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Note

High-voltage paper electrophoresis of zinc dialkyl- and diaryldithiophosphate lubricating oil additives

STANISŁAW PŁAZA
Department of Chemical Technology, Lodz University, 18 Nowotki Street, 91-416 Lodz (Poland)
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The O,O'-disubstituted dithiophosphates, particularly the zinc salts (ZDDPs), are commonly used in lubricating oils as multi-functional additives. The performance of these additives is influenced by the nature of the substituent groups.

Many analytical techniques have been used for the characterization of ZDDPs, but for most of them some intermediate stages are necessary, *e.g.*, pyrolysis[1], scission[2], hydrolysis[3] or oxidation[4]. All of these methods and also thin-layer chromatographic techniques[5,6] normally require some preliminary separation. Electrophoresis is a separation technique in which these obstacles do not occur.

Jamson and Hillman[7] described the electrophoresis of zinc dialkyl- and dialkylaryldithiophosphates, but their method does not distinguish between iso- and *n*-alkyl groups of ZDDPs and problems arise with the identification of used oils.

This paper describes the characterization of synthetic and commercial additives in oils by high-voltage paper electrophoresis in mixed aqueous–dimethylformamide (DMF) buffers. The conditions of separation give marked differences between *sec.*-, iso- and *n*-alkyl ZDDPs. Tetraacetoxymercurifluorescein (TMF) has been used successfully for the detection of ADDPs on paper chromatograms.

EXPERIMENTAL

Chemicals

The synthetic additives were prepared from the corresponding alcohols in accordance with the literature[8]; all alcohols were of analytical-reagent grade. TMF was obtained from POCh (Gliwice, Poland). All other reagents and solvents were of analytical quality.

Solutions

Electrolyte. The electrolyte was an aqueous solution of 0.1 mole/l sodium hydroxide and 0.05 mole/l borax (pH 10.6) and was mixed before use with DMF buffer (70:30).

Spray reagent. An aqueous $5 \cdot 10^{-4}$ *N* solution of TMF was prepared by dissolution of 17.1 mg of the reagent in 5 ml of 0.1 *M* sodium hydroxide solution, followed by dilution to 100 ml with water.

Sample concentration. Additive concentrates and synthetically prepared

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ZDDPs were applied as a 1% solution in *n*-hexane. Lubricating oils containing dialkyldithiophosphates were applied as a 50% (v/v) solution in *n*-hexane.

Electrophoresis

Paper electrophoresis was conducted in the apparatus described previously[9], using Whatman No. 1 chromatography paper and Whatman GF81 chromatography paper (glass-fibre paper) in 16 × 37 cm strips.

Electrophoresis was performed in the normal way in the horizontal mode. Samples were applied to the paper by means of a syringe as 1–3-μl spots. The separation was conducted at 2000–2500 V for 1–1.5 h. The paper was dried at room temperature before spraying it with TMF. After spraying, the ZDDPs gave dark spots on a yellow fluorescent background under ultraviolet light. All spots were 0.8 ± 0.2 cm in diameter. The ZDDPs can be identified by comparison with known standards.

RESULTS AND DISCUSSION

The recommended electrolyte was selected because it was found to promote faster and better separations of ZDDPs than others, the composition and pH of which were varied. Good separations were achieved on Whatman No. 1 paper at 2500 V for 1.5 h and on Whatman GF81 paper at 2000 V for 1 h.

The relative mobilites of 19 synthetic dialkyl- and dialkylaryldithiophosphates

TABLE I

RELATIVE RATES OF MIGRATION OF SYNTHETIC ZINC DITHIOPHOSPHATES

Substituent	*Derived ion, Mn**	
	Whatman No. 1 paper	*Glass-fibre paper*
Propanol-2	1.00	1.00
Propanol-1	0.96	0.95
Butanol-2	0.98	0.98
2-Methylpropanol-1	0.92	0.93
Butanol-1	0.86	0.83
3-Methylbutanol-1	0.85	0.85
Pentanol-1	0.79	0.77
Hexanol-1	0.75	0.73
Heptanol-1	0.71	0.67
2-Ethylhexanol-1	0.73	0.69
Octanol-1	0.66	0.64
Nonanol-1	0.62	0.60
Decanol-1	0.59	0.57
p-Butylphenol	0.56	0.55
Dodecanol-1	0.51	0.49
Tetradecanol-1	0.44	0.42
p-Octylphenol	0.40	0.37
p-Nonylphenol	0.36	0.33
Hexadecanol-1	—	0.35

* Mn values express mobilities relative to the diisopropyldithiophosphate anion, which moved approximately 25 cm.

are given in Table I. The values were calculated relative to the mobility of the diisopropyldithiophosphate anion and are average values of duplicate measurements.

Figs. 1 and 2 show the relationships between the relative mobilities and the number of carbon atoms present in the alkyl or alkylaryl group of the ZDDPs. Curves 1 correspond to members of the isoaliphatic series, curves 2 to the *n*-aliphatic series and curves 3 to dithiophosphates synthesized from alkylphenols.

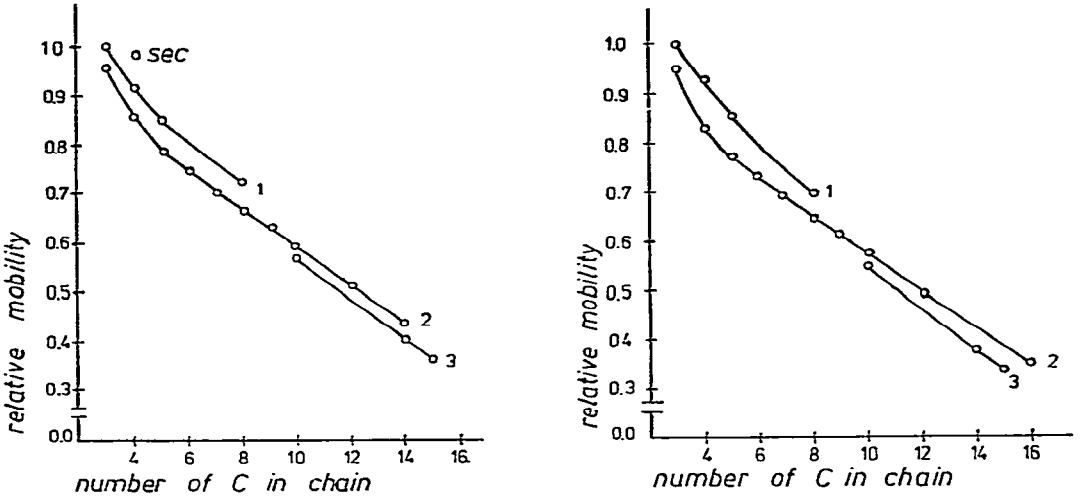

Fig. 1. Relationship between relative mobility and carbon number of ZDDPs prepared from: 1, *n*-alkyl alcohols; 2, isoalkyl alcohols; 3, *n*-alkylphenols; *sec*, *sec*.-butanol. Conditions of separation: Whatman No. 1 paper, 1.5 h, 2500 V.

Fig. 2. Relationship between relative mobility and carbon number of ZDDPs prepared from: 1, *n*-alkyl alcohols; 2, isoalkyl alcohols; 3, *n*-alkylphenols. Conditions of separation: Whatman GF81 paper, 1.0 h, 2000 V.

The velocity of migration decreased as the number of carbon atoms in the alkyl chain increased. The order of increasing velocity of electrophoretic migration of substituents is *n*-alkyl < isoalkyl < *sec*.-alkyl, and the migration distances of alkylaryl anions are smaller than those for the corresponding aliphatic series.

Fig. 3 shows the electrophoretic migration patterns of additive concentrates and used lubricating oils containing ZDDPs after testing in an engine. The identification of ZDDPs from an unknown mixture was carried out by comparison with reference additives (samples 1, 7, 8, 9 and 10). Using the recomended conditions of separation and detection there was no streaking and the ions migrated as compact spots. It has been shown that the presence of less than 0.1 % of ZDDPs in oil is easily detectable.

The unused oil (Fig. 3, sample 2) showed four spots consistent with a mixture of *n*-C_4, *iso*-C_8 and *n*-C_8 dialkyldithiophosphates. The additive concentrate (Fig. 3, sample 6) gave three spots, due to *iso*-C_3, *iso*-C_8 and a mixed additive with one of each of the two isoalkyl groups present. This was confirmed by hydrolysis–gas chromatography[4]. Samples 3, 4 and 5 shows the migration patterns obtained for such a series of used oils. These are lost, as is shown by the virtual disappearance of these spots after running the engine for 210 h. Unknown products, probably polymeric sulphur-

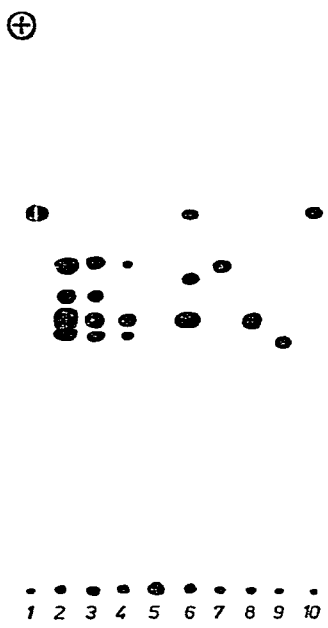

Fig. 3. Migration patterns of additive concentrate, unused and used oils and synthetic ZDDPs. 6, Additive concentrate; 2, unused oil; 3, oil after 100 h; 4, oil after 150 h; 5, oil after 210 h. Synthetic zinc dialkyldithiophosphates: 1,10, isopropyl; 7, *n*-butyl; 8, isooctyl; 9, *n*-octyl.

containing compounds, formed during the engine test remain at the point of application and can be seen to increase in concentration with increasing time. The technique is therefore easily applicable to the characterization of used oils.

The spots of the dithiophosphate anions were revealed well using TMF, the fluorescence of which is strongly quenched by some sulphur compounds. This reagent was very sensitive to the investigated additives and less than 0.5 μg of ZDDP per square centimetre of spot area was easily located.

CONCLUSIONS

The method described appears to be a general procedure for the rapid separation and sensitive detection of zinc dialkyl- and diaryldithiophosphates in unused and used lubricating oils, additive concentrates and additive packages.

The method has several advantages over that of Jamson and Hillman[7]: (a) shorter time of separation; (b) variations in migration distances for *n*-alkyl, isoalkyl and alkylaryl groups; and (c) the possibility of characterizing used oils.

Electrophoresis, however, possesses certain disadvantages: (a) it is possible for mixed dialkyldithiophosphates to have similar electrophoretic mobilities and thus be indistinguishable; (b) variations in migration distances for a few straight- and branched-chain alkyldithiophosphates may be small, so that great care must be exercised in interpreting the electrophoretic mobility patterns obtained.

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