Forschung, Wissenschaft

The Significance of Isomerism and Complexity of Composition, on the Performance of Triaryl Phosphate Plasticisers in PVC*

Angus J. Duke**
Ciba-Geigy, Manchester, UK

Abstract

The effectiveness, as PVC plasticisers, of alkylsubstituted triaryl phosphates of various isomer distributions and increasing degrees of complexity of composition, are assessed. The complexity factors in such mixture products include molecular symmetry / dissymmetry, relative distribution of substituted aryl groups between phosphate molecules, substituent positional isomerism, extent of concurrent polysubstitution on the aryl groups, and ultimately contributions of alkyl substituents of different sizes. The most important factors are shown to be substituent positional isomerism, coupled with degree of (mono)-substitution. This applies both for physical properties, such as plasticiser efficiency and especially low temperature flexibility, and the partially correlated fluid viscosity properties, and also for chemically-controlled stabilities, e.g. colour stability, compatibility in light. Secondary, but still important, factors are content of poly-substituted aryl groups, and distribution of substituent content between phosphate molecules—this latter primarily to ensure adequate low temperature fluidity of the liquid plasticiser. Poly-substituted content also appears to have some positive effect on light stabilities. Meta isomer contents, at least of methyl, ethyl or isopropyl groups, give very favourable effects on low temperature flexibilities. However, significant meta contents result in severe deterioration of the colour stabilities and compatibilities of PVC compositions. The preferred substituent type is shown to be orthoisopropyl, accompanied by substantial levels of unsubstituted phenyl groups, and a small content of polysubstitution.

Introduction

Plasticisers are commonly considered as single chemical entities. To vary their performance, they are usually mixed with different plasticiser types, as when phthalates are partially replaced by phosphates to gain fire retardancy or to speed up compounding operations, in preference to adjusting the composition of any one plasticiser. However, most technical plasticisers (bar di-(2 ethylhexyl)esters) are themselves fairly complex mixtures. The significance of this, for their performance in plasticising PVC, has been but little explored.

Triaryl phosphate plasticisers have always been highly complex mixtures. While they were made from the so-called "tar acids" assessment of the effect of this complexity was difficult, as the tar acids were of rather variable composition, and also contained non-phenolic contaminants. The advent of "synthetic" triaryl phosphates (CIBA-GEIGY REOFOS® ***) in the late '60s allowed more meaningful study, as their composition was more controllable, and their performance properties therefore less influenced by minor components of unkown nature.

Since the invention of REOFOS, CIBA-GEIGY have developed a great deal of data on the effect of the various molecular components present on the performance of molecularly complex isopropylated and butylated triaryl phosphates. Some of this data is used herein, to illustrate the ways in which plasticiser compositional complexity can affect performance in PVC. It will be seen that, at each level of increase of complexity, some positive advantage is gained: the commercial mixture plasticisers are thus technically superior to potential "equivalent" purer structures or compositions, and are not simply cheap technical crudes.

The introduction of synthetic feedstocks has also corrected various apparently inherent defects of the older triaryl phosphates based on by-product tar acids, in particular their poor colour stabilities.

A commercial triaryl phosphate (TAP) plasticiser is produced by phosphorylation of a mixture of mono-, di- and (even) tri-alkyl phenols, of various isomers, and with the various phenols distributed at random amongst the resulting TAP molecules. In consequence, six relevant levels of molecular complexity can be distinguished—as in table 1. Effects observed, at these various levels of complexity, will be examined successively.

Physical and efficiency properties

1. Symmetrical TAPs

Several of these pure compounds are solids (table 2) and therefore inefficient even if they could be incorporated into PVC, as they tend to crystallise in the PVC, and thus lose effectiveness on ageing. The effect of positional isomerism of the alkyl phenyl groups is already evident, predominating even over the nature of the alkyl substituent. The major influences of isomer type are on liquid viscosities (fig. 1) (meta giving the lowest viscosities and ortho the highest), and on the low temperature flexibility (tables 3 and 4), for which meta is far more effective, with para isomers being worst.

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** Dr. A. J. Duke, CIBA-GEIGY Plastics and Additives Company, Tenax Road, Trafford Park, Manchester M17 1WT, England.

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Table 1: Levels of TAP composition complexity.

1. Symmetrical single molecule, (from one phenol)	e.g. TPP,	$(C_6H_5O)_3PO$
	TmCP,	$(m\text{-}MeC_6H_4O)_3PO$
		$(o\text{-}i\text{-}PrC_6H_4O)_3PO$
2. Unsymmetrical single molecule, (from two phenols).	e.g. oCDP,	$(o\text{-}MeC_6H_4O)(C_6H_5O)_2PO$
		$(p\text{-}t\text{-}BuC_6H_4O)_2(C_6H_5O)PO$
3. Randomized mixture of four molecules, from phosphorylation of two mixed phenols: most usually phenol itself, plus one mono-alkyl phenol.	e.g.	$(o\text{-}i\text{-}PrC_6H_4O)_x(C_6H_5O)_{3-x}PO$, $0 < x < 3$
	m/pTCP,	$(m\text{-}MeC_6H_4O)_x(p\text{-}MeC_6H_4O)_{3-x}PO$, $0 < x < 3$
4. As 3 above, but containing isomeric forms of the alkyl phenol.	e.g. Commercial CDP,	$(m/p\text{-}MeC_6H_4O)_x(C_6H_5O)_{3-x}PO$, x = 0–3, average 1.
5. As 4 above, but containing also polysubstituted (di and/or tri-substituted) aryl groups.	e.g. REOFOS,	$(i\text{-}Pr_xC_6H_{5-x}O)_3PO$, x = 1,2(3), x differing in various aryls. Similar types, from sec- or tert-butylated phenol.
	PXP,	$(C_6H_5O)_x(Me_2C_6H_3O)_{3-x}PO$, x = 0–3
6. Mixtures contaning also various alkyl groups.	e.g. Commercial TXPs,	$(C_aH_{2a+1})_xC_6H_{5-x}O)_3PO$, a = 0 – ca. 4, x = 1,2(3), a and x differing in various aryls.

Table 2: Symmetrical TAP melting points.

$(C_6H_5O)_3PO$	49 °C
$(p\text{-}MeC_6H_4O)_3PO$	78 °C
[but $(o\text{-}MeC_6H_4O)_3PO$ – 19 °C] *	
[but $(m\text{-}MeC_6H_4O)_3PO$ – 31 °C] *	
$(o\text{-}i\text{-}PrC_6H_4O)_3PO$	+ 34 °C
[but $(m\text{-}i\text{-}PrC_6H_4O)_3PO$ – 50 °C]	
[but $(p\text{-}i\text{-}PrC_6H_4O)_3PO$ – 38 °C]	
$(p\text{-}t\text{-}BuC_6H_4O)_3PO$	+ 101 °C
$(2,3\text{-}Me_2C_6H_3O)_3PO$	61 °C
$(2,5\text{-}Me_2C_6H_3O)_3PO$	80 °C
$(3,4\text{-}Me_2C_6H_3O)_3PO$	72 °C
$(3,5\text{-}Me_2C_6H_3O)_3PO$	44 °C

* Ref. [1].

Table 3: Relative effects of alkyl type and of isomer, on efficiency properties in PVC, for symmetrical TAPs. (I, x = 3).

R		Me	Et	i-Pr	t-Bu
IRHD, 54 p.h.r.:	Meta	ca. 82	–	84.5	–
	Para		–	98	> 99
Clash & Berg	Meta	– 20	– 36	– 28	–
(°C, 82 p.h.r.)	Para	ca. – 7	–	– 4	> + 20

Table 4: Effect of isomer, alone, on efficiency in PVC, for symmetrical TAPs. (I, x = 3).

R		p.h.r.	ortho	meta	para
Me	Clash & Berg, °C	60	– 5	– 11	+ 2
	Shore hardness, 40 °C	60	78	80	80.5
	T.S., Kg/mm²	60	2.17	2.35	2.24
	ε_B, %	60	266	255	272
i-Pr	IRHD, 23 °C	54	97	84.5	98
	Clash & Berg, °C	82	– 9	– 28	– 4

TCP data, Ref. [1].

The effect of isomer on plasticisation efficiency at normal temperatures is far less (table 4), and at such temperatures, meta isomer is not uniformly best. With the equal number of alkyl groups per phosphate molecule (three), tertiary-butyl imparts significantly worse efficiency than is given by lower alkyl substituents (table 3).

However, those pure symmetrical TAPs which are not solids, are costly and difficult of access. Practical, economic and handleable liquid plasticisers have more complex compositions.

2. Unsymmetrical molecularly-pure TAPs.

Asymmetry commonly lowers melting points. In our studies, the second aryl introduced has usually been an unsubstituted phenyl, giving TAPs of formula:

$(RC_6H_4O)_x(C_6H_5O)_{3-x}PO$ (I)

A higher proportion of unsymmetrical TAPs are liquids than is the case for the symmetrical TAPs, but nevertheless, several are still solids (in contrast to literature statements: table 5). Other effects of the reduction in

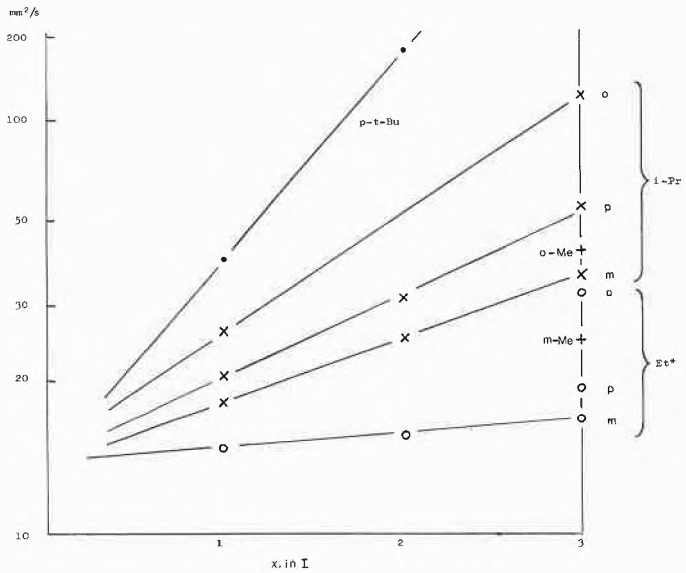

Fig. 1: Viscosity of phenyl/alkyl phenyl unsymmetrical TAPs, plotted as if blends of triphenyl phosphate with the corresponding symmetrical trialkyl TAP.* ref. [2].

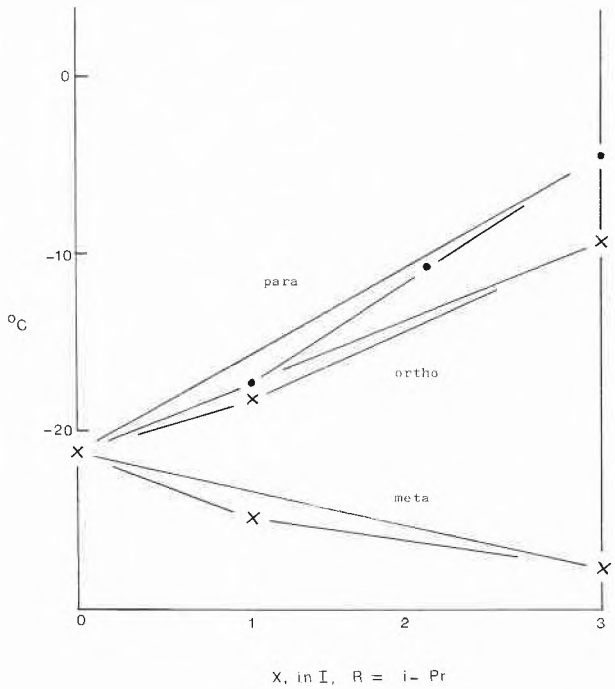

Fig. 2: Effect of introduction of a second aryl group (phenyl), yielding unsymmetrical structures, on low temperature flexibility in PVC (*Cash & Berg* temperatures, 82 p.h.r.).

the degree of alkyl substitution are shown in fig. 1 and 2.

As phenyl groups replace alkyl phenyl groups, viscosity decreases more than proportionately, the decrease being loglog-linear, as if two separate fluids were being blended (fig. 1). Meta isomers continue to give lowest viscosities, and viscosities of ortho isomers are much higher than those of equivalent para isomers. The lowest viscosities are found in the meta ethyl series: even incomplete tertiary-butyl substitution gives viscosities much higher than occur in the isopropyl series.

Table 5: Unsymmetrical TAP melting points.

$(p\text{-i-Pr}C_6H_4O)(C_6H_5O)_2PO$	28 °C
$(p\text{-t-Bu}C_6H_4O)(C_6H_5O)_2PO$	31 °C
$(p\text{-t-Bu}C_6H_4O)_2(C_6H_5O)PO$	41 °C

Low temperature flexibility also improves as phenyl groups are introduced, in parallel with the decline in liquid viscosity (unless the initial values are outstandingly good, as with meta isopropyl). Fig. 2 shows that for Clash & Berg temperatures, again, the improvement is slightly more than in proportion to the introduced phenyl content. For low temperature flexibility, however, isomer type remains as important as, or more so than, the extent of alkyl substitution.

The plasticising efficiency in PVC at normal temperatures also improves as alkyl phenyl groups are progressively replaced by unsubstituted phenyl groups, this effect being greater with the higher alkyl types, v.i. The decrease in molecular weight concurrently slightly worsens volatility-related properties, however.

3. Randomised phenyl/alkyl phenyl distribution

Unsymmetrical pure structures are even more costly to produce than symmetrical ones. Economic production nowadays demands co-reaction of two phenols, mixing them before phosphorylation. This produces a TAP in which the two aryl substituents are randomly distributed amongst the phosphate molecules, the product being a mixture of triphenyl phosphate, di-phenyl monoalkylphenyl phosphate, phenyl bis-alkylphenyl phosphate and tris-alkylphenyl phosphate molecules. Fortunately, the more costly 2-stage phosphorochloridate routes, required for synthesis of pure unsymmetrical types, prove completely needless (and in fact undesirable) for production of efficient plasticisers.

In such "randomised" mixtures, the problem of crystallisation is usually overcome: seeds of pure unsymmetrical components tend to dissolve in the product mixtures. However, randomisation has very slight, if any, effect on efficiencies or viscosities. Table 6 shows the very small further effect on viscosities on randomising meta cresyl di-phenyl phosphate, and table 7 the lack of any systematic trend on randomising various isomeric phenyl/isopropylphenyl phosphates.

Table 6: Lack of effect of randomizing aryl groups, on viscosities of meta-cresyl diphenyl phosphate (I, R = Me, x = 1: mm^2/s).

	25 °C	37.8 °C
Unsymmetrical single molecule	29.7	16.6
Mixture with randomized aryl groups	29.5	16.45

Table 7: Liquid viscosities, of unsymmetrical and randomized phenyl/isopropylphenyl phosphates (I, R = i-Pr: mm^2/s at 25 °C).

x	1		2	
	Unsymmetrical	Randomized	Unsymmetrical	Randomized
Ortho	52 *	47.4	-	125.4
Meta	32.5	39.6	48.1	49.6
Para	solid	39.0	59 *	68.5

* extrapolated.

Fig. 3 shows, on comparison with figure 2, that there is also negligible further effect on low temperature flexibilities on randomisation: however, the randomised materials provide no worse Clash & Berg temperatures than do the pure unsymmetrical equivalent TAPs, and the slight improvement, relative to linear interpolation between the values given by the appropriate two symmetrical TAPs, is still evident—and not confined to isopropyl substitution. Randomisation allows more flexibility in the choice of the extent of alkyl substitution, this being no longer restricted to exactly 1 or 2 (or 3) alkyls per molecule. This flexibility is important, allowing adjustment of exact degree of alkyl substitution to obtain compromises for particular applications, between efficiency at normal temperature or rates of gelation (which worsen as substitution and thus molec-

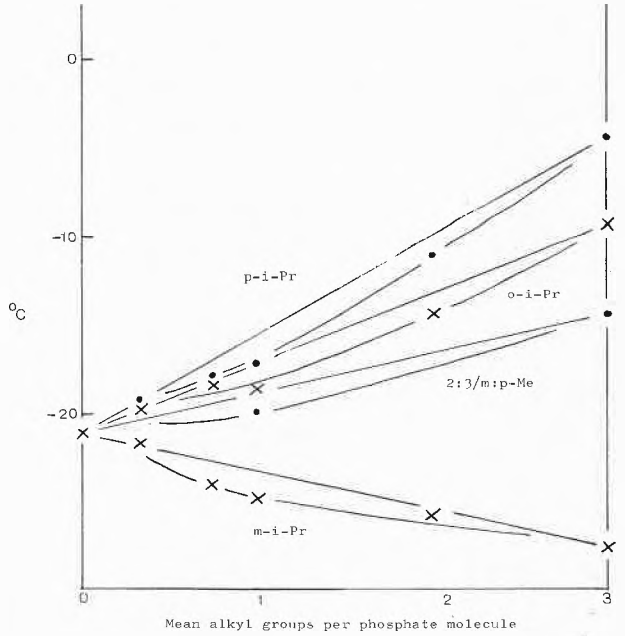

Fig. 3: Influence of phenyl: alkylphenyl ratio, and of isomer, on low temperature flexibility in PVC, in randomized compositions (*Clash & Berg* temperatures, 82 p.h.r.).

ular weight increases) and properties improved by increasing molecular weight or alkyl (non-polar) content, such as volatility or electrical properties.

Table 8: Clash & Berg temperatures* of blends of symmetrical structures (only), versus randomized compositions of equivalent isopropyl content (I, R = i-Pr: 82 p.h.r., °C).

x	0	1 Blended symmetrical TAPs	1 Coreacted (randomized) TAPs	3
Ortho	−18	−9.5	−13	−2.5
Meta	−18	−18.5	−20.5	−24
Para	−18	−9	−10.5	+0.5

* Results in this table are *not* determined by B.S. technique, and are therefore only comparable amongst themselves.

Randomised TAPs may also be compared with blends of two symmetrical TAPs, having equal average alkyl substitution and of the same isomeric type (table 8). Such blends, being two steps less complex due to absence of unsymmetrical structures, give worse low temperature flexibilities.

4. Effects of mixing alkyl phenyl isomers

For physical efficiency in randomised phenyl/alkylphenyl TAPs only meta isopropyl (or ethyl) substitution has yet shown any clear advantage, when replacing an unsubstituted phenyl group. However, in view of the serious oxidative stability problems associated with the presence of meta substituents (v.i.) it was interesting to explore the effect of mixing alkylphenyl positional isomers in already randomised TAP compositions. Such blending of isomers gives rise to another slight decrease in viscosity, relative to values interpolated (as blends) between randomised single isomer compositions (fig. 4).

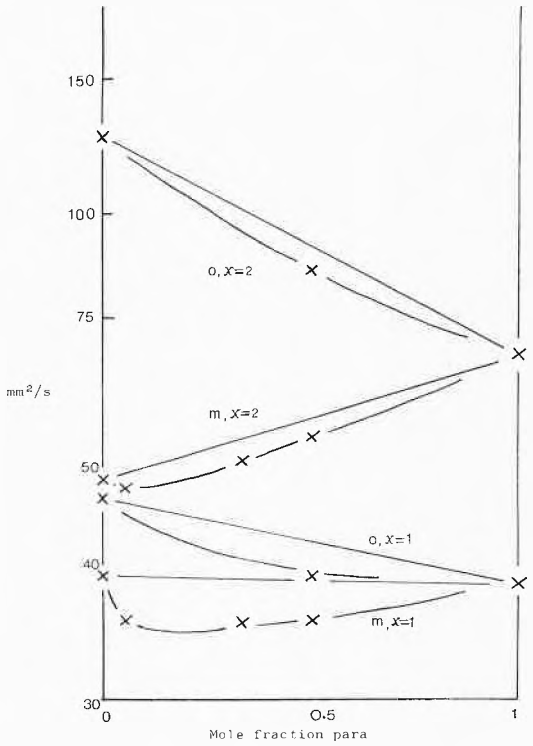

Fig. 4: Variation of viscosity (25 °C) with isomeric ortho:para and meta: para ratios, in co-reacted phenyl/isopropylphenyl TAPs.

However, on this occasion, this decrease is no longer paralleled by any further improvement in conferred low temperature flexibility of derived PVC compositions: fig. 5 shows that mixed isomer products give almost exactly the Clash & Berg values expected from interpolation.

Even at this level of complexity, the content of meta isomer is of more significance, in controlling low temperature flexibility properties, than are the isomeric natures of the other alkaryl groups present. Fig. 6 shows the substantially linear dependency of Clash & Berg temperature on meta content of various commercial and semi-commercial tricresyl phosphates. Even when other alkaryl groups present are in a majority, their isomeric nature has relatively little influence.

5. Poly-substituted content

The introduction of a limited content of poly-substituted aryl groups is an inevitable consequence of the (commercial) use of unseparated alkylated phenol products for phosphorylation. The small poly-substituted components, at least in the "alkylated" isopropylated and tertiary-butylated series, leave viscosities at equal average alkyl content lower than are predicted from those of corresponding pure unsymmetrical TAPs. The variation of viscosity with temperature is also less

(table 9): this latter effect is perhaps of more importance for hydraulic fiuid than for plasticiser uses, but is probably significant, in view of the correlation of low temperature flexibilities in PVC with fluid viscosity index (v.i., and figure 8).

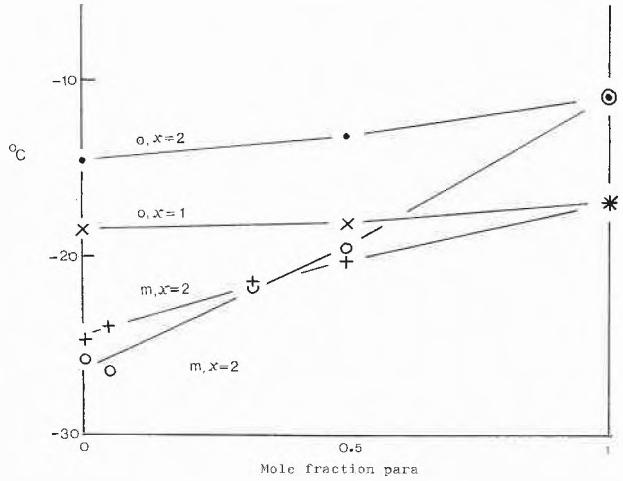

Fig.5: Variation of 82 p.h.r. *Clash & Berg* temperatures with isomer ratios, in co-reacted phenyl/isopropylphenyl TAPs.

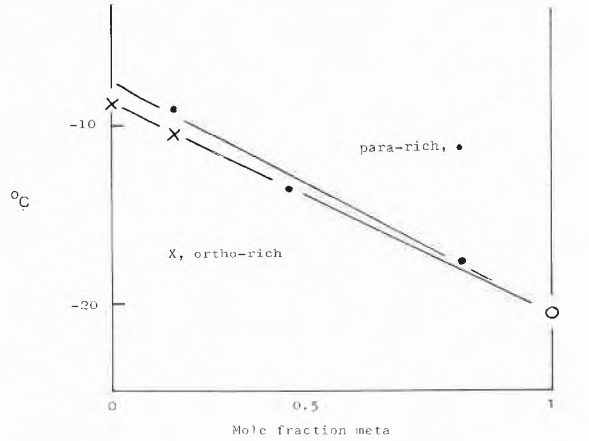

Fig.6: Effect of meta content on *Clash & Berg* temperatures of isomeric tricresyl phosphates, with varying other isomeric and non-isomeric aryl components. 82 p.h.r.

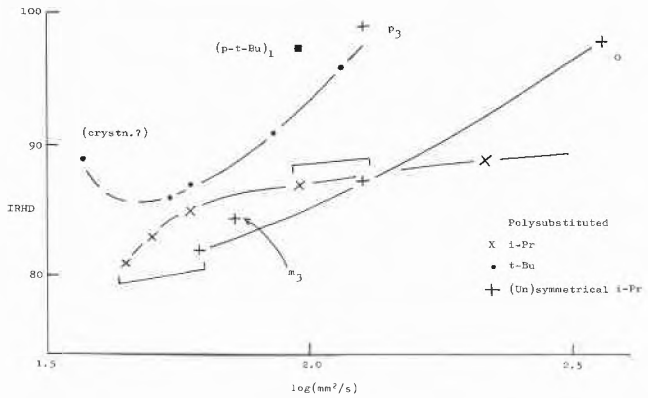

Fig.7: Plasticising efficiency versus log viscosity (25 °C) for polysubstituted (isopropylated and tertiary-butylated) TAPs, and symmetrical and unsymmetrical equivalents. 54 p.h.r.

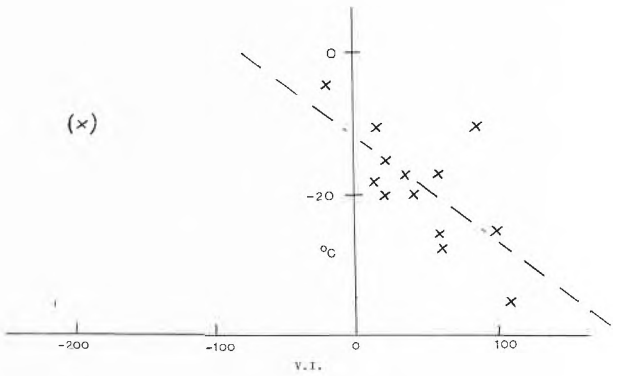

Fig.8: Correlation of *Clash & Berg* temperatures in PVC (82 p.h.r.) with liquid Viscosity Index, for compositions of symmetrical, randomized, isomeric, polysubstituted, and various alkyl types (Correlation coefficient of L.R., r −0.68, p ~99%, omitting extreme left hand point).

Table 9: Effect of polysubstituted components, from phosphorylation of whole alkylated phenol products, on liquid viscosity properties, relative to unsymmetrical single molecule TAPs of equal alkyl content.

R in I	x	Type	Isomer	Viscosity mm²/s at 37.8 °C	ASTM slope.
i-Pr	1	Unsymmetrical	ortho	26.2	0.844
			para	20.9	0.810
		Polysubstituted	ca. 80% ortho	22.7	0.831
t-Bu	1	Unsymmetrical	para	39.6	0.974
		Polysubstituted	> 95% para	36.7	0.840
	2	Unsymmetrical	para	178.4	0.886
		Polysubstituted	> 95% para	131.7	0.871

Polyalkyl content usually seems to improve softening efficiency. Normal temperature efficiency properties appear to be affected more than low temperature flexibilities. Table 10 shows the overall clearly beneficial effect of the poly-substituted level of complexity, on efficiency in PVC, when compared with symmetrical pure TAPs. Table 11 illustrates further that poly-substituted TAPs also show advantages relative to corresponding unsymmetrical pure TAPs.

Table 10: Efficiency in PVC, of polysubstituted TAPs (from alkylation) versus equivalent symmetrical single molecule TAPs. Average composition, one alkyl per aryl.

Alkyl	Property	p.h.r.	Symmetrical ortho	Symmetrical para	Poly-substituted *
i-Pr	IRHD, 23 °C	54	97	98	88
		82	70	70	66
	Clash & Berg, °C	82	−9	−4	ca. −5
t-Bu	T.S., MN/m²	100	–	16.3	15.9
	ε_B, %	100	–	90	260
	ε (load max), %	100	–	12	260

* Compositions (%): i-Pr: Phenol, 17; ortho, 33; para/meta, 14 (meta < 1); di, 29; tri, 7.
t-Bu: Phenol, 7; ortho, 2; para, 75; 2,4-di, 16.

Table 11: Efficiency in PVC, polysubstituted versus unsymmetrical TAPs: average composition, one tertiary-butyl per phosphate molecule. 54 p.h.r.

	IRHD	T_3(°C)	100% modulus (MN/m^2)
Unsymmetrical single molecule	97.5	19	18.4
Polysubstituted (alkylated)	91.5	14.5	15.8

Table 12: Clash & Berg temperatures for isopropylated (polysubstituted) TAPs, versus equivalent isomeric isopropylphenyl/phenyl mixture compositions. °C, 82 p.h.r.

Average isopropyl groups per phosphate molecule.	Type	
	Isomeric (Interpolated, assuming 80% ortho, 20% para)	Polysubstituted (by alkylation)
1	−18.5	−15 − −17.5
2	−14	−11.5 − −15

Introduction of poly-substitution can yield slight improvements relative to randomised mono-alkyl types. However, in the practically significant range of isopropyl contents, as used in commercial REOFOS, the effect of polysubstituted residues on efficiency properties may be marginally negative, as is shown by table 12, at least for low temperature flexibilities. Efficiency benefits of poly-substituted content are generally more evident at higher alkyl contents. For operational reasons, our production units tend to make TAP of a somewhat higher degree of poly-substitution complexity than is obtained from laboratory experiments. It seems plausible that the *slightly* lower viscosity at equal alkylation level we often observe on plant product, with associated improvements in related properties such as gelation rate (clear point), may be due to this slightly greater complexity.

6. Various alkyl content

The effects of mixing different alkyls have not been fully evaluated, and need more study. The properties imparted in PVC by TAPs containing mixed various alkyls are probably mostly controlled by the specific alkyl types present, rather than by interactions, as the differences between different alkyl types are much larger than any mixture effects found so far.

As has been noted, tertiary-butyl substituents give much higher viscosities than are found with lower alkyls: isopropyls give viscosities more comparable to those of methyl TAPs. Higher viscosities are expected to give rise to worse efficiencies, as is found (e.g. at polysubstituted level, fig. 7). Tertiary-butyl TAPs give comparable efficiencies to isopropylated ones, only when the viscosity of the former type is lower. The tertiary-butylated TAPs become less efficient as viscosity increases, whereas the efficiency of isopropylated types remains good, even at rather high viscosities. The isopropylated series is therefore less critical than the tertiary-butylated, as to alkyl contents giving efficient plasticisation, leaving more flexibility in choice of alkyl level to optimise properties controlled by molecular weight or polarity (volatility, fire retardance, gelation rates, etc.) for particular uses.

The apparent superiority of the pure unsymmetrical orthoisopropyl cases in fig. 7, over alkylated commercial types of equal viscosity, is due solely to the higher viscosity of the purer structures: bracketed pairs of points have equal isopropyl contents.

Secondary butyl groups generally give properties closer to those given by isopropyl than to those with tertiary-butyl, at equivalent carbon contents.

The greatest effects of mixture composition, upon both viscosity *and* low temperature flexibility, are by way of alkyl content and isomer type. Therefore, the correlation previously suggested by H. Jones [3], of low temperature liquid viscosity and/or viscosity index with low temperature flexibility, broadly holds for TAPs (fig. 8). This may imply that some microscopic plasticiser-rich "phase" still exists in the plasticised PVC, so that intermolecular interactions between plasticiser molecules still provide an effective "plasticiser viscosity": this supports "two-phase" models for plasticised PVC.

Overall, the effect of randomisation of distribution of the available aryl groups in a TAP is to somewhat lower viscosities, and thus also to lower minimum handling temperatures (pour points), as well as crystallisation temperatures. However, low temperature flexibilities in PVC are not improved significantly over those realised with equivalent unsymmetrical pure structures (where such exist). Softening efficiency at ambient temperatures is sometimes aided by polysubstitution, most significantly at alkyl contents giving inherently less good efficiencies.

Chemical stability properties, discolouration, and light induced incompatibility

For chemically-controlled properties, the nature of the alkyl substituent, and probably also the degree of alkyl substitution of the TAP molecule, was expected to be controlling. This expectation is surprisingly overridden by effects due to alkyl positional isomerism.

Table 13: Influence of isopropyl aryl isomer on fluid oxidation/corrosion test behaviours (Oxygenated, 218.3 °C, 48 h, in presence of antioxidant, copper deactivator, and metals).

Composition		Change in 37.8 °C viscosity, %	Change in acid value, mg/KOH/g
(o-i-$PrC_6H_4O)_3PO$		4	0.0
(m-i-$PrC_6H_4O)_3PO$		850	12.2
Polysubstituted:	Phenol 54 Ortho 29 Meta/para 10.5 di/(tri) 6.5	4	0.0_5

Table 14: Influence of light on PVC containing isopropyl TAPs: 180 h FSB exposure to fluorescent sunlamp/blacklamp combination.

	$(i\text{-}PrC_6H_4O)_3PO$			Randomized, average one isopropyl group per phosphate molecule.
	Colour stability	Exudation	I.R. C=O in exudate	Colour stability.
Ortho	Off-white	Nil	− ve	Off-white
Meta	Brown	Copious	+ ve	Dark yellow
Para	Fawn	Slight	+ ve	Light yellow

The inherent stabilities of the fluids can conveniently be assessed outside PVC from the results of standard hydraulic fluid tests. Table 13 shows that ortho-isopropyl TAPs are markedly more oxidatively resistant than their meta isomers. The worse chemical stability, thus indicated for the meta isomer, is paralleled by its severely worse behaviour in PVC exposed to light (table 14). Only ortho-rich isopropylated TAPs give satisfactory colour stability. The problem of discolouration of the other isomers is worsened, particularly in the case of meta isomers, by the development of gross incompatibility with the PVC on exposure to light: pools of orange to brown exudate appear on the surface of the PVC. Since this comparison is within a series of isomers of not greatly differing densities, it seems very unlikely that the development of this incompatibility is due to any significant differences in the initial inherent compatibility with PVC, as is controlled by solubility parameters. Rather, the incompatibility is attributed to rapid oxidative deterioration of the meta isomer near the surface of the exposed PVC: the exudate contains carbonyl compounds. Migration of deteriorating TAP to the surface may, of course, be facilitated by the lower viscosities in the meta series.

It would be of interest to explore how far the degradative problems with meta isomers have been a factor in the poor colour light stability and tack development problems which were always associated with the "prior art" tar acid TAPs, which had high contents of meta cresyl and the "meta-containing" 2,5/3,5-xylyl residues.

Table 15: Isomer effect on Volvo 90 °C fogging: symmetrical tris-isopropylphenyl phosphates (70 p.h.r.).

Isomer	Ortho	Meta
Reflectance, % (no fog = 100)	66	93

These chemical instabilities can have curiously distorting effects upon the apparent results even of physical property testing, particularly at high temperatures. This is well illustrated by the data in table 15, on the "Volvo fog" test, which assesses the extent to which plasticiser is lost by volatilisation from hot PVC. The data would suggest that the ortho isomer is *much* more volatile than the meta, which is surprising in view of the rather small difference in boiling points. However, as soon as we appreciate the relatively very bad oxidative stability of the meta isomer, it becomes clear that its apparent lack of volatilisation may be due to degradation to relatively non-volatile forms on or in the PVC: the material volatilised from PVC containing ortho TAP consists of the unchanged molecular components having lowest molecular weights (x = 0, 1, and a little 2). There seems little merit in avoiding loss of a plasticiser, if while being retained, it ceases to be a plasticiser at all! It may be significant that, while three companies hold patents covering meta-rich "synthetic" TAP types, none has chosen to commercialise them.

Conclusion

The ability, by phosphorylation of isopropylated mixed feedstocks, to produce ortho-rich TAPs which are substantially free of meta isomers, and which gain some advantage from the further randomisation due to minor para- and poly-substituted contents, has thus provided plasticisers having markedly better light stability properties than those which could be obtained so long as tar acid mixtures were used. This has been achieved without any of the sacrifice of efficiency properties which might have been expected on introduction of the bulkier isopropyl groups—particularly considering prior experience with TAPs bearing tertiary-butyl substituents. The products still, of course, provide that essential property which has become the chief raison d'être of the TAP plasticiser class—improved fire retardancy—to as great a degree (or, on some tests, even to a slightly greater extent) than was provided by the obsolete tar acid TAPs.

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