*	0	50	184	301	−40	$>10^{12}$	4.2

* None
TCP = tricrezyl phosphate

A Ratio of $(RO)_2PONH_2$ to DOP (dioctyl phthalate)
B Tensile strength
C Expansion
D Fragility point
E Surface specific resistance
F Flame resistance

dialkyl compounds are equal to DOP in tensile strength and better than DOP in expansion and thus are judged to possess good mechanical properties as plasticizer. They are also superior to DOP in cold resistance and have fairly good antistatic ability too and thus can be regarded as excellent flame-retardant plasticizers.

Flame retardants as (p.12) additives must be effective in small quantities and must not impair the property of the materials to which they are added. An example of such flame retardants; i.e., long-chain alkyl esters of trichloromethyl phosphonate, when added 1.5% to soft polyvinyl chloride, is shown in Table 5[22)]. It is apparent that these esters are effective flame-retardant additives which have also about the same chelating effect as the commercial chelate and are as antistatic as the commercial amine antistatic agent.

Other effective flame-retardant trihaloalkane phosphonates are 3-chloro-2,3-di-bromopropane phosphonate dialkyl esters that are synthesized by bromination of reaction products between 1,3-dichloropropane and trialkyl phosphites[23)], and these compounds when added in an amount of 15% to plastics

Table 5 Polyvinyl chloride to which 1.5% $Cl_3CP(O)(OR)_2$ is added22)

ポリ塩化ビニル

A 添　加　剤 (R)	B 透明性 (%)	C 難燃性 (sec)	D 帯電圧 (kV)
1) なし	86.1	5.0	0.90
DPDP	89.2	1.8	0.75
C_2H_5	88.4	1.3	0.65
C_4H_9	90.8	1.8	0.65
C_6H_{13}	88.5	2.8	0.65
C_8H_{17}	87.9	2.9	0.55
$C_{10}H_{21}$	87.9	4.2	0.58
$C_{12}H_{25}$	81.2	1.8	0.78
2) 市販帯電防止剤		—	0.70

A Additive (R)
  1) None
  2) Commercial antistatic agent
B Transparency
C Flame resistance
D Static voltage

DPDP: Commercial chelating additive, diphenyl decyl phosphite

with an oxygen index of 18.7 increased the oxygen index value to 23.9. Not only flameproofing plastics but also rendering them low-smoking are requested nowadays. According to a recent report24), combined use of isophthalic acid and phosphorus-containing flame retardants such as (diethanolamino)methane phosphonate dialkyl esters reduces smoke production of plastics by 30%.

When paints are flameproofed, vesicant paints that expand to foam on heating are used, and polyvalent alcohols and ammonium phosphate are employed as additives. Waterproof, vesicant and flame-retardant paints are also in demand. Blair <u>et</u> <u>al</u>.25) conducted a combustion test (ASTM D 1360-70) on paint films prepared by/coating 0.5 mm thick with an epoxy resin-based paint to which one of 21 different organophosphorus compounds as shown in Table 6 was added 10%. Fig. 5 shows the volume of carbonization and the foam height produced. Generally the flame-retarding effect varies with chemical structure of the phosphorus compounds and is approximately in the following order:

Table 6 List of organophosphorus compounds added to a paint and their abbreviation forms[25)]

Bis (hydroxymethyl) phosphinate	BHMP
Tris (2-chloroethyl) phosphate	TCEPA
Trimethylthiono phosphate	TMTPA
Trimethyl phosphate	TMPA
Triallyl phosphite	TAP
Tris (chloropropyl) phosphate	TCPPA
Triphenyl phosphite	TPP
Trimethyl phosphite	TMP
Diethyl trichloromethane phosphonate	DETCPH
Phosphoryl trianilide	PTA
Triallyl phosphate	TAPA
Phosphoric acid - aniline condensate	DIP
Tris (2-chloroethyl) phosphite	TCEP
Tributyl phosphite	TBP
Tributyl phosphate	TBPA
Diphenyl methane phosphonate	DPMPH
Dimethyl methane phosphonate	DMMPH
Diallyl propane phosphonate	DAAPH
Tricrezyl phosphate	TCPA
Polyol phosphonate	POPH
Tetraallyl phosphonosuccinate	TAPH

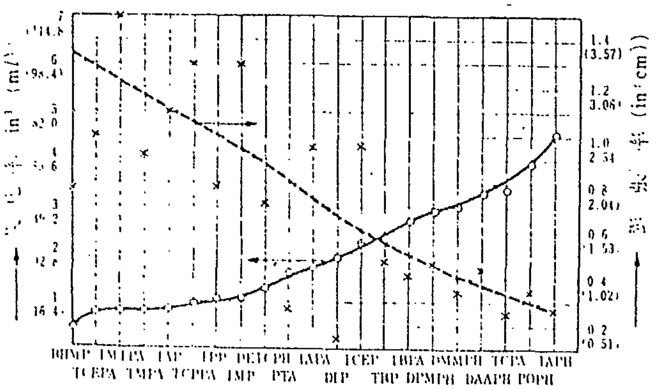


Fig. 5 Structure and flameproofing effect of organophosphorus compounds[25)] (See Table 6 for abbreviations)

Ordinate: (Left) Carbonization rate in in^3 (ml)
(Right) Expansion rate in in(cm)

acid > phosphate ester ≈ phosphite ester > phosphonate ester

3 Surfactants

Although inorganic phosphate and polyphosphate salts have been in use as detergent builders for a long time, it was only about 10 years ago that organophosphorus compounds were introduced into the field of surfactants. Since aliphatic phosphorus derivatives possess alkyl groups as hydrophobic groups on one hand and phosphonyl groups as hydrophilic groups on the other hand, there among these are very large numbers of compounds displaying surface active properties$^{26)}$.

Sakurai$^{27)}$ has carried out a detailed study with long- (p.13) chain alkane phosphonate derivatives possessing a variety of substitution groups to examine the relation between the substitution groups and surface active capacity of the derivatives. On the other hand, Maurer _et_ _al_.$^{28)}$ compared wetting, foaming, detergent, and/other surface-active properties of α-phosphono and α-sulfo fatty acids of C_9 to C_{18}.

Aliphatic phosphorus derivatives are used not only as surfactants themselves but also as surfactant ingredients depending on their characteristics; e.g., as inhibitors of lime soap dispersion and aggregation, stabilizers of bleaching solutions, solubilizers of cleaning liquids, germicides, anticorrosives, blocking agents of metallic ions, and builders. Properties and manufacturing procedures of these derivatives are discussed in detail in a treatise of Maier$^{29)}$. Comparisons of various surface-active properties between salts of sulfate esters and sulfonate esters are given in Table 7.

Phosphated castor oil has better surface-active quality but costlier than sulfated one (turkey-red oil). Similarly, dodecylbenzene phosphate salt is as effective as but costlier than the corresponding sulfonate salt and

Table 7 Surface-active properties of aliphatic phosphorus derivatives[29)]

A 化合物	B 湿潤力a) (sec)	C 洗浄力b)	D カルシウムセッケン分散力c)	E 表面張力d) (dyne/cm)
1 リン酸化ヒマシ油	180	70	42	39
2 ロート油	180	18	3	44
3 リン酸オクチルエステル	13.8	39	3	45
4 硫酸オクチルエステル	180	23	100	36
5 [illegible]	180	85	1	39
6 [illegible]	1.0	83	16	37
7 [illegible]	67	85	15	36
8 [illegible]	180	81	14	30

A Compound
- 1 Phosphated castor oil
- 2 Turkey-red oil
- 3 Octyl phosphate
- 4 Octyl sulfate
- 5 Sodium dodecyl benzenephosphonate
- 6 Sodium dodecyl benzenesulfonate
- 7 Sodium dodecyl phosphonate
- 8 Sodium nonyl phosphonate

B Wetting power[a)]
C Detergency[b)]
D Lime soap dispersion power[c)]
E Surface tension[d)]

a) Wetting time by the method of Draves in 25% solution.
b) 0.2% solution with hardiness of 300 ppm.
c) 100% being the maximum.
d) In 0.25% solution.

accordingly is limited in use. Also 4-(dimethyl dodecyl phosphonio) lactate salt $(C_{12}H_{25})(CH_3)_2PC_3H_7COONa$ has been patented as a detergent suitable for use at low temperatures of 4 to 35° C[30)].

Disodium phosphate salts of addition compounds of long-chain alcohol propylene oxide have been shown by Matsuda _et_ _al_.[31)] to be surfactants with low foaming and low bubble stability. Many compounds are patented as low-foaming additives of detergents; e.g., salts of phosphoric acid-acidified hexa- and octadecyls[32)], phosphoric acid-acidified polyoxyethylene-2-ethyl-hexyl[33)], salts of mono-dodecyl and monotetradecyl phosphites[34)] (all of which are alkaline metal or amine salts).

Krupin[35)] compared effectiveness of phosphoric acid ester salts and aromatic sulfonate salts (both sodium salts) as low-foaming solubilizers of non-ionic liquid detergents and has found that sodium salts of phosphoric acid-acidified esters are excellent hydrotropic agents. There is a patent in which addition of 0.1 - 0.2% per lb phosphine oxides such as $[(RO)_2P(O)CH_2]_3PO$ and $[(RO)_2P(O)CH_2]_2POH$ where $R = C_8H_{17}$ or $C_{12}H_{25}$, in lieu of sodium polyphosphite is claimed to be effective in preventing recontamination36).

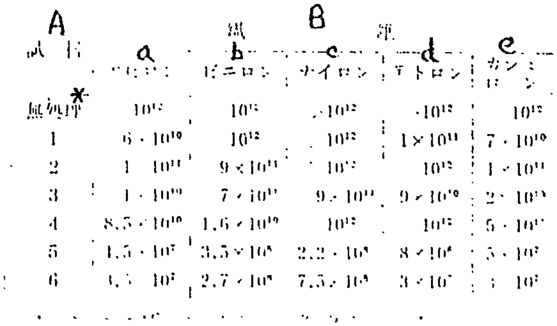
Surfactants are also in use in flotation. According to Yamada _et_ _al_.37), when monoalkyl (C_8 to C_{18}) phosphates (disodium salts) were used for ion flotation as collectors to remove Zn, Cd, Cu and Ca from aqueous solution, mono-octadecyl phosphate was found superior in elimination rate and selectivity.

4 Antistatic Agents

Detailed discussion of static electricity and its prevention are given in textbooks such as the one by Marushige38). Many of surface active phosphorus derivatives are effective also as antistatic agents, and such derivatives as mono and disalts (alkaline metals and amines) of phosphinate, phosphonate, phosphite, and phosphate esters are employed.

The method of synthesizing alkane phosphonate derivatives by blowing oxygen into trichloride solutions of hydrocarbons and various long-chain alkyl compounds was introduced at first by Clayton and Jensen39). When this method is applied to saturated fatty acids40) or wax esters41), unique phosphonate derivatives containing carboxyl groups are obtained. Sakurai and Okamoto[41)] have shown that phosphonate derivative sodium salts obtained from sperm whale solid wax are effective not only as antistatic agents but also as softners of synthetic fibers and these useful properties have been attributed largely to the presence of ester groups. They[42)] also examined antistatic properties toward synthetic fibers of a variety of phosphonate derivatives obtained as addition compounds of dialkyl phosphites containing long-chain unsaturated alkyl bonds. A part of the results is shown in Table 8. The diethyl phosphonate derivatives

Table 8 Antistatic capacity (surface resistance, Ω) of long-chain alkane phosphonate derivatives[42)]



A 試料	B a テビロン	b ビニロン	c ナイロン	d テトロン	e カシミロン
無処理*	10^{12}	10^{12}	10^{12}	10^{12}	10^{12}
1	6×10^{10}	10^{12}	10^{12}	1×10^{11}	7×10^{10}
2	1×10^{11}	9×10^{11}	10^{12}	10^{12}	1×10^{11}
3	1×10^{10}	7×10^{11}	9×10^{11}	9×10^{10}	2×10^{11}
4	8.5×10^{10}	1.6×10^{10}	10^{12}	10^{12}	5×10^{11}
5	1.5×10^{7}	3.5×10^{8}	2.2×10^{8}	8×10^{8}	5×10^{7}
6	[illegible]	2.7×10^{8}	7.5×10^{8}	3×10^{7}	[illegible]

A Compound
- * No treatment
- 1 Reaction product between ethyl oleate and diethyl phosphite
- 2 Reaction product between oleyl acetate and diethyl phosphite
- 3 Reaction product between oleyl alcohol and diethyl phosphite
- 4 Reaction product between liquid wax ester from sperm whales and diethyl phosphite
- 5 Sodium salt of 1-hydrolyzate
- 6 Sodium salt of 2-hydrolyzate

B Fiber
- a Tevilon
- b Vinilon
- c Nylon
- d Tetlon
- e Kashimilon

designated as compounds 1 to 4 in Table 4 have almost no effect, whereas the sodium salts (compounds 5 and 6) are highly effective antistatic agents.

Also there is a patented method in which dialkaline (p.14) metal salts of mono dodecyl phosphite are added 0.5 to 5% to fiber materials before spinning43). Other compounds such as polyoxyethylene alkyl ether ($C_{12} - C_{16}$ ethylene oxides 2 to 10 mol), phosphoryl chloride, N-aminopropane phosphonamide ester synthesized from N,N-dimethyl-1,3-propanediamine are also patented as effective antistatic agents44).

Rendering plastics antistatic is carried out in two ways; an exterior process in which antistatic agents are painted and an interior one in which agents are incorporated into plastic materials, the latter being in wider use than the former. The long-chain dialkyl phosphoro amidates shown in Table 3 (should be 4: Translator's note) are effective not only as plasticizers for polyvinyl chloride but also as antistatic agents. When phosphate ester metal salts of addition compounds of higher alcohol ethylene oxides, for example di(polyoxyethylene dodecyl ether) phosphate barium salt, are combined with metallic salts of ampholitic surfactants as internal antistatic agents for polyvinyl chloride sheets, it is claimed that the product possesses good thermostability with high antistatic property in the order of $10^{10}\,\Omega$ surface specific resistance45).

As for antistatic agents of exterior type, there is a report by Suga <u>et al</u>.46) that antistatic capacity of mono octyl phosphite and mono 2-ethylhexyl phosphite when painted on vinyl chloride resin is remarkable. As antistatic agents for photographic film, monoalkyl phosphates, alkane phosphonates47) and monoalkyl alkane phosphonate salts48) are patented.

5 Additives for Lubricating Oil and Gasoline

Sometime in the last half of the 19th century the practice of adding beef tallow to mineral oil to improve the lubricating quality of steam cylinder oil began, and this is said to be the beginning of lubricating oil additives. In recent years, with increasing quality of machines the demand for better lubricating oil also become increasingly severe, and development of new additives is being carried out at a good pace. A number of organophosphorus derivatives are in practical use as antioxidants, detergents, extreme pressure resistance agents, and anticorrosives for lubricating oil.

5.1 Antioxidants

Of high temperature antioxidants for internal combustion engine lubricating oil, the most widely used are metal (mainly zinc) salts of dialkyl dithio phosphates $(RO)_2P(S)S-ZnS(S)P(OR)_2$ where R = straight or branched chain alkyl groups having C_3 to C_8. Akamatsu and Negoro49) have examined oil solubility and antioxidant properties of dithio phosphate esters having different alkyl groups and observed synergism between these esters and amine and phenolic antioxidants.

In addition to the dithio esters, phosphate esters obtained by reaction among 2,6-di-tertiary butyl hydroquinone, phosphoryl chloride (or thiophosphonyl chloride), and octadecanol display antioxidant properties such as suppression of chain reactions and decomposition of peroxides50). A byproduct of the above reaction, bis (3,5-di-tertiary butyl-4-hydroxyphenyl) octadecyl phosphate, is reported to show synergism with didodecyl thiodipropionate51). On the other hand, reaction products among dimeric acids, N-beef tallow-1,3-propylene diamine, and 2-ethylhyxyl phosphate are found effective as antioxidants and antistatic agents for diesel oil52).

5.2 Detergents

As detergents as well as dispersants that prevent engine deposits, effective are phosphate compounds obtained by neutralization with metal oxide (barium) or amines or esterification with ethylene oxide of a hydrolyzate of a reaction product between polybutane polymer and phosphorus pentasulfide, and each class of these compounds, be it salt, amide, or ester type, is used for different kinds of engines (ref. - 53). Monobutyl phosphate54) is effective as a detergent for airplane gas turbine engines, whereas N-oleylpropane diamine salt of octyl phosphate55) and vanadium and chrome salts of decyl phosphate56) for gasoline engines. Dioctadecyl ester of N-propyl-N-dodecyl phosphoroamidate is also effective as a gasoline detergent57).

5.3 Extreme pressure additive

Additives of this class are added to prevent seizure of metal surface by allowing these compound to react with metal surface at high temperature under high pressure to form low-shearing compounds. However, these additives at the same time are required to exhibit some lubricating property to reduce the wear and tear.

Davey[58)] determined a few properties of 21 esters of phosphate and phosphite compounds, both aliphatic and aromatic and when used as extreme pressure additives, in a four-ball testing machine, and has found that phosphite esters are superior to phosphate esters, that long-chain aliphatic derivatives are better than the aromatic ones, and that phosphorus derivatives containing Cl and S are effective, especially those containing Cl_3C-groups being extremely so even at low concentrations. It is generally said that phosphorus derivatives are inferior to additives of halogen-sulfur series in extreme pressure resistance but that they are about equal to lead soap - sulfur series additives.

On the other hand, Sakurai and Sato[59)] examined reactivity at high temperature toward iron of lubricating oil to which was added one of the following five aliphatic phosphorus derivatives: didodecyl phosphite, tridodecyl phosphite, a mixture of mono and didodecyl phosphates, tridodecyl phosphate, and tridodecyl trithiophosphite. Reaction products formed between iron and the treated lubricating oil preparations were also examined to determine seizure load capacity of the five derivatives. Neutral esters showed low reactivity, whereas acidic esters and the thiophosphite ester were high in reactivity. X-ray analyses confirmed that some of the reaction products; i.e., $2FeFe_4(PO_4)_3(OH)_5$, $Fe_3(PO_4)_2$, and $FePO_4$, contributed to the extreme pressure-resisting effect. The extreme pressure-resistant effectiveness of compounds formed as films on the metal surface were in the following increasing order: chloride, sulfide, phosphate and phosphide, whereas the antiwear effectiveness were in the order of phosphide < phosphate < sulfide.

Table 9 shows seizure load and friction coefficients of C_{18} phosphono fatty acid methyl esters obtained as radical addition compounds of diethyl phosphite to methyl oleate, methyl linoleate, or acetylated methyl ricinoleate and used as 10% additives[60]. Dialkyl (long-chain) esters of Cl_3C-group-containing trichloromethane phosphonate are also very effective extreme pressure additives[22], and comparison of these with the corresponding trialkyl phosphites, when both are used as 1% additives, is shown in Table 10 and some extreme pressure-resistant properties of the phosphonate esters when used in low (p.15)

Table 9 Properties of C_{18} phosphono fatty acids as extreme pressure additives[60] (four-ball machine testing)

(A)	(B) (kg/cm²)	(C)	(A)	(B) (kg/cm²)	(C)
1	6.0	0.1099	3	9.5	0.1145
2	7.0	0.0931	B	3.5	0.1181

(A) Additive
- 1 Methyl diethylphosphonostearate
- 2 Reaction product between methyl linoleate and diethyl phosphite
- 3 Reaction product between acetylated methyl ricinoleate and diethyl phosphite
- B Spindle oil (no additive)

(B) Seizure load
(C) Friction coefficient

Table 10 Extreme pressure-resistant properties of trichloromethane phosphonate diesters and phosphite triesters22) (Top) (Four-ball machine testing)

A Additive
* None
B Seizure Load
C Friction coefficient

Table 11 Extreme pressure-resistant properties of trichloromethane phosphonate diesters at various concentrations (ref. 22) (Bottom)

A Additive
B Amount added
C Seizure load
D Friction coefficient

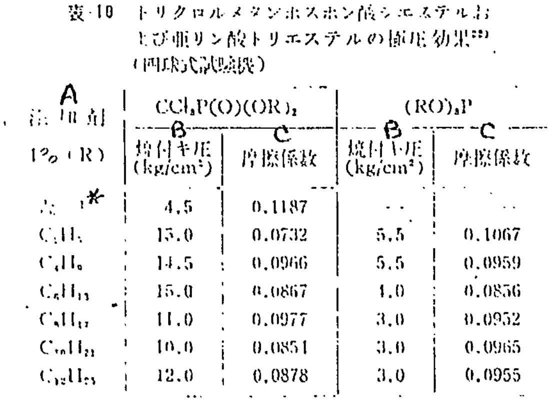


表-10 トリクロルメタンホスホン酸ジエステルおよび亜リン酸トリエステルの極圧効果22)（四球式試験機）

A 添加剤 1% (R)	$CCl_3P(O)(OR)_2$ B 焼付キ圧 (kg/cm²)	 C 摩擦係数	$(RO)_3P$ B 焼付キ圧 (kg/cm²)	 C 摩擦係数
無し*	4.5	0.1187		
C_3H_7	13.0	0.0732	5.5	0.1067
C_4H_9	14.5	0.0966	5.5	0.0959
C_6H_{13}	15.0	0.0867	4.0	0.0856
C_8H_{17}	11.0	0.0977	3.0	0.0952
$C_{10}H_{21}$	10.0	0.0851	3.0	0.0965
$C_{12}H_{25}$	12.0	0.0878	3.0	0.0955

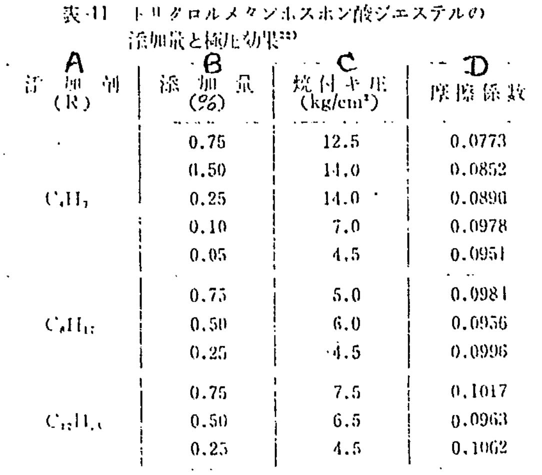


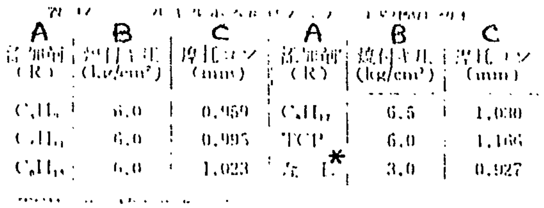
表-11 トリクロルメタンホスホン酸ジエステルの添加量と極圧効果22)

A 添加剤 (R)	B 添加量 (%)	C 焼付キ圧 (kg/cm²)	D 摩擦係数
C_4H_9	0.75	12.5	0.0773
	0.50	14.0	0.0852
	0.25	14.0	0.0890
	0.10	7.0	0.0978
	0.05	4.5	0.0951
C_8H_{17}	0.75	5.0	0.0981
	0.50	6.0	0.0956
	0.25	4.5	0.0996
$C_{12}H_{25}$	0.75	7.5	0.1017
	0.50	6.5	0.0963
	0.25	4.5	0.1062

concentrations are demonstrated in Table 11.

Table 12 shows properties of dialkyl (long-chain) phosphoryl amidates as 5% extreme pressure additives in comparison with tricrezyl phosphate21). Also Forbes and Silver61) determined extreme pressure- and wear-resistant effects of 12 N-substitutes of dibutyl phosphorylamidate and 14 amine

Table 12 Extreme pressure-resistant properties of alkyl phosphoryl amidates21)



A 添加剤 (R)	B 焼付キ圧 (kg/cm²)	C 摩耗コン (mm)	A 添加剤 (R)	B 焼付キ圧 (kg/cm²)	C 摩耗コン (mm)
C_4H_9	6.0	0.959	C_8H_{17}	6.5	1.030
C_6H_{13}	6.0	0.995	TCP	6.0	1.166
C_8H_{16}	6.0	1.023	無し*	3.0	0.927

A Additive
TCP = tricrezyl phosphate
* None
B Seizure load
C Friction coefficient

salts of dibutyl phosphate, and have found that the N-substitutes are more effective than tricrezyl phosphate, monosubstitutes being superior to disubstitutes, and that the phosphate ester amines have higher seizure load, though the effect is independent of the extent of N-substitution. Seizure load capacity of Sn, Zn and Ba salts of monoalkyl (C_6 to C_{18}) phosphates when used as additives at different levels has been determined by Suga *et al.*62). Although these salts have high seizure load, they are sparingly soluble in lubricating oil. There is also a report stating that amine salts of dialkyl phosphites have large extreme pressure-resistant effect but that amine salts of mono alkyl phosphates have little63). Dibutyl phosphite β-phenylamine salt serves as an extreme pressure additive for synthetic lubricating oil of ester series64), whereas dioctadecyl phosphite or dioleyl sulfide of a mixture of ~~amine~~ animal and vegetable oils (P 0.1%, S 0.9%) exhibits synergistic extreme pressure-resistant properties and registers as high a value as above 70 lbs in the Temken's testing machine65). Other effective compounds found in patent records are dialkyl phosphites, ZnF_2, complex salts of t-alkyl amines66), mixtures of a partial hydrolyzate of trioctadecyl phosphite and alkenyl succinimide67) and reaction products between trialkyl phosphites and polybutenyl succinic acid anhydride68).

5.4 Wear-resistant agents

One% addition of dialkylphenyl phosphates (R = C_8 to

C_{18}) results in a wear constant of 0.26 mm[69], whereas lubricating oil to which is added 1% a reaction product among 2-methyl-2-octadecyl-propanediol-1,3, phosphoryl chloride, and 3-amino-1,2,4-triazol shows a value of 0.39 mm[70]. Another recent patent states that use of an addition compound of tetradecan phosphonate ethylene oxide as a 0.04% additive to turbine oil or diesel oil results in a reduction in the wear constant from 0.49 mm to 0.36 mm and the product is also anticorrosive[71].

5.5 Additives for rolling oil

Although palm oil and beef tallow have been used as lubricating oil in the cold rolling process of iron, the recent trend is the use of emulsifiable soluble oil. Triethanolamine salt of oleyl phosphate[72], dodecan phosphonate disodium salt[73], and phosphate esters of addition compounds of alkylamine (C_{16}, C_{18} and oleyl) ethylene oxides[74] are claimed to act as emulsifiable, extreme pressure-resistant and anticorrosive additives.

5.6 Motor oil

Phosphate esters as fireproof, flame-resistant oil usable at high temperature under high pressure are an important ingredient of synthetic motor oil preparations[75]. Flashing and combustion points of various types of motor oils are listed in Table 13 and the temperature at which their spontaneous combustion in the air occurs and the time required for recognition of their ignition (ignition lag) are shown in

Table 13 Flashing and combustion points of various types of motor oil[76]

A 作動油	B 引火点 (°C)	C 燃焼点 (°C)
1. 鉱油系 #90 タービン油	211	240
2. 油中水滴型油	· ·	…
3. 水-グリコール系油	…	—
4. リン酸エステル系油	229	352
5. リン酸エステル-塩素化油系油	221	357
6. リン酸エステル-塩素化油-鉱油系油	198	243

A Motor oil type
  1 Mineral oil, type #90 Turbine oil
  2 Water droplet type oil
  3 Water-glycol series oil
  4 Phosphate ester series oil
  5 Phosphate ester - Chlorinated oil series oil
  6 Phosphate ester - Chlorinated oil - Mineral oil series oil
B Flashing point (°C)
C Combustion point (°C)

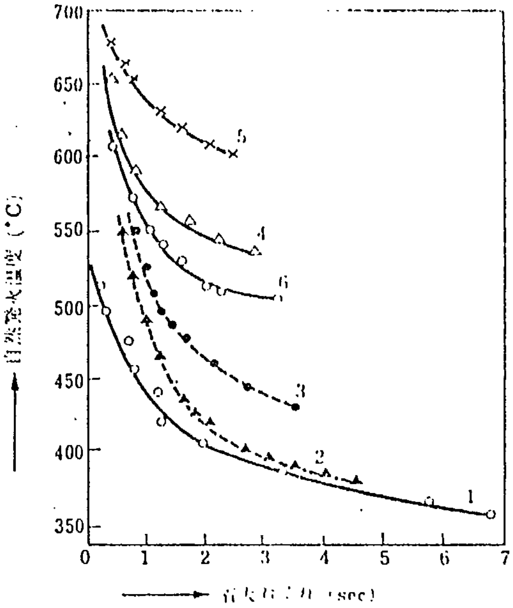


Fig. 6 Relation between spontaneous combustion temperature and ignition lag[76] (ASTM D 2155) (See Table 13 for sample numbers)

Ordinate: Spontaneous combustion temperature
Abscissa: Ignition lag

Fig. 6[76]. Oils of phosphate ester series are about the same in flashing point as but have about 100° C higher combustion points than mineral oil. Also the former does not continue to burn for more than 7 or 8 seconds, has considerably high spontaneous combustion temperature and accordingly, can be considered safe motor oil.

6 Anticorrosives

(p.16)

Anticorrosives for metals, both oil-soluble and aqueous, some of which have already been mentioned in this paper as additives for lubricating oil and gasoline, are in wide use and include a very large variety of compounds. These agents exhibit their anticorrosive effect by forming adsorptive films by way of adsorptive orientation of polar molecules on the metal surface. Hence aliphatic phosphorus derivatives possessing suitable hydrophilic as well as hydrophobic groups are naturally considered highly effective.

As for oil-soluble anticorrosives, there is a report by Sakurai _et al_.77) of anticorrosive effect of long-chain alcane phosphonates and alcane phosphinates possessing carboxyl and hydroxyl groups when used as additives. They also compared the anticorrosive effect among 9(10)-phosphonostearic acid and stearic acid derivatives obtained by introducing carboxyl, hydroxyl, mercapto, or amino groups into 9(10) position and have found that the phosphono derivatives are highly effective78).

As aquous anticorrosives, sodium salts of octyl phosphate, dioctyl thiophosphate and octyl mercaptomethane phosphonate have been compared by Umehara and Kato79). Also comparison among sodium salts of 1-oxynonan phosphonate, octyl oxymethane phosphonate and octyl mercaptomethane phosphonate has been conducted by them. The same group of investigators has pointed out that there is a large difference in the anticorrosive effectiveness of aliphatic phosphorus derivatives between moisture-rich and moisture-poor environment80).

Hydrolyzates of a reaction product between phosphoryl amidate and phosphorus pentachloride, dialkyl N-phosphono-phosphoryl amidates $(RO)_2P(O)NHP(O)(OH)_2$, are water soluble, and aqueous solutions of their free salts, monoalkaline salts and dialkaline salts in concentrations of 10^{-3} to 10^{-4} mol/liter at a wide pH range of 3 to 10 exhibit excellent anticorrosive quality to iron and aluminum[81]. Also solutions in ethyleneglycol monoethyl ether of monophosphate esters of unsaturated, long-chain alcohols such as oleyl alcohol, linoleyl alcohol and linolenyl alcohol are effective as anticorrosives for iron and aluminum[82]. Trimethyl phosphate in vapor phase is also effective in preventing corrosion of aluminum products during storage and for this purpose it has been ~~foundx~~ used at vapor tension ranging from 0.1 to 10 mmHg[83].

Hellsten and others[84] have stated that mono long-chain alkyl phosphate esters are effective in preventing metal corrosion caused by detergents containing trichloroacetate or super borate salts of nitroso compounds. The effect of alkyl phosphates having C_{10} to C_{18} at various concentrations on corrosion of copper in the presence of nitroso trichloroacetate is shown in Fig. 7. The esters of C_{12} to C_{16} show anticorrosive effect above a level of about cmc, but the C_{18} ester is effective even below cmc level. Also the anticorrosive effect of alkyl phosphates is augmented by addition of long-chain alcohols or alkyl polyglycol ethers, and thus

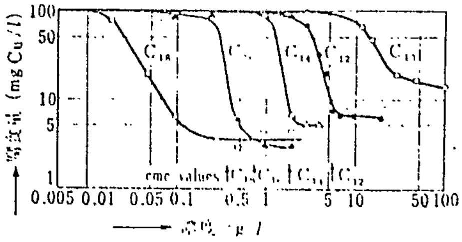


Fig. 7 Effect of alkyl phosphates at various concentrations on copper corrosion[84]

Ordinate: Amount of corrosion
Abscissa: Concentration

these phosphorus derivatives may be of value as ingredients of heavy-duty detergents. Also addition of disodium salt of hexadecyl or octadecyl phosphite in the order of 0.02% to alkaline detergents has been found to be an effective anti-corrosive procedure85).

7 Conclusion

Aliphatic organophosphorus compounds have extremely various uses and among them there are a large number of derivatives of good quality. However, it is a fact that their use is limited because of their high price. It can be expected that perfecting any suitable methods of synthesizing these as low-priced industrial materials; e.g., a direct synthetic method of organophosphorus compounds from red or yellow phosphorus86), results in development of more interest- (p.17)
ing and larger areas of their application. However, in doing so sufficient consideration must be given to some negative effects such as those which were observed in the past as in contamination and toxicity of organophosphorus agricultural chemicals.

In this paper recent advances in a few main application areas of aliphatic phosphorus derivatives are outlined. However, the areas covered represent only a very small portion of the total. Alos the data quoted herein were obtained under different conditions by different methods and therefore it is difficult to comapre these on equal bases. Especially in the case of additives, when they are put to practical use, the effects including synergism of coexisting additive(s) must be considered. The author will be pleased to hear any comments from specialists in each application field.

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