# Viscosity Characteristics of Long-Chain Phosphorus Compounds

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PHOSPHORUS-CONTAINING organic compounds are important additives for lubricants. Patents are the main source of information about such additives probably because most of them are ill-defined reaction products of organic compounds with various reactive inorganic phosphorus compounds.

A broad program on the synthesis and evaluation of pure, well characterized, long-chain phosphorus-containing compounds of various structural types was initiated in this laboratory in 1954. Methods of preparation, physical and chemical characteristics (*1*, *3*), and evaluation of these materials as plasticizers (*3*, *5*) and lubricity additives (*2*) have been published. The determination of the viscosity over a range of temperatures (+98° to −60° C., whenever possible), the viscosity index (V.I.) and ASTM slope, and the pour or freezing point of these substances with the object of correlating structure with these properties are presented here.

Five general classes of long-chain phosphorus compounds were examined. These were dialkyl acyloxyalkyl phosphates (I), dialkyl acyloxyalkylphosphonates (II), *P,P*-dialkylphosphono esters (III), dialkyl 11-phosphonoundecanoates (IV), and *P,P*-dialkyl 9(10)-phosphonostearates (V).

The specific compounds studied and the controls are listed in Table I.

Structural similarities and differences among these five classes of compounds are worth noting here. I, II, and III have the phosphorus-containing and carboxyl ester groups relatively close together; in IV and V these groups are widely separated. In III, the polar groups are not only close together, but a long-chain branch ($C_4$, $C_{10}$, or $C_{16}$) is symmetrically placed between them. V is similar to III, and in many cases the compounds are positional isomers, but in V the long-chain branch ($C_8$ or $C_9$) is adjacent to the phosphonate and distant from the carboxyl ester group. I, II, and IV are more nearly linear; III and V are more highly branched. None of the compounds described in this paper is strictly linear, because of the two pendant groups on phosphorus; in some cases R′ in the carboxyl ester is also branched.

Viscosity characteristics were determined by physical test methods used in an earlier report (*4*). Stiffness or Clash-Berg temperatures listed in Table I have been taken from earlier publications (*3*, *5*). These temperatures were obtained on compositions containing 34 to 35% by weight of the listed compound and 65% by weight of poly(vinyl chloride-acetate) copolymer (95 to 5) (VYDR) (*4*, *5*). They are the temperatures at which these compositions have an apparent modulus of elasticity of 135,000 p.s.i. As in a previous study (*4*), there has been an attempt to correlate viscosity at low temperatures with low stiffness temperatures in plasticized poly(vinyl chloride).

## RESULTS AND DISCUSSION

**Class I.** Dialkyl acyloxyalkyl phosphates are characterized by a high V.I., usually above 150 and in one case as high as 180 (compound 4, Table I). The pour or freezing points of this class, however, are relatively high; in no case is a value below −37° C. obtained (compounds 2 and 4). No correlation can be made between their viscosity at low

Table I. Viscosity Characteristics of Long-Chain Phosphorus Compounds and Controls

| | Phosphorus Compounds | Kinematic Viscosity, Centistokes at ° C. | | | | | | | A.S.T.M. | | Pour | Stiffness Temp.,$^{a}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 98.6 | 38 | 10 | −10 | −30 | −50 | −60 | Slope | V.I. | Point, ° C. | ° C. |
| | | | | | Dialkyl Acyloxyalkyl Phosphates (I) | | | | | | | |
| 1 | Diethyl lauroyloxyethyl phosphate | 1.91 | 5.22 | $^{b}$ | ... | ... | ... | ... | 0.70 | 158 | 7$^{c}$ | $^{d}$ |
| 2 | Diethyl oleoyloxyethyl phosphate | 2.72 | 8.39 | 20.9 | 31.2(0°)$^{e}$ | ... | ... | ... | 0.68 | 160 | −37 | $^{d}$ |
| 3 | Diethyl oleoyloxypropyl phosphate | 4.61 | 19.8$^{e}$ | ... | ... | ... | ... | ... | 0.67 | 167 | ... | −67 |
| 4 | Diethyl oleoyloxybutyl phosphate | 4.56 | 18.3 | 55.8 | $^{b}$ | ... | ... | ... | 0.65 | 180 | −37 | −54 |
| 5 | Dibutyl lauroyloxypropyl phosphate | 2.97 | 10.7 | $^{b}$ | ... | ... | ... | ... | 0.72 | 149 | −28$^{c}$ | −53 |
| | | | | | Dialkyl Acyloxyalkyl Phosphonates (II) | | | | | | | |
| 6 | Dibutyl lauroyloxyethyl phosphonate | 2.98 | 11.2 | 33.9 | 110–112$^{f}$ | ... | ... | ... | 0.73 | 138 | −13$^{c}$ | −52 |
| 7 | Dibutyl lauroyloxypropyl phosphonate | 3.89 | 17.1 | 57.5 | 100 | 910 | ... | ... | 0.75 | 143 | −31$^{c}$ | −48 |
| 8 | Dihexyl lauroyloxyethyl phosphonate | 3.50 | 13.9 | 42.8 | 132 | ... | ... | ... | 0.70 | 151 | −16$^{c}$ | −53 |
| | | | | | Dialkyl Phosphono Esters (III) | | | | | | | |
| 9 | Triethyl phosphonostearate | 3.85 | 18.3 | 69.2 | $^{b}$ | ... | ... | ... | 0.71 | 118 | −1$^{c}$ | −37 |
| 10 | Tributyl phosphonolaurate | 2.92 | 12.2 | 40.5 | 133 | 610 | 4,660 | 27,600 | 0.76 | 99 | −69 | −43 |
| 11 | Trihexyl phosphonocaproate | 1.84 | 5.86 | 15.7 | 40.4 | 145 | 835 | 3,170 | 0.81 | 115 | < −74$^{g}$ | −55 |
| 12 | Butyl *P,P*-diethyl phosphonolaurate | 2.57 | 10.5 | 34.1 | 117 | 595 | 7,880 | ... | 0.79 | 76 | −69 | −45 |
| 13 | Butyl *P,P*-diethyl phosphonostearate | 4.08 | 18.8 | 56.3 | $^{b}$ | ... | ... | ... | 0.70 | 138 | −15$^{c}$ | −33 |
| 14 | 2-Ethylhexyl *P,P*-diethylphosphonostearate | 4.26 | 20.2 | 92.0 | $^{b}$ | ... | ... | ... | 0.72 | 138 | −18$^{c}$ | −41 |
| 15 | Ethyl *P,P*-dihexyl phosphonolaurate | 3.25 | 13.8 | ... | 161 | 815 | 9,720 | ... | 0.79 | 111 | −70 | −47 |
| 16 | Phenyl *P,P*-diethyl phosphonostearate | 4.40 | 21.8 | $^{b}$ | ... | ... | ... | ... | 0.72 | 129 | 7$^{c}$ | $^{d}$ |

temperatures and the stiffness temperatures of poly(vinyl chloride) compositions containing them, because not enough of these compounds are compatible.

Diethyl oleoyloxypropyl phosphate (compound 3) is unusual in having equaled the lowest stiffness temperature we have observed in evaluating hundreds of compounds as plasticizers at the 35% level in poly(vinyl chloride).

**Class II.** Only three members of the dialkyl acyloxyalkylphosphonates were available (compounds 6, 7, 8); conclusions, therefore, are tentative. The V.I. is relatively high and in the range of bis(2-ethylhexyl) sebacate—values of the control obtained in this laboratory at different times range from 145 to 155. Freezing points are also relatively high. The three compounds are efficient low temperature plasticizers and, as anticipated, the viscosity of these compounds at −10° C. is low—100 to 132 centistokes.

**Class III.** No unusually high V.I. is observed with the *P,P*-dialkyl phosphono esters (compounds 9 to 16); the range is 76 to 138. Several pour points are strikingly low—notably those of trihexyl phosphonocaproate, below −74° C.

| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | Dialkyl Phosphonoundecanoates (IV) | | | | | | |
| 17 | Trimethyl 11-phosphonoundecanoate | 2.84 | 10.3 | 30.5 | 51.0(0°) | ... | ... | ... | 0.75 | 140 | −20[c] | −39 |
| 18 | Triethyl 11-phosphonoundecanoate | 2.64 | 9.09 | ... | 71.3 | [b] | ... | ... | 0.71 | 142 | −25[c] | −43 |
| 19 | Tributyl 11-phosphonoundecanoate | 3.37 | 13.2 | 37.5 | 108 | 250(−20°) | ... | ... | 0.71 | 148 | −44[c] | −43 |
| 20 | Trihexyl 11-phosphonoundecanoate | 4.74 | 20.2 | 65.2 | 193 | 860 | [b] | ... | 0.65 | 170 | −35[c] | −45 |
| 21 | Tris(2-ethylhexyl) 11-phosphonoundecanoate | 5.74 | 30.5 | 115 | 432 | 2,840 | 39,000 | ... | 0.73 | 138 | −56 | −50 |
| 22 | Tridodecyl 11-phosphonoundecanoate | Crystalline at room temperature | | | | | | ... | ... | ... | ... | ... |
| 23 | Ethyl *P,P*-dibutyl phosphonoundecanoate | 3.01 | 11.0 | 30.2 | 86.0 | [b] | ... | ... | 0.71 | 148 | −41[c] | −45 |
| 24 | Ethyl *P,P*-bis(2-ethylhexyl) phosphonoundecanoate | 4.70 | 22.4 | 80.1 | 177 | 1,470 | 17,800 | ... | 0.69 | 146 | −65 | −47 |
| 25 | Butyl *P,P*-bis(2-ethylhexyl) phosphonoundecanoate | 7.59 | 39.6 | 195 | 800 | 4,950 | 60,900 | ... | 0.65 | 148 | −61 | −49 |
| 26 | 2-Ethylhexyl *P,P*-diethyl phosphonoundecanoate | 3.93 | 17.4 | 58.5 | 142 | 1,020 | 12,500 | ... | 0.72 | 143 | −68 | −38 |
| 27 | 2-Ethylhexyl *P,P*-dibutyl phosphonoundecanoate | 4.44 | 18.7 | 60.9 | 198 | 960 | 2790(−40) | ... | 0.67 | 169 | −56 | −44 |
| 28 | Dodecyl *P,P*-dibutyl phosphonoundecanoate | 5.12 | 24.3 | 78.0 | [b] | ... | ... | ... | 0.71 | 152 | −15[c] | −43 |
| 29 | Phenyl *P,P*-dibutyl phosphonoundecanoate | 4.87 | 25.1 | 95.0 | 393 | [b] | ... | ... | 0.65 | 132 | −20[c] | −24 |
| | | | | | | *P,P*-Dialkyl 9(10)-Phosphonostearates (V) | | | | | | |
| 30 | Trimethyl 9(10)-phosphonostearate | 4.71 | 25.5 | 106 | 543 | 2,630 | 52,500 | ... | 0.71 | 116 | −55 | −31 |
| 31 | Triethyl 9(10)-phosphonostearate | 4.56 | 21.9 | 78.4 | 281 | 1,390 | 19,300 | ... | 0.68 | 141 | −61 | −38 |
| 32 | Tributyl 9(10)-phosphonostearate | 5.21 | 25.2 | 86.1 | 282 | 1,250 | 12,800 | ... | 0.58 | 149 | −64 | −46 |
| 33 | Tris(2-ethylhexyl) 9(10)-phosphonostearate | 6.14 | 32.8 | 128 | 476 | 2,580 | 28,000 | ... | 0.62 | 140 | −52 | −48 |
| 34 | Ethyl *P,P*-dibutyl 9(10)-phosphonostearate | 4.40 | 19.9 | 61.0 | 203 | 920 | 8,000 | 40,000–45,000[f] | 0.72 | 152 | −63 | −41 |
| 35 | Butyl *P,P*-diethyl 9(10)-phosphonostearate | 4.04 | 18.7 | 60.7 | 199 | 965 | 10,460 | 43,600 | 0.67 | 135 | −63 | −45 |
| 36 | 2-Ethylhexyl *P,P*-diethyl 9(10)-phosphonostearate | 4.96 | 25.7 | 94.8 | 349 | 2,010 | 26,700 | ... | 0.70 | 132 | −56 | −41 |
| | | | | | | Controls | | | | | | |
| | Bis(2-ethylhexyl) sebacate (DOS) | 3.26 | 12.6 | 37.2 | 118 | 550 | 4,220 | 21,300 | 0.71 | 145 | −67 | −59 |
| | Tris(2-ethylhexyl) phosphate (TOP) | 2.22 | 8.13 | 22.8 | 72.0 | 340 | 2,400 | 11,400 | 0.80 | 84 | <−71 | −60 |
| | Bis(2-ethylhexyl) phthalate (DOP) | 4.22 | 29.9 | 163 | 1050 | 14,100 | ... | ... | 0.86 | 12 | −37 | −28 |

[a] Temperatures were obtained on compositions containing 34 to 35% by weight of plasticizer and 65% by weight of poly(vinyl chloride–acetate) copolymer (VYDR) 95:5.

[b] Crystallized in capillary of viscometer.

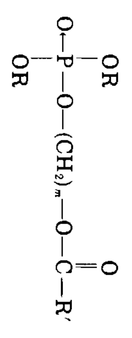
[c] Freezing point.

[d] Incompatible at the 35% level with copolymers.

[e] Material no longer available to obtain complete data.

[f] Erratic results obtained.

[g] Lowest temperature of freezing bath.



$\mathrm{O{\leftarrow}P(OR)_2\text{—}O\text{—}(CH_2)_m\text{—}O\text{—}C(=O)\text{—}R'}$

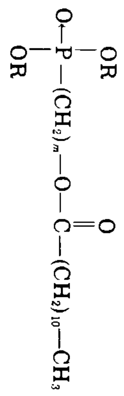
(I)

Dialkyl acyloxyalkyl phosphates

R = ethyl or *n*-butyl

*m* = 2, 3, or 4

R′ = $CH_3$—$(CH_2)_{10}$ or $CH_3$—$(CH_2)_7$—CH=CH—$(CH_2)_7$



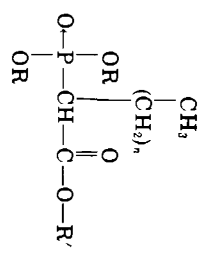
$\mathrm{O{\leftarrow}P(OR)_2\text{—}(CH_2)_m\text{—}O\text{—}C(=O)\text{—}(CH_2)_{10}\text{—}CH_3}$

(II)

Dialkyl acyloxyalkylphosphonates

R = *n*-butyl or *n*-hexyl

*m* = 2 or 3



$\mathrm{O{\leftarrow}P(OR)_2\text{—}CH[(CH_2)_n CH_3]\text{—}C(=O)\text{—}O\text{—}R'}$

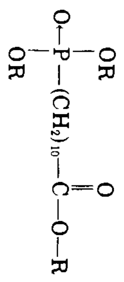
(III)

*P,P*-Dialkyl phosphono esters

R = ethyl, *n*-butyl or *n*-hexyl

R′ = ethyl, *n*-butyl, *n*-hexyl, 2-ethylhexyl, or phenyl

*n* = 3, 9, or 15



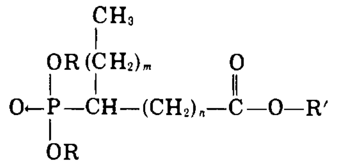
$\mathrm{O{\leftarrow}P(OR)_2\text{—}(CH_2)_{10}\text{—}C(=O)\text{—}O\text{—}R}$

(IV)

*P,P*-Dialkyl 11-phosphonoundecanoates

R = methyl, ethyl, *n*-butyl, *n*-hexyl, 2-ethylhexyl, or *n*-dodecyl

R′ = methyl, ethyl, *n*-butyl, *n*-hexyl, 2-ethylhexyl, *n*-dodecyl, or phenyl



$$O \leftarrow \underset{\underset{OR}{|}}{\overset{\overset{OR}{|}}{P}} - \overset{\overset{\overset{CH_3}{|}}{(CH_2)_m}}{\overset{|}{C}H} - (CH_2)_n - \overset{\overset{O}{\|}}{C} - O - R'$$

(V)

*P,P*-dialkyl 9(10)-phosphonstearates

R and/or R′ = methyl, ethyl, *n*-butyl, or 2-ethylhexyl

$m = 8$ and $n = 7$ or $m = 7$ and $n = 8$

(compound 11); ethyl *P,P*-dihexyl phosphonolaurate, -70° C. (compound 15); tributyl phosphonolaurate, -69° C. (compound 10); and butyl *P,P*-diethyl phosphonolaurate, -60° C. (compound 12). This is to be expected as this class and V are the most highly branched. Trihexyl phosphonocaproate (compound 11) has an unusually low viscosity, even at -60° C.

Many of the dialkyl $\alpha$-phosphonates have a low viscosity at -10° C.—40 to 160 centistokes—and they are also efficient low temperature plasticizers. As indicated earlier (*4*), a low viscosity at -10° C.—preferably 250 centistokes or less—still appears to be a prerequisite in most cases for an efficient low temperature plasticizer. The compounds with the lowest viscosity at -10° C., however, do not necessarily have the best low temperature characteristics. A low viscosity is only one desirable property, if an efficient low temperature plasticizer for poly(vinyl chloride) is to be obtained.

**Class IV.** There was particular interest in the dialkyl phosphonoundecanoates and *P,P*-dialkyl 9(10)-phosphonostearates because they are so similar structurally to compounds which are extremely useful as synthetic lubricants and as other functional fluids. This class of compounds closely resembles diesters of dibasic acids except that one of the carboxyl ester groups is replaced by a phosphonate group.

The V.I. of this class is generally high, equaling or exceeding that of conventional diesters in most cases. Members of this class with the highest V.I., in descending order, are trihexyl 11-phosphonoundecanoate, 170 (compound 20); 2-ethylhexyl *P,P*-dibutyl phosphonoundecanoate, 169 (compound 27); dodecyl *P,P*-dibutyl phosphonoundecanoate, 152 (compound 28); tributyl 11-phosphonoundecanoate, ethyl *P,P*-dibutyl phosphonoundecanoate, and butyl *P,P*-bis(2-ethylhexyl) phosphonoundecanoate, 148 (compounds 19, 23, 25); ethyl *P,P*-bis(2-ethylhexyl) 11-phosphonoundecanoate, 146 (compound 24); and 2-ethylhexyl *P,P*-diethyl phosphonoundecanoate, 143 (compound 26).

In addition to a high V.I., some of these compounds also have a low pour point. The members of this class with the best combination of V.I. and pour point are compounds 24, 25, 26, 27 (pour points of -65°, -61°, -68°, and -56° C. coupled with V.I. of 146, 148, 143, and 169, respectively).

Tentatively it can be concluded that the 2-ethylhexyl group is desirable in order to obtain this good combination of properties. Mixed phosphonoundecanoates, as expected, have lower pour or freezing points than the symmetical ones with the exception of dodecyl *P,P*-dibutyl phosphonoundecanoate (compound 28) and phenyl *P,P*-dibutyl phosphonoundecanoate (compound 29). These two compounds, as well as the trimethyl and triethyl 11-phosphonoundecanoates (compounds 17, 18) have relatively high freezing points.

Most of the dialkyl 11-phosphonoundecanoates impart low stiffness temperatures to poly(vinyl chloride) and, with the exception of compounds 21 and 25, they are also characterized by a low viscosity at -10° C. of 50 to 200 centistokes. Tris(2-ethylhexyl) 11-phosphonoundecanoate (compound 21) and butyl *P,P*-bis(2-ethylhexyl) 11-phosphonoundecanoate (compound 25) have a higher viscosity at -10° C., 430 and 800 centistokes, respectively; but in spite of this they are the two most efficient members of this class as low temperature plasticizers. This apparent anomaly emphasizes the danger of selecting a single physical property and of overgeneralizing the relationship between it and an evaluation which is the resultant of many complex phenomena operating simultaneously.

**Class V.** The V.I. of the *P,P*-dialkyl 9(10)-phosphonostearates is not unusual, but two members have a high V.I., in the range of that of diesters of dibasic acids. These are ethyl *P,P*-dibutyl phosphonostearate (compound 34) of V.I. 152 and tributyl 9(10)-phosphonostearate (compound 32) of V.I. 149.

More important, however, is that all members of this class have low pour points in the narrow range of -52° to -64° C. The dialkyl $\alpha$-phosphonates, on the other hand, display a wide range of pour or freezing points from +7° to below -74° C., although they have the same number of branches as the 9(10)-series. The wide range appears to be related in a general way to the length, rather than to the position of the alkyl branch. In the *P,P*-dialkyl phosphonates, the alkyl branch is $C_4$, $C_{10}$, or $C_{16}$. In the first case ($C_4$ branch), the pour point of the phosphonate is below -74° C.; in the second case, the pour point is about -69° C.; and in the last case, the pour points are from +7° to -18° C. In the 9(10)-series, the branch is of relatively constant length (either $C_8$ or $C_9$) and the pour points do not vary much.

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