# Long-Chain Phosphorus Compounds as Low Temperature Plasticizers for Vinyl Chloride Polymers

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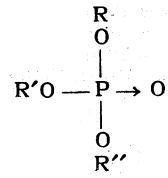
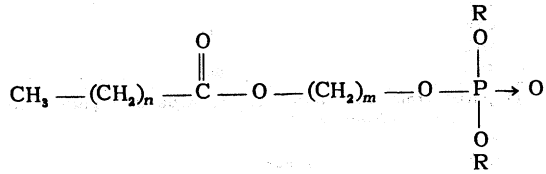
Research on plasticizers derivable from fats being conducted in this laboratory has been directed mainly toward the correlation of structure with compatibility and certain other important characteristics desired in a plasticizer (low temperature properties, lack of volatility, etc.). The authors have described the effect of introducing the oxirane (*6*) or acetoxy (or higher acyloxy) (*4*) group into fatty acid esters. These groups, singly or together, are effective in compatibilizing long-chain compounds with vinyl chloride polymers, and compositions with outstanding low temperature properties are obtained.

Groups containing the phosphorus atom are also known to impart useful properties to plasticizers, and a number of phosphorus-containing plasticizers are commercially available. None of these, however, contains long chain or other structures derived from fats.

For the past 4 years the authors have been systematically preparing long-chain phosphorus compounds of various types (*1–3*): trialkyl phosphates (I), dialkyl acyloxyalkyl phosphates (II), dialkyl acyloxyalkylphosphonates (III), 1 (α-dialkylphosphono)alkanoates (IV), and some miscellaneous compounds.



(I)
R = R′ = R″ = Dodecyl, octadecyl or oleyl
R = Dodecyl or oleyl, and R′ = R″ = ethyl



(II)
$n = 10$, $m = 2$–$4$, and R = ethyl or *n*-butyl

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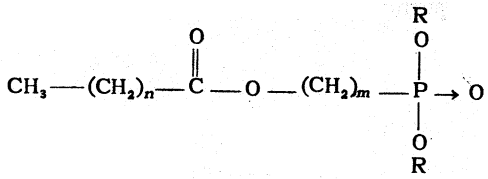
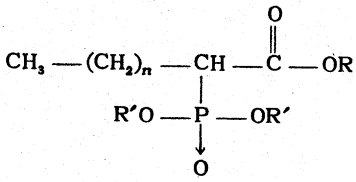


(III)

$n = 4$–$16$, $m = 2$ or $3$, R = ethyl, *n*-butyl, or *n*-hexyl



(IV)

$n = 3$–$15$, R = ethyl, *n*-butyl, *n*-hexyl, or 2-ethylhexyl, R′ = ethyl, *n*-butyl, or *n*-hexyl

These compounds have been evaluated as plasticizers for poly(vinyl chloride) with the object of extending knowledge of the relationship between plasticizer structure and properties of the plasticized polymer. The results have been compared with those obtained with some commercially available phosphorus-containing plasticizers and also with some of the better known low temperature plasticizers for vinyl chloride polymers. This paper describes the results of this evaluation program.

## EXPERIMENTAL

**Starting Materials.** The following commercial plasticizers were used as received: tri(2-ethylhexyl) phosphate (normally referred to as trioctyl phosphate); tricresyl phosphate; triphenyl phosphate; tri(butoxyethyl) phosphate; tri-*n*-propyl phosphate; tri-*n*-butyl phosphate; cresyl diphenyl phosphate; alkyl aryl phosphate (Santicizer 141); di(2-ethyl-hexyl) azelate; di(2-ethylhexyl) sebacate; di(2-ethyl-hexyl) adipate; and di(2-ethylhexyl) phthalate. Methods of preparation and physical characteristics of many of the (α-dialkylphosphono) alkanoates and acyloxyalkylphosphonates and of diethyl dodecylphosphonate and diethyl palmitoylphosphonate have been published (*1–3*). The preparation of the other long-chain phosphorus compounds is given below.

**Trialkyl phosphates.** Diethyl Dodecyl Phosphate. To a stirred solution of 56 grams (0.3 mole) of pure dodecanol in 24 grams (0.3 mole) of pyridine and 54 grams of benzene, 33 grams (0.3 mole) of freshly distilled diethyl chlorophosphate (boiling point 95° to 100° at 20 mm.) were slowly added at a reaction temperature not exceeding 35°. After about 5 hours, the pyridine hydrochloride was filtered off and washed with benzene. The wash and filtrate were combined and the benzene was removed by evaporation at 30 mm. Distillation of the residue yielded 48 grams (55% yield) of moderately pure diethyl dodecyl phosphate, boiling point 146° to 148° at 0.1 mm. Redistillation yielded the analytically pure material, boiling point 157° to 160° at 1 mm., $n_D^{30}$ 1.4305.

Diethyl Oleyl Phosphate, boiling point 205° to 207° at 1 mm., $n_D^{30}$ 1.4460, was similarly prepared (65% yield) from diethyl chlorophosphate and pure oleyl alcohol (*5*) in pyridine-benzene.

Diethyl Octadecyl Phosphate was similarly prepared from diethyl chlorophosphate and pure octadecanol in pyridine-benzene, but was not distilled.

Trioleyl Phosphate, molecularly distilled at 240° and 10 to 11 microns, $n_D^{30}$ 1.464, was similarly prepared in 50% yield from phosphorous oxychloride (0.1 mole) and pure oleyl alcohol (0.3 mole) in pyridine-benzene.

Tridodecyl Phosphate and Trioctadecyl Phosphate were similarly prepared from phosphorus oxychloride and pure dodecanol and octadecanol, respectively, in pyridine-benzene, but the products were not distilled.

**Dialkyl Acyloxyalkyl Phosphates.** Dibutyl Lauroxypropyl Phosphate. 3-Hydroxypropyl laurate [boiling point 137° to 145° at 0.1 to 0.15 mm., $n_D^{30}$ 1.4442 and hydroxyl oxygen, 6.56% (calculated 6.56%)] was prepared in 50 to 70% yield by refluxing 80 grams (0.2 mole) of lauric acid, 305 grams (4.0 mole) of 1,3-propanediol (Eastman practical grade), 200 ml. of toluene, and 2 grams of concentrated sulfuric acid for 4.5 hours with azeotropic removal of water. The reaction product was washed several times with water to remove excess glycol and catalyst, and it was then fractionally distilled. Dibutyl chlorophosphate (46 grams, 0.2 mole) was slowly added to a stirred solution of 3-hydroxypropyl laurate (38.7 grams, 0.15 mole), pyridine (11.9 grams, 0.15 mole) and anhydrous ether (150 ml.), and reaction was continued for an additional 3 hours at 25° to 35°. The product was then worked up as described above under the preparation of trialkyl phosphates. Dibutyl lauroxypropyl phosphate [boiling point 169° to 185° at 0.13 mm., $n_D^{30}$ 1.439] was obtained in 50% yield as a colorless, odorless liquid.

Diethyl Lauroxypropyl Phosphate [boiling point 151° to 158° at 0.1 mm., $n_D^{30}$ 1.437] was similarly prepared in 58% yield from 3-hydroxypropyl laurate and diethyl chlorophosphate in pyridine-ether.

Diethyl Oleoxypropyl Phosphate [boiling point 181° to 190° at 0.24–0.28 mm., $n_D^{30}$ 1.4491] was similarly prepared in 60% yield from 3-hydroxypropyl oleate [boiling point 195° to 200° at 0.2 mm., $n_D^{30}$ 1.4571, hydroxyl oxygen 5.02% (calculated 4.99%)] and diethyl chlorophosphate in pyridine-ether.

Diethyl Oleoxybutyl Phosphate [$n_D^{30}$ 1.4495, $d_4^{30}$ 0.9726, iodine number 51.9 (calculated 51.4)] was similarly prepared in 95% yield from 4-hydroxybutyl oleate [boiling point 191–4° at 0.2 mm., $n_D^{30}$ 1.4590, hydroxyl oxygen, 4.83% (calculated 4.79%); prepared from 1,4-butanediol and oleic acid by the procedure used for 3-hydroxypropyl laurate] and diethyl chlorophosphate in pyridine-ether except that the filtrate after separation of the pyridine hydrochloride was freed of solvent and employed directly for analysis and plasticizer evaluation.

Diethyl Lauroxybutyl Phosphate [boiling point 169° to 180° at 0.02 mm., $n_D^{30}$ 1.4390, $d_4^{30}$ 0.9833] was similarly prepared from 4-hydroxybutyl laurate [boiling point 140° to 150° at 0.05 mm., $n_D^{30}$ 1.4462, hydroxyl oxygen, 6.19% (calculated 6.25%)] and diethyl chlorophosphate in pyridine-ether. A small amount of solid material which it contained was separated by filtration and discarded. The filtrate was employed for evaluation and analysis.

Diethyl Oleoxyethyl Phosphate [boiling point 170° to 190° at 0.1–0.4 mm., $n_D^{30}$ 1.4498] was similarly prepared from 2-hydroxyoleate [boiling point 180–1° at 0.1 mm., $n_D^{30}$ 1.4588, hydroxyl oxygen, 5.13% (calculated 5.20%)] and diethyl chlorophosphate in pyridine-ether.

Diethyl Lauroxyethyl Phosphate [boiling point 175–77° at 0.3 mm., $n_D^{30}$ 1.4365] was similarly prepared in 50% yield from 2-hydroxyethyl laurate [boiling point 138° to 150° at 0.3 mm., $n_D^{35}$ 1.4428, hydroxyl oxygen, 6.94% (calculated 6.99%)] and diethyl chlorophosphate in pyridine-benzene.

Dibutyl Lauroxypropyl Phosphonate [boiling point 178° to 185° at 0.25 mm., $n_D^{30}$ 1.4451] was prepared in the usual way (*1*) in a 47% yield from 3-bromopropyl laurate [boiling point 142–5° at 0.2 mm., $n_D^{30}$ 1.4585; obtained in 83% yield by esterification of lauric acid (0.35 mole) with 3-bromo-1-propanol (0.5 mole) and concentrated sulfuric acid (3 grams) as catalyst, with azeotropic removal of water by toluene] and freshly distilled tri-*n*-butyl phosphite, boiling point 120–4° at 9 mm.

## EVALUATION OF PLASTICIZERS

**Recipes Used.** A commercial copolymer (Vinylite VYDR) containing 95 parts by weight of vinyl chloride and 5 parts by weight of vinyl acetate was used throughout. The following recipes were employed.

| Recipe A | | Recipe B | | Recipe C | |
|---|---|---|---|---|---|
| VYDR | 63% | VYDR | 60.5 | VYDR | 63.5 |
| Plasticizer | 35 | Plasticizer | 35 | Plasticizer | 35.0 |
| Epoxidized soybean oil | 1 | Tribase | 4 | Lead carbonate | 1.0 |
| Advastab 52 or | 1 | Stearic acid | 0.5 | Stearic acid | 0.5 |
| Nuodex V-81 | 1 | | | | |

Compositions were milled and then molded at 300° F. (*6*). The finished molded sheet, from which test samples were taken, was 6 × 6 × 0.075 inches. The test procedures were standard ASTM methods whenever possible (*6*). Volatility and migration were studied in approximately 2-mil sheets which were milled only.

**Mechanical Properties.** Table I lists the properties of VYDR plasticized with the various long-chain phosphorus compounds. For comparison the authors have also listed

**Table I. Comparison of Properties of Vinyl Copolymer (VYDR) Plasticized with Long-chain Phosphorus Compounds and Commercial Plasticizers**

| Long-Chain Phosphorus Compound | Recipe | Tensile Strength, P.S.I. | Elongation, % | Modulus, 100% P.S.I. | Clash-Berg T-200, °C. | Migration, % Wt. Loss after 14 Days | Volatility, Wt. Loss, % |
|---|---|---|---|---|---|---|---|
| 1. Diethyl dodecyl phosphate | B | 2220 | 355 | 1020 | −53 | 16.6 | 12.7 |
| 2. Diethyl oleyl phosphate | B | 2345 | 395 | 1030 | −61 | 14.4 | 1.4 |
| 3. Diethyl lauroxypropyl phosphate | A | 3140 | 350 | 1520 | −41 | 12.3 | 1.0 |
| 4. Diethyl oleoxypropyl phosphate | A | 2545 | 380 | 1180 | −67 | 23.0 | 3.1 |
| 5. Dibutyl lauroxypropyl phosphate | A | 2540 | 330 | 1390 | −53 | 16.4 | 5.2 |
| 6. Diethyl lauroxybutyl phosphate | C | 2540 | 360 | 1050 | −52 | 13.8 | 2.3 |
| 7. Diethyl oleoxybutyl phosphate | A | 2740 | 360 | 1375 | −54 | 20.7 | 3.4 |
| 8. Diethyl dodecylphosphonate | C | 2110 | 320 | 970 | −55 | 20.0 | 4.3 |
| 9. Diethyl caprooxyethylphosphonate | A | 2270 | 395 | 1060 | −47 | 18.0 | 22.5 |
| 10. Diethyl lauroxyethylphosphonate | C | 2580 | 360 | 1040 | −45 | 14.9 | 4.1 |
| 11. Dibutyl lauroxyethylphosphonate | A | 2640 | 380 | 1200 | −52 | 17.3 | 1.9 |
| 12. Dihexyl lauroxyethylphosphonate | A | 2720 | 370 | 1420 | −53 | 16.3 | 1.5 |
| 13. Dibutyl lauroxypropylphosphonate | A | 2600 | 340 | 1390 | −48 | 15.7 | 1.2 |
| 14. Triethyl α-phosphonostearate | A | 2735 | 330 | 1560 | −37 | 16.5 | 1.3 |
| 15. Tributyl α-phosphonolaurate | A | 2800 | 270 | 1550 | −43 | 14.9 | 0.8 |
| 16. Trihexyl α-phosphonocaproate | A | 2550 | 335 | 1250 | −55 | 18.7 | 7.3 |
| 17. Ethyl (α-dibutylphosphono)laurate | A | 2570 | 350 | 1220 | −42 | 15.3 | 1.9 |
| 18. Ethyl (α-dihexylphosphono)laurate | A | 2520 | 290 | 1390 | −47 | 19.7 | 1.1 |
| 19. Butyl (α-diethylphosphono)laurate | A | 2200 | 380 | 940 | −45 | 19.7 | 5.1 |
| 20. Butyl (α-diethylphosphono)stearate | A | 2470 | 370 | 1240 | −33 | 23.3 | 1.6 |
| 21. 2-Ethylhexyl (α-diethylphosphono)stearate | A | 2470 | 340 | 1395 | −41 | 24.6 | 4.7 |
| Commercial Controls | | | | | | | |
| Tricresyl phosphate | B,C | 3610 | 270 | 2015 | −1 | 0.5 | 0.3 |
| Tri(2-ethylhexyl) phosphate | A,B | 2600 | 390 | 1275 | −60 | 17.0 | 3.6 |
| Tri(*n*-propyl) phosphate[a] | B | 2705 | 260 | 1805 | ... | ... | ... |
| Tri(*n*-butyl) phosphate[a] | A | 2135 | 310 | 1190 | ... | ... | ... |
| Tributoxyethyl phosphate | B | 2625 | 365 | 1200 | −44 | 13.5 | 2.5 |
| Triphenyl phosphate[b] | B | 3290 | 320 | 1450 | −8 | ... | ... |
| Cresyl diphenyl phosphate | B | 3335 | 265 | 1610 | −7 | 1.8 | 1.1 |
| Alkylarylphosphate | B | 2560 | 310 | 1215 | −28 | 7.6 | 2.3 |
| Di(2-ethylhexyl) phthalate | C | 2930 | 370 | 1390 | −28 | 6.0 | 1.1 |
| Di(2-ethylhexyl) adipate | C | 2490 | 345 | 1000 | −58 | 23.7 | 4.1 |
| Di(2-ethylhexyl) azelate | C | 2700 | 280 | 1170 | −59 | 22.6 | 1.2 |
| Di(2-ethylhexyl) sebacate | C | 2670 | 345 | 1090 | −61 | 24.2 | 0.7 |
| Butyl epoxystearate | B,C[c] | 2440 | 460 | 1010 | −51 | 22.3 | 3.6 |

[a] Large amounts of plasticizers were obviously driven off during milling. Final sheet did not contain 35% of plasticizer.
[b] Considerable bloom observed.
[c] Metallic stabilizer omitted from recipe.

the properties of the compositions containing commercial plasticizers, as determined in their laboratory under the same conditions used for the research compounds. The following long-chain phosphorus compounds were incompatible with VYDR at a 35% level of plasticizer.

Tridodecyl phosphate
Trioctadecyl phosphate
Trioleyl phosphate
Diethyl octadecyl phosphate

Diethyl lauroxyethyl phosphate[a]
Diethyl oleoxyethyl phosphate

Diethyl palmitoxyethyl phosphonate
Diethyl oleoxyethyl phosphonate[b]
Diethyl palmitoyl phosphonate[c]

[a] Slight exudation on standing. Clash-Berg T-200, °C., −42°.
[b] Slight exudation on standing. Clash-Berg T-200, °C., −58°.
[c] Considerable decomposition on mill. Not studied further.

**Trialkyl Phosphates (I).** Because all of the commercially available phosphorus-containing plasticizers are phosphates, the first class of long-chain phosphorus compounds prepared and evaluated was trialkyl phosphates. The primary objective was to determine whether symmetrical trialkyl phosphates with long alkyl chains were compatible with VYDR. Tridodecyl phosphate was the trialkyl phosphate of shortest chain length prepared, because it was thought that any species of lower molecular weight would probably be too volatile. Tridodecyl phosphate, trioctadecyl phosphate, and trioleyl phosphate were incompatible; in fact, these compounds could not even be milled into the polymer at 300° F.

Because short-chain trialkyl phosphates (triethyl, tripropyl, and tributyl phosphates) are good solvent type plasticizers for VYDR, although admittedly much too volatile (Table I), it was thought that possibly one of these short alkyl chains could be replaced by a much longer aliphatic chain without loss in compatibility. A mixed trialkyl phosphate, diethyl dodecyl phosphate, was prepared and evaluated. This compound could easily be milled with VYDR and yielded a very flexible sheet on molding. The mechanical properties of the sheet were very good (Table I) and a low Clash-Berg temperature was obtained (−53 °C.). Diethyl dodecyl phosphate, however, showed poor volatility characteristics, indicating that a longer alkyl chain should be introduced to reduce the volatility still further. Diethyl octadecyl phosphate was then prepared and evaluated. Although it could be milled with VYDR and yielded a flexible sheet, after 12 hours profuse exudation occurred.

On the other hand, diethyl oleyl phosphate (compound 2, Table I) milled easily and yielded a well plasticized sheet with good mechanical properties and low Clash-Berg temperature (−61° C.). Apparently the interruption of the long aliphatic chain by a double bond provides a site for interaction with VYDR so that the compound is compatible at the 35% level, in contrast to the octadecyl compound.

**Dialkyl Acyloxyalkyl Phosphates (II).** As the mixed trialkyl phosphates (I) showed promise, dialkyl acyloxyalkyl phosphates were investigated to determine the effect of additional oxygen atoms in the alkyl portion of the molecule on the compatibility of compounds containing a long alkyl

chain. Diethyl oleoxyethyl phosphate and diethyl lauroxyethyl phosphate, the first members of this class to be prepared, both yielded dark sheets on milling. The former showed some exudate after 24 hours, which became excessive after 1 week; the latter showed only slight exudation after 1 week and the sheet appeared unchanged thereafter. Although diethyl lauroxyethyl phosphate was somewhat unstable to milling, the final milled and molded sheet showed good mechanical properties (tensile strength 2840 p.s.i.; elongation 380%; 100% modulus, 1280 p.s.i.) and a low brittle temperature (Clash-Berg, T-200, –42°C.).

On the other hand, dialkyl acyloxypropyl and acyloxybutyl phosphates (II, $n = 3$ or 4) milled readily and were stable to milling conditions, they showed good compatibility, efficiency, and other mechanical properties, and they had exceptionally good low temperature characteristics. Five compounds were evaluated; their Clash-Berg temperatures ranged from –41° to –67°C. (compounds 3 to 7, Table I). The latter value, the lowest the authors have observed for a plasticizer at the 35% level, was obtained with diethyl oleoxpyropyl phosphate.

**Dialkyl Acyloxyalkylphosphonates (III).** These were selected for study next because of their structural interest, phosphonates (C-P linkage) are known to be more stable to heat and hydrolysis than are the analogous phosphates (C-O-P linkage), and no information could be found in the literature on such compounds. Dialkyl acyloxyalkylphosphonates (compounds 9 to 13, Table I) milled well and showed good over-all properties comparable to those of closely related phosphates. The heat stability at 160° C. of the milled and molded sheets containing 35% of phosphonates was far superior to that of sheets containing phosphates.

The maximum length of the alkyl chain which yielded a compatible plasticizer was about $C_{12}$, a chain length similar to that observed previously. Diethyl oleoxyethylphosphonate, listed among the incompatible plasticizers, showed only slight exudation on standing for 1 week, but the sheet had good mechanical properties (tensile strength, 2790 p.s.i. elongation 360%, 100% modulus, 1560 p.s.i.) and an extremely low Clash-Berg temperature (–58° C.). It was not studied at low plasticizer levels or in combination with other plasticizers.

**Trialkyl α-Phosphonates (IV).** Based on studies with over 100 compounds prepared in the authors' laboratory, the longest unsubstituted saturated chain which can be present in a plasticizer to be compatible at the 35% level in poly(vinyl chloride) is about $C_{12}$. The trialkyl α-phosphonates, however, are one of the two classes of long-chain compounds (*4*) of which the authors are aware, in which an unsubstituted chain of at least 16 carbon atoms can be present and an efficient low temperature plasticizer for poly(vinyl chloride) be obtained. The dialkyl phosphono group in the α-position of a fatty acid ester has an unusually high compatibilizing effect.

Triethyl α-phosphonostearate (compound 14, Table I) showed good over-all properties as a plasticizer. It was compared with two of its isomers (compounds 15 and 16). Tributyl α-phosphonolaurate (compound 15) gave substantially similar mechanical properties but a slightly lower Clash-Berg temperature (–43° C.). Trihexyl α-phosphonocaproate (compound 16), although exceedingly effective at low temperatures, had a much higher volatility in a thin sheet than the other two compounds. Although compounds 14, 15, and 16 are isomeric, the last has a much lower boiling point (higher vapor pressure) than the first two. Compounds 17 to 21, the other examples of α-phosphonates studied including two stearates, were also efficient plasticizers.

## GENERAL COMMENTS

All of the long-chain phosphorus compounds studied, in common with other efficient low temperature plasticizers, such as the dialkyl adipates, azelates, and sebacates, show high migrations. This characteristic of low temperature plasticizers is not understood but may be related to the ability of these compounds to solvate more effectively with the polymer at low temperatures than at the temperature at which the test is conducted (30° C.). In most cases, however, the long-chain phosphorus compounds are superior to the available low temperature plasticizers in this test.

The shape of the torsional modulus versus temperature curves, in the case of many of the long-chain phosphorus compounds, is flatter than that of most of the commercial arylphosphate plasticizers and resembles that of tri(2-ethylhexyl)phosphate. As the temperature is lowered, the modulus of the compositions containing the long-chain phosphorus compounds increases fairly uniformly.

After 6 months' storage at room temperature all of the molded sheets were examined visually. No exudation was observed in sheets containing compounds 1, 16, 17, and 19 (Table I), only slight exudation was observed with compounds 2, 6, 14, 15, 18, and 20, and the other sheets had marked exudation but without any significant changes in mechanical properties. No attempt was made to study mixtures of plasticizers or compositions containing less than about 35% of plasticizer.

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