Evaluation of Dialkyl 11-Phosphonoundecanoates and *P,P*-Dialkyl 9(10)-Phosphonostearates as Plasticizers for Vinyl Chloride Polymers

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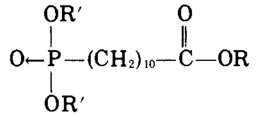
TWO NEW CLASSES of long-chain phosphorus compounds—namely, dialkyl 11-phosphosphonoundecanoates and *P,P*-dialkyl 9(10)-phosphonostearates—have been evaluated as plasticizers for poly(vinyl chloride). Most of them are efficient, primary plasticizers imparting good low temperature flexibility to poly(vinyl chloride) compositions containing them. All the 9(10)-phosphonostearates and two of the undecanoates are outstanding in having low migration losses in addition to imparting low stiffening temperatures to poly(vinyl chloride). This desirable combination of characteristics has not been observed previously.

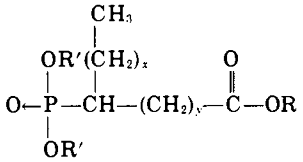
The structural requirements for obtaining efficient, low-temperature primary plasticizers for vinyl chloride polymers from four important classes of long-chain phosphorus compounds have been published (*4*). A similar study on two new classes of long-chain phosphorus compounds is presented here—namely, dialkyl 11-phosphonundecanoates and *P,P*-dialkyl 9(10)-phosphonostearates. Preparation and characterization methods have been described (*2, 3*). Both classes of compounds are colorless, odorless, high boiling, thermally stable liquids.



$O \leftarrow P(OR')_2-(CH_2)_{10}-C(=O)-OR$

Dialkyl 11-Phosphono-undecanoates

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



$O \leftarrow P(OR')_2-CH[(CH_2)_xCH_3]-(CH_2)_y-C(=O)-OR$

P,P-Diakyl 9(10)-phosphono-stearates
(x = 7, y = 8 or x = 8, y = 7)

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

The dialkyl 11-phosphonoundecanoates were of special interest because structurally they are similar to diesters of dibasic acids. Also, they represent a novel type of long-chain phosphorus compound in that the dialkylphosphono and carboalkoxy groups area t opposite ends of a long chain and these polar groups are farther apart than in any other class of phosphorus compound reported to date.

The *P,P*-dialkyl 9(10)-phosphonostearates are also unusual because they not only have widely separated polar groups, but they also contain a C_8 or C_9 branch. As a result of their method of preparation, they are mixtures of two (the 9- and 10-) isomers. These phosphorus-containing long-chain compounds are unique in providing both low temperature plasticization and exceptionally low migration losses.

EVALUATION OF PLASTICIZERS

The long-chain phosphono compounds were prepared as reported previously (*3, 4*). The commercial, control plasticizers were used as received.

Recipe 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 in the following recipe (all parts by weight):

Copolymer (VYDR)	64	Advastab stabilizer	1
G-60 stabilizer	1	Plasticizer	34

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

Plasticizer Properties. Table I lists the properties of VYDR plasticized with the dialkyl 11-phosphonoundecanoates (compounds 1 to 12) and *P,P*-dialkyl 9(10)-phosphonostearates (compounds 13 to 19). For comparison some commercial controls are included.

11-Phosphonoundecanoates. The phosphonoundecanoates are efficient plasticizers for poly(vinyl chloride), as shown by the figures for 100% modulus and elongation (Table I). The undecanoates are more efficient than the stearates, although the difference is not a gross one. The 11-phosphonoundecanoates closely resemble dialkyl esters of dibasic acids in many respects. They are not quite as effective in modifying the low temperature characteristics of poly(vinyl chloride), however, but they have superior migration characteristics.

Compositions containing trimethyl or triethyl 11-phosphonoundecanoate (compounds 1 and 2) are extremely well plasticized but plasticizer volatility is high. For all practical purposes, tributyl 11-phosphonoundecanoate (compound 3) is as efficient and has satisfactory volatility characteristics. Trihexyl and tris(2-ethylhexyl) 11-phosphonoundecanoates (compounds 4 and 5) are similar to the tributyl ester except for a somewhat higher 100% modulus and, possibly, slightly lower stiffening temperatures.

Of the mixed alkyl 11-phosphonoundecanoates, ethyl *P,P*-dibutyl 11-phosphonoundecanoate (compound 6) has the best combination of properties, including one of the lowest 100% modulus values thus far obtained. With the exception of phenyl *P,P*-dibutyl 11-phosphonoundecanoate (compound 12), the remaining mixed undecanoates (compounds 7 to 11) are similar in almost all respects, showing good all-round properties. As expected, a phenyl group in the molecule (compound 12) decreases the efficiency and markedly raises the stiffening temperature.

9(10)-Phosphonostearates. The phosphonostearates (compounds 13 to 19) are similar in almost all respects, showing a good all-round combination of characteristics with no gross inadequacy evident and exceptionally low migration losses (discussed below). The dialkylphosphono group is a sufficiently powerful compatibilizing group, in the same class as the oxirane and acetoxy groups (*1*), that these phosphonostearates are readily compatible with vinyl chloride polymers, and they are efficient plasticizers as shown

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

	Tensile Strength, P.S.I.	Elongation, %	Modulus, 100%, P.S.I.	Clash-Berg, T-200, ° C.	Migration, % Wt. Loss after 14 Days^a	Volatility Wt. Loss, %
1. Trimethyl 11-phosphonoundecanoate	2300	350	970	−39	18	7.7
2. Triethyl 11-phosphonoundecanoate	2150	360	920	−43	20	4.6
3. Tributyl 11-phosphonoundecanoate	2400	350	1000	−43	15	1.5
4. Trihexyl 11-phosphonoundecanoate	2850	350	1450	−45	14	2.1
5. Tris(2-ethylhexyl) 11-phosphonoundecanoate	2600	400	1350	−50	14	1.6
6. Ethyl *P,P*-dibutyl 11-phosphonoundecanoate	2300	370	950	−45	17	1.7
7. Ethyl *P,P*-bis(2-ethylhexyl) 11-phosphonoundecanoate	2650	360	1350	−44	8	1.4
8. Butyl *P,P*-bis(2-ethylhexyl) 11-phosphonoundecanoate	2550	330	1300	−49	10	1.5
9. 2-Ethylhexyl *P,P*-diethyl 11-phosphonoundecanoate	2500	355	1200	−38	16	1.6
10. 2-Ethylhexyl *P,P*-dibutyl 11-phosphonoundecanoate	2600	340	1250	−44	15	1.1
11. Dodecyl *P,P*-dibutyl 11-phosphonoundecanoate	2600	380	1300	−43	18	1.3
12. Phenyl *P,P*-dibutyl 11-phosphonoundecanoate	3000	330	1300	−24	8	1.1
13. Trimethyl phosphonostearate	2900	345	1200	−31	8	2.1
14. Triethyl phosphonostearate	2700	345	1350	−38	8	2.0
15. Tributyl phosphonostearate	2700	360	1350	−46	8	1.6
16. Tris(2-ethylhexyl) phosphonostearate	3000	310	1700	−48	8	2.1
17. Ethyl *P,P*-dibutyl phosphonostearate	2850	340	1400	−41	8	1.5
18. Butyl *P,P*-diethyl phosphonostearate	2750	360	1350	−45	9	1.1
19. 2-Ethylhexyl diethyl phosphonostearate	2900	370	1450	−41	9	1.0
	Commercial Controls					
Bis(2-ethylhexyl) phthalate (DOP)	2950	370	1400	−28	6	1.1
Bis(2-ethylhexyl) sebacate (DOS)	2600	400	1200	−59	23	2.0
Tris(2-ethylhexyl) phosphate (TOP)	2600	390	1275	−60	17	3.6
Tritolyl phosphate (TCP)	3600	270	2000	−1	0.5	0.3

[a] Weight loss of 15% means that 15/34 × 100 or 44% of the original quantity of plasticizer has migrated out of the sheet into the silicic acid adsorbent.

by the figures for 100% modulus. The composition plasticized with trimethyl 9(10)-phosphonostearate (compound 13) has a higher stiffening temperature than the others. With the exception of compound 13, the phosphonostearates are clearly superior to DOP in low temperature performance but not as good as DOS or TOP in this respect.

Low Temperature Flexibility and Migration Loss. With esters of hydroxystearic and epoxystearic acids a relationship exists between stiffening temperature and plasticizer migration in plasticized poly(vinyl chloride): the lower the stiffening temperature the higher the migration loss (*1*). Among plasticizers commercially available for low temperature use, high migration at room temperature occurs when these plasticizers are used alone, which is the case when the lowest flexibility temperatures are required. This high migration loss is reduced by blending with nonmigrating plasticizers—TCP, for example—but then a sacrifice must be made in the low temperature flexibility attainable in the plasticized poly(vinyl chloride).

The *P,P*-dialkyl 9(10)-phosphonostearates (compounds 13 to 19) are outstanding in that they not only have a low and constant migration loss [8 to 9% compared to 23% for bis(2-ethylhexyl)sebacate] but they impart good low temperature flexibility characteristics to poly(vinyl chloride) (−40° to −50° C. in most cases). The dialkyl 11-phosphonoundecanoates show somewhat higher migration losses, but even here two compounds (compounds 7 and 8) give outstandingly low migration losses for the low stiffness temperatures attainable (−44° and −49° C., respectively). This desirable combination of characteristics has not been observed previously. Re-examination of the previous results (*4*) shows that many long-chain phosphorus compounds have relatively low migration losses even though they are effective low temperature plasticizers.

Comparison of the structures of these two new classes of plasticizers shows a close similarity. The *P,P*-dialkyl 9(10)-phosphonostearates, however, have an additional long branch on the carbon atom to which the dialkylphosphono group is attached, whereas the phosophonoundecanoates do not. The lowest migration losses occur when the polar groups are widely deparated and when an additional branch is present in the molecule. In support of this conclusion, *P,P*-dialkyl 9(10)-phosphonostearates have less than half of the migration losses of isomeric dialkyl α-phosphonostearates, in which the polar groups are close together; and significantly lower migration losses than the dialkyl 11-phosphonoundecanoates, in which the additional branch is absent. Whether the position of this branch with respect to a polar group is important cannot be decided until more compounds are available.

Miscellaneous. The poly(vinyl chloride) compositions containing phosphonostearates and undecanoates stiffen gradually with decrease in temperature. The shape of their torsional modulus–temperature curves is similar to that obtained with DOP, with one exception. The curve for the phenyl derivatives (compound 12) resembles that of poly(vinyl chloride) plasticized with TCP.

All of the plasticized sheets were exposed to the usual laboratory conditions of temperature and humidity and examined periodically. The composition containing triethyl 9(10)-phosphonostearate showed slight exudation after 1 week. The composition containing ethyl *P,P*-bis(2-ethylhexyl) phosphonoundecanoate showed slight exudation after 1 month. The other compositions showed no evidence of exudation after 6 months.

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