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CHARACTERIZATION OF ZINC DIALKYL DITHIOPHOSPHATE LUBRICATING OIL ADDITIVES BY HIGH-VOLTAGE ZONE ELECTROPHORESIS

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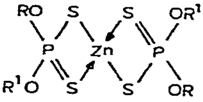
SUMMARY

A method is described for the rapid qualitative characterization of zinc dialkyl dithiophosphate oil additives by high-voltage zone electrophoresis, on a silica gel substrate. Samples of lubricating oils and lubricating oil additive packages can be analysed directly, as solutions in light petroleum (b.p. 80–100°).

INTRODUCTION

Dialkyl dithiophosphates, usually as the zinc salts, are widely used in motor oils as anti-oxidant and extreme-pressure additives. They have the general formula:



where R and R^1 may be *n*-alkyl, branched alkyl or alkaryl groups. The performance of these additives is influenced by the nature of the substituent groups[1].

In our department there is a requirement for methods to identify the nature of these additives for the quality assurance of service oils and additive packages, for the characterization of proprietary oils and packages and for studies of the depletion of oil additives during engine testing.

Various analytical techniques have been described, including:

(1) Pyrolysis–gas chromatography[2,3]. In this technique olefins produced by pyrolysis can be related to the chain length of the original alkyl groups present.

(2) Thin-layer chromatography[4–6]. Fingerprint chromatograms of the oil additives may be obtained although overlap occurs between the dialkyl and dialkaryl additives.

(3) Infrared spectroscopy[7–9]. This technique is not usually applicable to dialkyl dithiophosphate additives containing mixed alkyl groups.

(4) Chemical scission followed by gas chromatography[10]. In this technique the alkyl side chains present are converted by hydriodic acid to alkyl iodides which are identified by gas chromatography–mass spectrometry. Dialkyl sulphides can be formed which may complicate interpretation.

(5) Hydrolysis followed by gas chromatography. The alkyl side chains are converted to the corresponding alcohols which are then identified by gas chromatography.

All these methods normally require some degree of preliminary separation.

The application of high-voltage electrophoresis to non-aqueous or mixed aqueous (alcohol–water) buffer media has been described by Leighton et al.[11], who studied the separation of oil additives including zinc dialkyl dithiophosphates. This report describes work with a wider range of synthetic and commercial additives and their qualitative determination in commercial lubricating oils and additive packages.

EXPERIMENTAL

High voltage electrophoresis apparatus. The apparatus consisted of a high-voltage electrophoresis cell (Camag) fitted with a water-bath and a refrigeration unit to ensure maximum cooling of the thin-layer plate.

Chemicals. Analar-grade chemicals were used throughout.

Buffer solution. The buffer solution was prepared by dissolving boric acid (20 g) and anhydrous sodium acetate (10 g) in de-ionized water (150 ml) and ethanol (400 ml).

Thin-layer plates. Commercial pre-coated silica gel thin-layer plates (500 μm, 20 × 40 cm; Anachem, Luton, Great Britain).

Preparation of zinc dialkyl and dialkaryl dithiophosphates. Synthetic additives were prepared by the method of Brazier and Elliott[12].

Sample concentration. Additive concentrates, additive packages and synthetically prepared zinc dialkyl dithiophosphates were applied as a 1% (v/v) solution in light petroleum (b.p. 80–100°). Lubricating oils, with a dialkyl dithiophosphate content of approximately 1%, were applied as a 50% (v/v) solution in light petroleum.

Spray reagents. Spots were visualized by spraying with palladium chloride solution [100 ml 0.5% (w/v) in aqueous acetone, 50% (v/v), acidified with 5 ml dilute hydrochloric acid] which gives brown spots on a pale brown background for dithiophosphate anions.

Electrophoresis procedure. The apparatus was set up in accordance with the manufacturer's instructions. The silica gel plate was impregnated with buffer solution by immersion in a trough containing the boric acid–sodium acetate buffer (see above) and excess of buffer solution was removed by light blotting with filter paper. Adequate heat transfer from the silica gel plate to the cooled base of the unit was ensured by smearing the bottom of the plate with silicone grease (Dow Corning MS4; Midland, Mich., U.S.A.). Sample solutions were applied across the centre of the moist plate as 0.5- or 1.0-μl spots using a microsyringe.

The safety case of the electrophoresis unit was then closed and a potential of 1000 V applied for 5 h. The silica gel plate was then removed and allowed to dry at room temperature before spraying with the visualizing reagent (see above). Warming of the electrophoresis plate to 50° increased the spot intensity, allowing the migration distance of the dithiophosphate anions to be measured.

RESULTS AND DISCUSSION

Calibration

The results reported below show that it is possible to correlate migration distance with the carbon number of the *n*-alkyl group for a series of synthetically prepared zinc di-*n*-alkyl dithiophosphates (*n*-C_3–*n*-C_8). The range C_3–C_8 covered most of the commercial dialkyl dithiophosphate additives in lubricating oils. A series of *para*-substituted dialkaryl dithiophosphates was also prepared.

Figs. 1 and 2 show the electrophoretic migration patterns of the dithiophosphate anions obtained for the series of di-*n*-alkyl and dialkaryl dithiophosphates, when examined under the standard conditions described above.

Fig. 3 shows the linear relationship between migration distance and carbon chain number of the *n*-alkyl group for the synthetically prepared aliphatic series of dithiophosphates. The dialkyaryl series also shows a linear relationship though the migration distances of the anions are smaller.

Analysis of lubricating oils and lubricating oil additive packages

A qualitative analysis of the zinc dialkyl dithiophosphates present in oils and additive packages was performed. Samples and standards containing synthetic *n*-C_3, *n*-C_5, and *n*-C_8 dialkyl dithiophophates were applied to the thin-layer plate as 0.5-μl

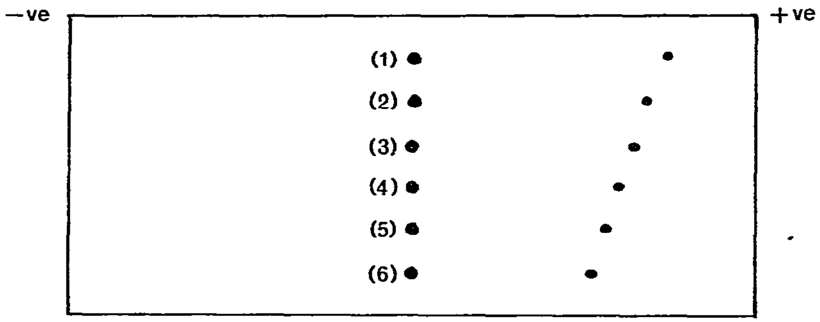


Fig. 1. Migration patterns if synthetic zinc dialkyldithiophosphates; 1 = n-propyl, 2 = *n*-butyl, 3 = *n*-pentyl, 4 = *n*-hexyl, 5 = *n*-heptyl, 6 = *n*-octyl.

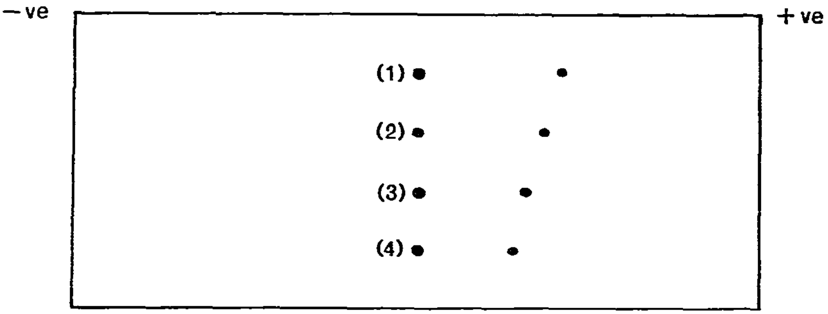


Fig. 2. Migration patterns of synthetic dialkaryldithiophosphates. 1 = *p*-methylphenyl, 2 = *p*-ethylphenyl, 3 = *p*-*n*-propylphenyl, 4 = *p*-*tert.*-amylphenyl.

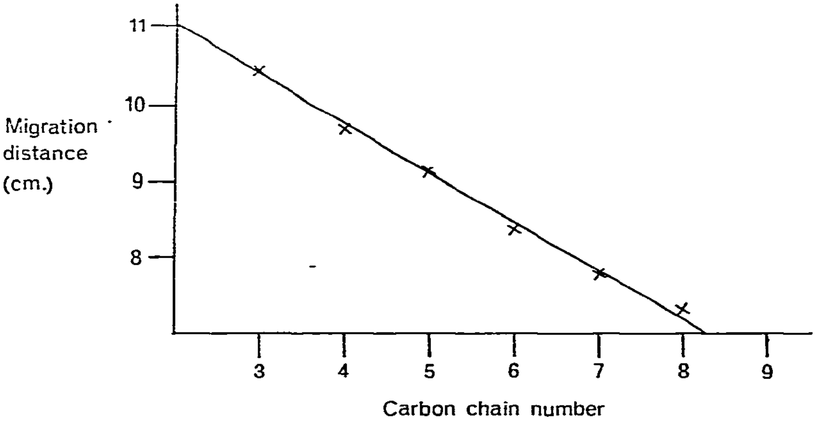


Fig. 3. Relationship of migration distance to carbon chain number.

spots. Fig. 4 shows a typical electrophoretic migration pattern for various additive concentrates (A–E). Additive E, known to be a dialkaryl dithiophosphate, can be readily distinguished from dialkyl dithiophosphates by its low electrophoretic mobility. Although a similar low mobility might be shown by a dithiophosphate with a very long alkyl chain, it is believed that such materials are not commercially used.

The best visualization of dithiophosphate anions was obtained using the palladium chloride spray, which is specific for sulphur-containing compounds. No interference from other ionic additives occurs as is the case when using other non-specific reagents, *e.g.* 2,6-dibromo-*p*-benzoquinone chlorimine. Development of the thin-layer plate shows that polymeric sulphur-containing additives remain at the point of application.

The standard mixtures of n-C_3, n-C_5 and n-C_8 zinc dialkyl dithiophosphates were applied at either side of the test surface of the thin-layer plate in order to show that uniform migration occurred across the plate. Plates showing an unequal migration of the standard components, resulting from unequal cooling of the plates or of variations in the thickness of coating, were rejected. From the calibration graph of migration distance against carbon chain number of the components in the applied standard solutions, the characterization of the particular dithiophosphates present was achieved.

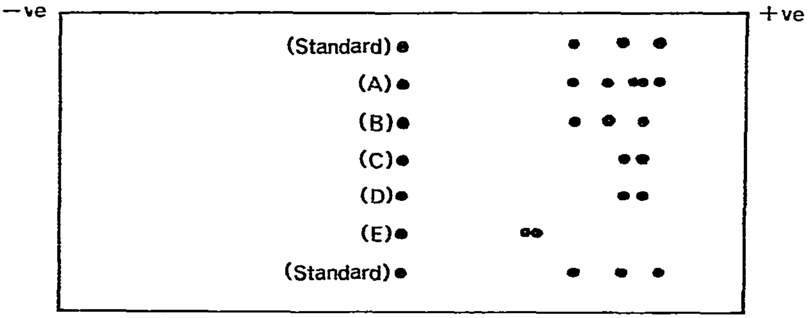


Fig. 4. Migration patterns of additive packages and concentrates. A–E = additive concentrates listed in Table I.

TABLE I

QUALITATIVE CHARACTERISATION OF ADDITIVE PACKAGES AND CONCENTRATES

Sample type	*Sample Ref.*	*Detected by electrophoresis*	*Detected by hydrolysis–GC*
ZDDP concentrate	A	C_3, C_4, mixed C_4–C_5, C_6, C_8	iso-C_3, iso-C_4, iso-C_5, n-C_5, n-C_6, branched-C_8
	B	C_4, C_6, C_8	iso-C_3, iso-C_4, n-C_4, n-C_6, branched-C_8
	C	C_4, C_5	iso-C_4, n-C_5
	D	C_4, C_5	iso-C_4, iso-C_5, n-C_5
	E	C_{30} + C_{12} alkyl phenyl	approx. C_{10}–C_{12} alkyl phenyl
	F	C_4, C_5	iso-C_3, iso-C_4, iso-C_5, n-C_5
EP Additive Packages	G	C_6	4-methyl-2-pentyl
	H	C_6	Branched C_6
Oil (Multigrade)	I	C_4, C_5	—

Table I shows the results obtained for a series of lubricating oils, additive packages and additive concentrates compared with results obtained by hydrolysis–gas chromatography technique. In general there is good agreement between the two methods. Exceptions are additives B and F where the isopropyl derivative is not found by electrophoresis because of the very low level present. The position of the third spot from additive A was intermediate between those for C_4 and C_5, probably being a mixed additive with one of each of the two alkyl groups present. All these anomalies, however, occur with minor components.

Analysis of used oils

The technique was applied to a series of used lubricating oils containing zinc dialkyl dithiophosphate additives, after Petter W1 testing (IP/176/69). As the concentrations of dialkyl dithiophosphate additives in used oils are extremely low, sample sizes were increased to 3.0 μl in order to be able to visualize the additives. Sample application consisted of three separate 1.0-μl spots placed directly on the previous spot, allowing sufficient time for the applied spot to dry.

Fig. 5 shows the electrophoretic migration patterns obtained for such a series of used oils after development with palladium chloride spray. The unused oil shows

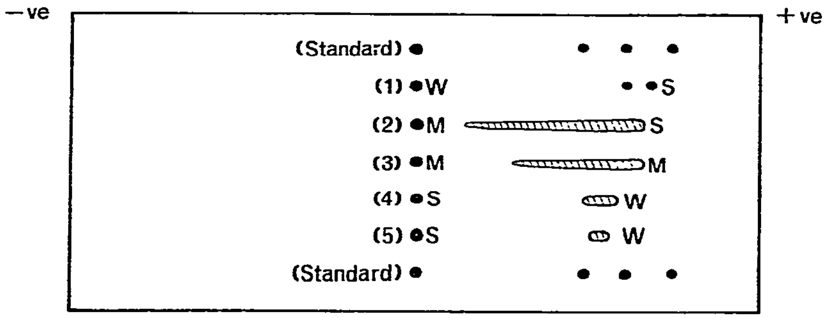


Fig. 5. Migration patterns of a used oil series; 1 = unused oil, 2 = after 9 h, 3 = after 18 h, 4 = after 27 h, 5 = after 36 h; S = strong, M = medium and W = weak.

two spots consistent with C_4 and C_5 dialkyl dithiophosphates. These are rapidly lost, shown by the virtual disappearance of these spots after 36 h engine running. Unknown products resulting from the test give streaking. Other products remain stationary at the point of application and can be seen to increase in concentration with increasing time. The technique is therefore not easily applied to the characterisation of used oils although the conditions of the Petter W1 test are very severe.

CONCLUSIONS

Electrophoresis can be used as a simple method for the qualitative identification of zinc dialkyl and dialkaryl dithiophosphate additives present in lubricating oils, additive concentrates and additive packages.

The advantages of electrophoresis over conventional methods include:

(i) lubricating oils can be analysed directly without any intermediate 'clean-up' stage necessary;

(ii) electrophoresis, as it involves the fission of the dithiophosphate salt, containing four alkyl groups into two dithiophosphate anions containing two alkyl or alkaryl groups, provides a better resoltuion than thin-layer chromatography;

(iii) electrophoresis readily distinguishes between dialkyl and dialkaryl dithiophosphates in a single analysis;

(iv) electrophoresis can attempt to identify the common mixed alkyl additives used in lubricating oils, whereas hydrolysis of the alkyl group followed by gas chromatography shows only which alkyl groups are present;

(v) ammonium dialkyl dithiophosphates can be analysed by the same procedure as for zinc salts. The presence or absence of zinc cations can be determined by visualizing with dithizone reagent whereby zinc cations produce pink spots, remaining stationary at the point of application.

Electrophoresis does, however, possess certain disadvantages, namely:

(i) it is difficult in the electrophoretic migration patterns to distinguish between isomeric alkyl groups, whereas hydrolysis of the alkyl side chain to form the appropriate alcohol followed by gas chromatography shows accurately which alkyl groups are present, including isomers;

(ii) it is possible for mixed dialkyl dithiophosphates to have similar electrophoretic mobilities and thus be indistinguishable;

(iii) variations in migration distances for successive alkyl dithiophosphates may be small, thus great care must be exercised in interpreting the electrophoretic mobility patterns obtained.

(iv) problems may arise with used oils where severe operating conditions may lead to streaking in the electrophoretic pattern.

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