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## IDENTIFICATION AND DETERMINATION OF PRIMARY PLASTICISERS IN POLYVINYL CHLORIDE CALENDERED FORMULATIONS

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### SUMMARY

A method has been developed for the rapid identification and determination of single primary and certain mixed plasticisers in polyvinyl chloride sheetings. Direct injection of tetrahydrofuran solutions of sheet samples containing dibutyl phthalate as internal standard gave excellent quantitative results; individual analyses can be completed in less than 1 h.

### INTRODUCTION

Primary plasticisers used in polyvinyl chloride calendered formulations have similar physical properties and separations are thus difficult. Plasticisers such as relatively pure dibutyl phthalate, tritolyl phosphate and diethyl phthalate, reported as being separable by gas chromatography<sup>1-3</sup>, are not used in current formulations. Plasticisers in current use are made from mixed alcohol feedstocks and can contain up to twelve components.

### EXPERIMENTAL

#### *Materials and formulations*

The plasticisers used are specified in Table I. The solvent used, tetrahydrofuran, was of technical reagent grade (BDH, Poole, Great Britain). The dibutyl phthalate internal standard was supplied by Geigy (U.K.).

The specially prepared sheeting formulations were milled at 140° and stripped out at 0.01-in. thickness. Samples were prepared covering the range 5–40% plasticiser at 5% intervals, varying the amount of polyvinyl chloride and keeping the amounts of stabiliser and pigment constant, as shown in Table II.

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TABLE I  
PLASTICISERS

No.	Name	Code/abbreviation	Source
1	Dialphanol phthalate	DAP	Geigy (U.K.) (Manchester, Great Britain)
2	Linear 7,9-alcohol phthalate	L79P	B.P. Chemicals (U.K.) (Glamorgan, Great Britain)
3	Diisooctyl phthalate	DIOP	Geigy (U.K.)
4	Diisodecyl phthalate	DIDP	Geigy (U.K.)
5	Diisooctyl azelate	DIOZ	Geigy (U.K.)
6	Trisphenyl/isopropyl phenyl phosphate	Reofos	Geigy (U.K.)

TABLE II  
FORMULATION COMPOSITIONS %

Plasticisers 1-6	40-5
Polyvinyl chloride	55.5-90.5
Stabilizer system	{ Epoxy 2.0
	{ Marc C 0.5
	{ DP 5296 1.0
Pigments	{ TiO <sub>2</sub> 0.5
	{ Blue BHL 0.5

#### Apparatus

A Pye 104 Model 64, twin-column, chromatograph equipped with a flame ionisation detector was used. Glass columns were 1.5-3.0 m in length and 4 mm I.D. A Phillips PR 4069M/04 recorder, 1 mV f.s.d. was coupled to a Kent Chromalog I integrator for the quantitative work.

#### Columns

Stationary phases, loadings and supports are given in Table III. In addition, a porous polymer, Chromosorb 101, was examined.

The separating ability of the various columns at various temperatures was

TABLE III  
STATIONARY PHASES, SUPPORTS AND LOADINGS

Chromosorb W was 60-80 mesh, non-acid-washed grade; glass beads were 60-80 mesh, HF etched.

Stationary phase	Code	Loadings and supports
Dimethyl silicone gum	SE-30	1, 3, 10, 25% on Chromosorb W 0.5% on glass beads
Methyl phenyl silicone fluid (50% phenyl)	OV-17	5, 10% on Chromosorb W
Methyl phenyl silicone fluid (75% phenyl)	OV-25	10% on Chromosorb W
Trifluoropropyl methyl silicone fluid	QF-1	10% on Chromosorb W
Poly(neopentyl glycol) adipate	NGA	10% on Chromosorb W 0.5% on glass beads
Poly(diethylene glycol) succinate	DEGS	15% on Chromosorb W
Polyethylene glycol succinate	PEGS	10% on Chromosorb W
Polyethylene glycol	Carbowax 20M	10% on Chromosorb W 0.5% on glass beads
Polyvinylpyrrolidone	PVP	2.5, 5, 10% on Chromosorb W

examined by direct injection of 1- $\mu$ l volumes of 5% (v/v) solutions of each plasticiser and of various mixtures in hexane, containing 0.2% (w/v) dibutyl phthalate. In appropriate cases calibration graphs were prepared by integrating areas of all the peaks from each plasticiser.

Sheeting samples (1 cm<sup>2</sup>) were cut into small pieces and 25 mg dissolved in 0.5 ml tetrahydrofuran containing 0.2% (w/v) dibutyl phthalate as internal standard pipetted into glass vials. 1- $\mu$ l volumes of each formulation were injected directly on column and calibration graphs prepared. Batch manufactured sheet material was analysed in a similar manner using the calibration data obtained from the specially prepared series of formulations.

## RESULTS

Preliminary experiments showed that of the columns examined (Table III) only SE-30 and OV-25 columns gave useful separations and that dibutyl phthalate was a good internal standard.

A 1.5-m column of 3% SE-30 separated DAP, DIOZ and DIDP; retention data and conditions are shown in Table IV. The separations were of no use for quantitative purposes because of the long retention times and the shapes of the peaks.

TABLE IV

### SEPARATION OF DIOZ, DIDP AND DAP

Column, 1.5 m, 3% SE-30, 200°; nitrogen carrier flow-rate, 45 ml/min.

<i>Plasticiser</i>	<i>Peaks (min)</i>
DAP	15, 18.5, 23.4, 33.8
DIOZ	15.4, 43.1, 48.8
DIDP	76.9

Reofos, DIOP and L79P had similar retention times on the 3% SE-30 column to DAP and could not be distinguished; indeed DIOP, L79P and DAP, which are all based on octyl alcohol, could not be separated on any of the columns examined. If present singly, identification of each is possible, as chromatograms are quite different. Increased loadings from 3 to 10% and column lengths from 1.5 to 3 m increased resolution of components in single plasticisers but did not improve significantly the separation of admixtures.

A 10% OV-17 column gave partial separation of Reofos from DAP, but better separation was achieved using OV-25. QF-1, the most polar silicone phase examined, gave similar chromatograms to SE-30, hence it was concluded that polarity was not the major factor in the separation of Reofos from DAP. The separation is affected by the phenyl content of the stationary phase, OV-17 (50%) or OV-25 (75%); however, an increase in phenyl content to 85% gave no improvement in separation over that obtained using OV-25. The optimal conditions for reasonably fast analysis times using 10% OV-25 on 60-80 mesh Chromosorb W are a nitrogen carrier flow-rate of 100 ml/min and a column temperature of 260°. Chromatograms for DAP, L79P, DIOP, DIDP, DIOZ and Reofos are shown in Fig. 1. The first peak

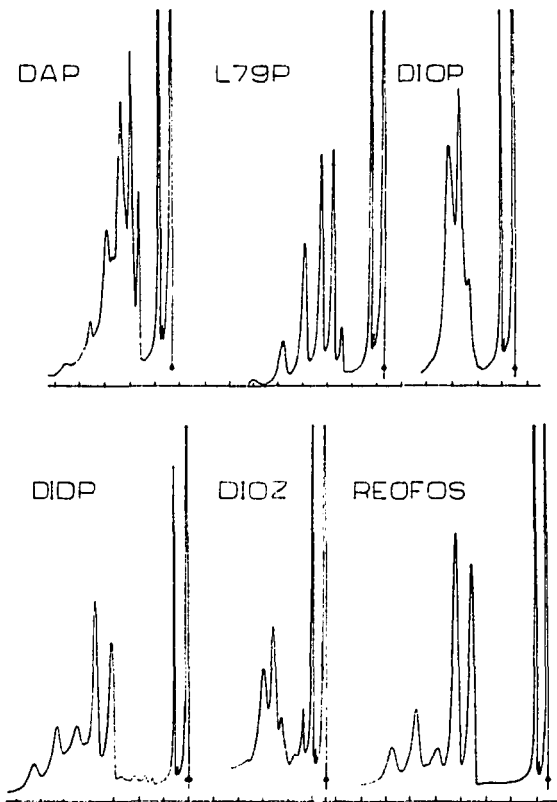


Fig. 1. Chromatograms of DAP, L79P, DIOP, DIOZ and Reofos using a 7-ft. column of 10% OV-25 on 60-80 Chromosorb W at 260°.

in each case is due to tetrahydrofuran and the second to the internal standard.

The analysis of standard production sheet materials was attempted. Results are given in Table V. Material containing a single plasticiser, DAP, was analysed using the calibration graphs as indicated earlier. Since separation of Reofos and DAP was not complete on an OV-25 column, further calibration graphs were prepared, taking the area up to the fourth major peak of DAP as a measure of DAP

TABLE V  
ANALYSIS OF NORMAL PRODUCTION SHEET SAMPLES

<i>DAP %</i>		<i>Reofos %</i>	
<i>Specification</i>	<i>Found</i>	<i>Specification</i>	<i>Found</i>
30.3	30.0	—	—
9.24	9.52	22.2	21.4
7.5	7.1	22.5	22.1
15.0	15.4	15.0	15.9
22.5	21.0	7.5	13.2

and peaks thereafter as a measure of Reofos, ignoring the slight overlap. This procedure is satisfactory for DAP-to-Reofos ratios of 1:1 and 1:3 for a total plasticiser content of 30%.

## DISCUSSION

The multi-component nature and the overall similar physical properties of the plasticisers examined made it difficult to obtain separations of mixed systems suitable for quantitative purposes. Mixed phthalate-phosphate systems can be quantitatively analysed provided the w/w ratio of phthalate to phosphate is not greater than 1:1 (coefficients of variation 2–5% on five results). Identification and estimation of single plasticisers can be made by the use of reference chromatograms and prepared calibration formulation samples.

Identification and estimation of plasticisers by solvent extraction<sup>4</sup> is lengthy and problems arise with mixed systems which co-extract. Extracts may be examined by thin-layer chromatography<sup>3</sup>, by infrared spectroscopy<sup>4</sup>, or after hydrolysis<sup>5</sup> by gas chromatography. The present work shows that it is possible to avoid the lengthy extraction and hydrolysis stages and examine chromatographically solutions of polyvinyl chloride formulations by direct injection. Filtration of solutions is not necessary for samples with low solid contents. Up to 200 samples can be analysed without noticeable deterioration of columns by the build-up of polymeric material on the column. The accuracy and precision of results obtained using production materials compare favourably with those attainable by more classical procedures. There is a considerable saving of time in that overall analysis per sample is completed in less than 1 h provided calibration data are available.

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