Separation and Identification of Zinc Dithiophosphates by Partition Paper Chromatography*

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Summary: This paper describes the method for the separation and identification of zinc dithiophosphates having alkyl or aryl substituents by partition paper chromatography.

Of a variety of solvent systems examined, the solvent system of cresyldiphenyl phosphate (stationary phase)—90/10 isooctane-*n*-cetane (mobile phase) was most suitable for the separation and identification of zinc dialkyldithiophosphates. Their R_f values with this solvent system increase with the number of carbon atoms in the alkyl group. Among zinc dialkyldithiophosphates having isomeric alkyl groups respectively of straight primary, branched primary and secondary, the R_f values increase in this order. The solvent system of liquid paraffin—*isopropyl* alcohol was found to be satisfactory for partition paper chromatography of zinc dialkyldithiophosphates having long chain alkyl groups.

A large difference in the R_f values between zinc dialkyldithiophosphates having isomeric alkyl groups respectively of primary and secondary, was observed when the solvent system of polyoxyethylene octylphenylether (E.O.10 mol)—*n*-heptane was used and similarly, a large difference in the R_f values between zinc dialkyldithiophosphates having isomeric alkyl groups respectively of straight primary and branched primary, was observed when the solvent system of chlorinated paraffin—*isopropyl* alcohol was used. It is effective especially for the analysis of mixtures of zinc dialkyldithiophosphates to use these solvent systems together with the solvent system of cresyldiphenyl phosphate—90/10 isooctane-*n*-cetane.

It was found that zinc diaryldithiophosphates can be distinguished from zinc dialkyldithiophosphates by the solvent system of chlorinated paraffin—*isopropyl* alcohol and identified by the solvent system of cresyldiphenyl phosphate—90/10 isooctane-*n*-cetane or liquid paraffin—*isopropyl* alcohol.

Zinc dithiophosphates in commercial antioxidants and EP hydraulic oils could be identified by the above mentioned solvent systems.

1 Introduction

Zinc dithiophosphates have been used widely in lubricating oils as antioxidants and antiwear/load carrying additives. Since the activity of zinc dithiophosphates, both as antioxidants and antiwear/load carrying additives, depends on the chemical structure of the substituents of zinc dithiophosphates^{1)~5)}, the structural analysis of the substituents is very important in their application.

The infrared spectra of zinc dialkyldithiophosphates were published by Rockett⁶⁾, Zimina et al.⁷⁾, Gallopoulos⁸⁾ and Shimazu et al.⁹⁾. Legate et al.¹⁰⁾ and Perry¹¹⁾ described the structural analysis of the substituents of zinc dialkyldithiophosphates by pyrolytic-gas chromatography. Geldern¹²⁾, Murata et al.¹³⁾ and Hiroki et al.¹⁴⁾ also described the structural analysis of the substituents of zinc dialkyldithiophosphates

by thin-layer chromatography. The determination of the decomposition products of zinc dialkyldithiophosphates in gear oils was studied by Goodwin et al.¹⁵⁾ by means of paper chromatography using water as the stationary phase. This method is not suitable for the separation and identification of zinc dialkyldithiophosphates since they are generally water insoluble. Then the author described the structural analysis of the substituents of zinc dialkyldithiophosphates by paper chromatography using organic solvents as the stationary phase¹⁶⁾.

The separations with paper chromatography are due to partition between two solvents. As for thin-layer chromatography, the separations proceed by adsorption. Generally partition chromatography has an advantage that good separations of homologues or isomers are obtained more easily than by adsorption chromatography. In the case of samples containing zinc dialkyldithiophosphates of two kinds or more, or having different alkyl groups in a molecule, it is difficult to identify the components by infra-

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red spectroscopy⁹) and also difficult to confirm the molecular structure of the components by pyrolytic-gas chromatography and thin-layer chromatography as these two methods are accompanied by the decomposition of zinc dialkyldithiophosphates^{10)~14)}. The molecular structure of the components can be confirmed by partition paper chromatography¹⁵⁾ as this method is carried out without the decomposition of zinc dialkyldithiophosphates. It has previously been reported¹⁶⁾ that the solvent system of aniline as the stationary phase and *n*-heptane as the mobile phase is suitable for partition paper chromatography of zinc dialkyldithiophosphates. With this solvent system, some attention should be paid to the developing operation as aniline is slightly volatile¹⁶⁾.

The present work was undertaken to investigate new solvent systems for partition paper chromatography of zinc dialkyldithiophosphates and also to investigate suitable solvent systems for partition paper chromatography of zinc diaryldithiophosphates.

2 Experimental

2.1 Materials

The zinc dithiophosphates used as standard samples are listed in **Table 1**. These were prepared essentially in the manner described by Negoro and Akamatsu¹⁷⁾. Each zinc dithiophosphate will be hereafter represented by the name of its substituent.

Typical commercial antioxidants and EP hydraulic oils containing zinc dithiophosphates were also used. They are listed in **Table 2**.

2.2 Partition Paper Chromatography

2.2.1 Solvent Systems

The solvent systems examined are shown in **Table 3**. Non-volatile solvents were applied as the stationary phase.

Properties of the stationary solvents used are as follows.

Cresyldiphenyl phosphate (hereafter abbreviated as CDP): P 8.9%, d_4^{20} 1.2096, n_D^{25} 1.5601, acid value 0.05.

Polyoxyethylene octylphenyl ether (E. O. 10 mol) (hereafter abbreviated as POE): cloud point 74°C, solidifying point 6°C, hydroxyl value 86, water 0.29%.

Liquid paraffin (hereafter abbreviated as LP): viscosity 79.26 cSt @ 37.8°C, 7.789 cSt @ 98.9°C, VI 58.5, d_4^{20} 0.8885, n_D^{25} 1.4840, M_{403} , S 0.01%, aniline point 105.2°C, ring analysis (*n-d-M*) C_A 0.0%, C_N 47.4%, C_P 52.6%, R_A 0.00, R_N 2.95.

Chlorinated paraffin (hereafter abbreviated

Table 1 Properties of Zinc Dithiophosphates (ZDTP) Used for the Experiments

ZDTP (Substituent R*)	m.p. (°C)	% Zinc	
		Found	Calcd.
<i>n</i> -Butyl	Liquid	12.1	11.9
<i>n</i> -Hexyl	Liquid	10.2	9.9
<i>n</i> -Octyl	Liquid	8.1	8.5
<i>n</i> -Dodecyl	Liquid	6.3	6.6
Isobutyl	106~107	11.9	11.9
Isoamyl	Liquid	10.9	10.8
2-Ethylhexyl	Liquid	8.4	8.5
Isopropyl	140~141	13.5	13.3
<i>sec</i> -Butyl	55~57	12.1	11.9
1,3-Dimethylbutyl	Liquid	10.2	9.9
<i>sec</i> -Octyl	Liquid	8.2	8.5
<i>p-tert</i> -Butylphenyl	203~204	7.7	7.7
<i>p-tert</i> -Octylphenyl	Liquid	6.1	6.1
<i>p-sec</i> -Nonylphenyl	Liquid	6.0	5.8

Table 2 Properties of Commercial Antioxidants and EP Hydraulic Oils Used for the Experiments

Commercial Antioxidant or Oil		% Zinc	P-O-C Absorption Band (cm ⁻¹)
Antioxidant	A	7.8	995
	B	8.8	1,000
	C	8.9	1,005
	D	9.0	982
	E	9.2	980
	F	8.5	978
	G	8.7	977
	H	3.3	920
	I	3.1	920
EP Hydraulic Oil	A	0.09	1,000
	B	0.07	975

as CP): Cl 40.8%, viscosity 26.15 cSt @ 98.9°C, d_4^{25} 1.1565, n_D^{25} 1.5020, acid value 0.02.

2.2.2 Preparation of Impregnated Paper

Strips of Toyo Roshi No.50 filter paper (25 cm × 12 cm) were dipped in a solution of the stationary solvent in volatile diluent and then taken out. The volatile diluent was allowed to evaporate at room temperature.

The volume ratio of volatile diluent to the stationary solvent was four to one in the case of CDP and six to one in the case of the others. Acetone was used as the volatile diluent of CDP and POE, and petroleum ether as that of LP and CP.

2.2.3 Developing Procedure

The base line was drawn at a distance of 3 cm from one edge of the paper when isopropyl alcohol was used as the mobile solvent and 6 cm when the others was used. The solutions of zinc dithiophosphates in benzene or ethyl alcohol were applied at 1 cm intervals on the base line. The diameter of each spot was adjusted to about 0.5 cm. The chromatograms were allowed to

develop until the solvent front travelled about 10 cm from the base line at 10°C or 20°C by the ascending technique. The zinc dithiophosphates to be compared were developed always on a single paper.

Unless otherwise stated, standard samples were used at a concentration of 0.2 g/100 ml except *n*-dodecyl, *p*-*tert*-butylphenyl, *p*-*tert*-octylphenyl and *p*-*sec*-nonylphenyl, which were used at a concentration of 0.5 g/100 ml. Antioxidant A, B and F were used at a concentration of 0.3 g/100 ml, Antioxidant C, D, E and G, 0.5 g/100 ml and Antioxidant H and I, 1.0 g/100 ml. In the case of EP hydraulic oils, their benzene eluates on silica gel adsorption chromatography were used being adjusted to a concentration of 3 g/100 ml.

2.2.4 Detection

After development, the chromatograms were allowed to dry in air and then sprayed with 0.01% solution of dithizone in carbon tetrachloride. All of the zinc dithiophosphates were revealed as purplish red spots.

2.3 Adsorption Chromatography

Wako Gel Q-12, 28 to 200 mesh silica gel from Wako Pure Chemical Industries, Ltd., activated at 150°C for 3 hrs, was used as the adsorbent.

The glass column of diameter about 20 mm was partially filled with *n*-hexane. Into the column, 100 g of the silica gel suspended in *n*-hexane was poured and settled. Then the excess *n*-hexane was drained. A solution of 0.5 g of zinc dithiophosphate or 10 g of EP hydraulic oil dissolved in 20 ml of *n*-hexane was poured into the column and the collection of the effluent was started. The column was eluted first with

n-hexane until 250 ml of the effluent were collected and then eluted successively with 50/50 benzene-*n*-hexane, benzene, 30/70 ethyl alcohol-benzene and methyl alcohol until 100 ml, 150 ml, 300 ml, and 100 ml of the effluent were collected respectively.

The eluates were divided into four groups by the composition of the eluent; hexane eluate from 0 to 300 ml fraction of the effluent, benzene eluate from 300 to 600 ml, ethanol eluate from 600 to 800 ml and methanol eluate from 800 to 900 ml.

3 Results and Discussion

3.1 R_f Values of Zinc Dithiophosphates

R_f values of zinc dithiophosphates are shown in Table 3. Fig. 1 and 2 show the relation between the carbon number in the substituent of zinc dithiophosphates and their R_f values.

In all of the solvent systems using CDP as the

Fig. 1 Effect of the Carbon Number in Substituent of Zinc Dithiophosphates on the R_f Values with Solvent System C

Table 3 R_f Values of Zinc Dithiophosphates

Solvent System	A		B		C	D	E	F
Stationary Phase	CDP				POE		LP	CP
Mobile Phase	<i>n</i> -Heptane	Isooctane		90/10 Isooctane· <i>n</i> -Cetane	<i>n</i> -Heptane	Isopropyl Alcohol		
Temp. °C	20		10	20				
<i>n</i> -Butyl	0.30	0.24	0.19	0.22	0.08	0.94	0.80	
<i>n</i> -Hexyl	0.61	0.52	0.45	0.48	0.24	0.89	0.72	
<i>n</i> -Octyl	0.83	0.77	0.72	0.67	0.43	0.76	0.67	
<i>n</i> -Dodecyl	0.95	0.94	0.93	0.90	0.85	0.39	0.52	
Isobutyl	0.42	0.35	0.28	0.31	0.12	0.95	0.85	
Isoamyl	0.52	0.45	0.38	0.40	0.18	0.94	0.82	
2-Ethylhexyl	0.92	0.89	0.86	0.77	0.67	0.79	0.77	
Isopropyl	0.33	0.27	0.22	0.24	0.12	0.96	0.83	
<i>sec</i> -Butyl	0.56	0.48	0.41	0.42	0.33	0.93	0.80	
1,3-Dimethylbutyl	0.90	0.87	0.82	0.73	0.77	0.87	0.78	
<i>sec</i> -Octyl	0.93	0.91	0.89	0.82	0.89	0.70	0.69	
<i>p</i> - <i>tert</i> -Butylphenyl	0.07	0.03	0.02	0.03	0.01	0.89	0.48	
<i>p</i> - <i>tert</i> -Octylphenyl	0.38	0.26	0.20	0.24	0.05	0.71	0.46	
<i>p</i> - <i>sec</i> -Nonylphenyl	0.57	0.41	0.33	0.38	0.09	0.60	0.45	

Fig. 2 Effect of the Carbon Number in Substituent of Zinc Dithiophosphates on the R_f Values with Solvent System E

stationary phase, the R_f values of zinc dialkyldithiophosphates increase with the number of carbon atoms in the alkyl group. Among zinc dialkyldithiophosphates having isomeric alkyl groups respectively of straight primary, branched primary and secondary, the R_f values increase in this order. These tendencies are similar to those observed with the solvent system of aniline-*n*-heptane¹⁶⁾.

The R_f values of zinc dialkyldithiophosphates having long chain alkyl groups with the solvent system of CDP-*n*-heptane are too high to be used for their identification. Their R_f values were reduced a little by using isooctane instead of *n*-heptane as the mobile phase and lower R_f values could be obtained by reducing developing temperature from 20°C to 10°C or by adding *n*-cetane to isooctane as the mobile phase.

When the solvent system of CDP-90/10 isooctane-*n*-cetane (solvent system C) was used, the range of R_f values of the zinc dialkyldithiophosphates listed in **Table 1** was from 0.22 to 0.90. Of a variety of solvent systems examined, this solvent system was most suitable for the separation and identification of zinc dialkyldithiophosphates.

The R_f values of zinc diaryldithiophosphates with solvent system C, increase with the number of carbon atoms in the substituent similarly to zinc dialkyldithiophosphates. Solvent System C is suitable for the identification of zinc diaryldithiophosphates as well as zinc dialkyldithiophosphates. The R_f values of zinc diaryldithiophosphates are very low compared with those of zinc dialkyldithiophosphates. This tendency may be due to the selective solvent power of CDP for aromatic compounds.

The solvent system of POE-*n*-heptane (solvent system D) shows similar tendencies on the whole to the case of solvent system C toward the R_f values of zinc dialkyldithiophos-

phates, but has a special feature that there is a large difference in R_f values between zinc dialkyldithiophosphates having isomeric alkyl groups respectively of primary and secondary. This feature appears distinctly in the ratio of R_f value with solvent system D to that with solvent system C. The ratio was calculated as 0.79 and 1.05 for *sec*-butyl and 1,3-dimethylbutyl respectively, and as 0.36, 0.39 and 0.50 for *n*-butyl, isobutyl and *n*-hexyl respectively. Thus, the ratio is affected by the carbon number in the alkyl group as well as the type of the alkyl group. As the carbon number in the alkyl group is reflected in the R_f values with solvent system C, the ratio of R_f value with solvent system D to that with solvent system C is plotted against the R_f values with solvent system C in **Fig. 3**. From the figure, the type of alkyl group (primary or secondary) can be estimated.

The R_f values of zinc diaryldithiophosphates with solvent system D are extremely low.

When the solvent system of LP-isopropyl alcohol (solvent system E) is used, the R_f values of zinc dialkyldithiophosphates decrease with the number of carbon atoms in the alkyl group as previously reported¹⁶⁾. Solvent system E is not suitable for the separation and identification of zinc dialkyldithiophosphates having alkyl groups of short chain of six and less carbon atoms because the R_f values of these zinc dialkyldithiophosphates are close each other. This solvent system is applicable to zinc dialkyldithiophosphates having alkyl groups of long chain of eight and more carbon atoms.

The R_f values of zinc diaryldithiophosphates with solvent system E decrease with the number of carbon atoms in the substituent similarly to

Fig. 3 Relation between the Structure of Substituent of Zinc Dithiophosphates and the Ratio of the R_f Values with Solvent System D to Those with Solvent System C

- Solvent System: F
- 1, 9 *sec*-Octyl
  - 2 Zinc dibutyldithiocarbamate
  - 3 Zinc diamyldithiocarbamate
  - 4 *p*-*tert*-Butylphenyl
  - 5 *p*-*tert*-Octylphenyl
  - 6 Isobutyl
  - 7 2-Ethylhexyl
  - 8 *sec*-Butyl

Fig. 4 Paper Chromatogram of Zinc Containing Antioxidants

zinc dialkyldithiophosphates. This solvent system is suitable for the identification of zinc diaryldithiophosphates.

The solvent system of CP—isopropyl alcohol (solvent system F) is a unique one in that the R_f values are not affected so much by the carbon number in the substituent of compounds, but are greatly affected by the type of compounds. The author previously reported that zinc dialkyldithiocarbamates can be distinguished from zinc dialkyldithiophosphates by using the characteristics of solvent system F¹⁶. Similarly,

Fig. 5 Relation between the Structure of Substituent of Zinc Dithiophosphates and the R_f Values with Solvent System F

the R_f values of zinc diaryldithiophosphates with solvent system F are not affected so much by the carbon number of the substituent. Thus, zinc diaryldithiophosphates can be distinguished from zinc dialkyldithiophosphates by solvent system F as shown in Fig. 4. Solvent system F has another special feature in that there is a large difference in R_f values between zinc dialkyldithiophosphates having isomeric alkyl groups respectively of straight primary and branched primary. The R_f values of zinc dialkyldithiophosphates with solvent system F are affected to some extent by the carbon number in the alkyl group. As the carbon number in the alkyl group is reflected in the R_f values with solvent system C, the R_f value with solvent system F is plotted against the R_f values with solvent system C in Fig. 5. The type of alkyl group (straight primary or branched primary) can be estimated from the figure.

3.2 Effect of Various Factors on the R_f Values of Zinc Dithiophosphates

The effect of the concentration of zinc dithiophosphate solution applied to the impregnated paper is shown in Table 4 and the R_f values of mixtures of zinc dithiophosphates are shown in Table 5. The effect of coexisting lubricating oil is shown in Table 6. Solvent refined 150 neutral oil was used as the lubricating oil.

The data of Table 4 indicate that the R_f values are not affected by the concentration of zinc dithiophosphate solution when solvent system C is used. The R_f values with solvent systems E and F become a little lower at higher concentration, but those with solvent system D become lower at lower concentration. So higher concentration over 0.1 g/100 ml must be used in the case of solvent system D.

The data of Table 5 indicate that the R_f values are affected a little by coexisting other zinc dithiophosphates. This tendency is similar to that observed with the solvent system of aniline—*n*-heptane¹⁶. In the case of mixtures of zinc

Table 4 Effect of Concentration of Zinc Dithiophosphate Solution on the R_f Values

	Concn. of ZDTP (g/100 ml)	Solvent System			
		C	D	E	F
Isobutyl	0.05	0.31	0.11	0.95	0.85
	0.1	0.31	0.12	0.95	0.85
	0.2	0.31	0.12	0.95	0.85
	0.5	0.31	0.13	0.95	0.85
	1.0	0.31	0.13	0.94	0.84
<i>sec</i> -Butyl	0.05	0.42	0.31	0.93	0.80
	0.1	0.42	0.32	0.93	0.80
	0.2	0.42	0.33	0.93	0.80
	0.5	0.42	0.33	0.93	0.79
	1.0	0.42	0.33	0.92	0.78

Table 5 R_f Values of Mixtures of Zinc Dithiophosphates

Solvent System	Number of ZDTP	<i>n</i> -Octyl	Isoamyl	2-Ethyl-hexyl	Isopropyl	<i>sec</i> -Butyl	1,3-Dimethyl-butyl	<i>p</i> - <i>tert</i> -Butyl-phenyl
C	1	0.67	0.40	0.77	0.24	0.42	0.73	0.03
	2	0.67	—	—	0.25	—	—	—
		—	0.40	—	0.26	—	—	—
		—	—	0.77	0.25	—	—	—
		—	—	—	0.26	0.42	—	—
		—	—	—	0.26	—	0.73	—
		—	0.42	0.76	—	—	—	—
		—	—	0.76	—	0.44	—	—
		—	0.38	—	—	—	—	0.05
	3	—	0.41	0.76	0.27	—	—	—
F	1	0.67	0.82	0.77	0.83	0.80	0.78	0.48
	2	0.70	—	—	0.82	—	—	—
		—	0.82	—	—	—	—	—
		—	—	0.80	—	—	—	—
		—	—	—	0.81	—	—	—
		—	—	—	0.81	—	—	—
		—	0.80	—	—	—	—	—
		—	—	0.78	—	—	—	—
		—	0.82	—	—	—	—	0.49
	3	—	—	0.80	—	—	—	—
		—	—	—	0.80	—	—	—

dithiophosphates of two kinds, the R_f values of upper spot become lower by 0.01 and those of lower spot become higher by 0.02 on the whole. In the case of mixtures of zinc dithiophosphates of three kinds, the R_f values of upper spot become lower by 0.01 and those of middle and lower spot become higher by 0.01, and 0.03 respectively on the whole, therefore, it is necessary to make a correction for the R_f values of components of the mixtures. When the R_f values of zinc dithiophosphates comprising the mixture are close each other, a single spot is obtained and the R_f value of the spot is nearly the average of those of the components.

The data of **Table 6** indicate that the R_f values with solvent systems C and D are little affected by the coexisting lubricating oil but

those with solvent systems E and F become lower under coexistence of great quantities of lubricating oil. From the results, it was found that commercial additives can be applied to partition paper chromatography without pretreatment and lubricating oils must be treated beforehand in order to concentrate zinc dithiophosphates.

3.3 Analysis of Zinc Dithiophosphates in Commercial Antioxidants and EP Hydraulic Oils

Zinc dithiophosphates in EP hydraulic oils must be concentrated beforehand to apply to partition paper chromatography as previously stated. Fujita¹⁸⁾ described that adsorption chromatography is useful for concentrating various additives in lubricating oils and Jenkins and Humphreys¹⁹⁾ reported that zinc dialkyl-dithiophosphates are eluted with diethyl ether on silica gel adsorption chromatography. In this paper, the method for concentrating zinc dithiophosphates in lubricating oil by silica gel adsorption chromatography was investigated, using the eluting agents previously used for concentrating metal dialkyl-dithiocarbamates²⁰⁾ and, trialkyl and triarylphosphates²¹⁾ in lubricating oils. The results of silica gel adsorption chromatography of isobutyl and *p*-*tert*-butylphenyl are shown in **Table 7**. From the data, it was found that zinc dithiophosphates are eluted

Table 6 Effect of Coexisting Lubricating Oil on the R_f Values of Zinc Dithiophosphates

	Ratio of Oil to ZDTP	Solvent System			
		C	D	E	F
<i>n</i> -Octyl	0	0.67	0.43	0.76	0.67
	10	0.67	0.43	0.76	0.67
	25	0.67	0.43	0.76	0.66
	50	0.68	0.43	0.75	0.63
	100	0.68	0.43	0.74	0.54
<i>sec</i> -Butyl	0	0.42	0.33	0.93	0.80
	10	0.42	0.33	0.93	0.80
	25	0.42	0.33	0.93	0.80
	50	0.43	0.33	0.93	0.79
	100	0.43	0.33	0.91	0.74

Table 7 Silica Gel Adsorption Chromatography of Zinc Dithiophosphates

Fraction	Yield (%)	
	Isobutyl	<i>p</i> - <i>tert</i> -Butylphenyl
Hexane Eluate	0.0	0.0
Benzene Eluate	98.4	97.2
Ethanol Eluate	0.4	1.2
Methanol Eluate	0.0	0.0
Recovery	98.8	98.4

with benzene. As a greater part of lubricating oils is eluted with *n*-hexane, the zinc dithiophosphates in lubricating oils can be concentrated by this method.

The yield of each benzene eluate obtained from EP hydraulic oil A and B was 19.6% and 14.3%, respectively. These benzene eluates and commercial antioxidants were chromatographed on the impregnated paper. The results are shown in Fig. 3 and 5. In case two or three spots were obtained, measured R_f values were corrected according to the results of 3.2.

An example of the paper chromatograms is shown in Fig. 6.

Solvent System: C			
1, 8	Isopropyl	5	<i>n</i> -Dodecyl
2, 9	2-Ethylhexyl	6	Antioxidant D
3	<i>n</i> -Hexyl	7	Antioxidant E
4	<i>n</i> -Octyl		

Fig. 6 Paper Chromatogram of Commercial Antioxidants

The chemical structure of the substituents of zinc dithiophosphates in commercial antioxidants and EP hydraulic oils listed in Table 2 was estimated as follows.

Antioxidant A : isooctyl.

Antioxidant B and EP hydraulic oil A : mixed alkyl of isobutyl and isoamyl.

Antioxidant C : Three spots were obtained

with solvent system C. The substituents of the upper, lower and middle spots are 2-ethylhexyl, mixed alkyl of isobutyl and isoamyl, and mixed alkyl of isobutyl, isoamyl and 2-ethylhexyl respectively.

Antioxidant D : Two spots were obtained with solvent system C. The substituents of the upper and lower spots are straight primary alkyl of about seven carbon atoms and isopropyl respectively. In the infrared spectra of this antioxidant, P-O-C absorption by secondary alkyl appears strongly.

Antioxidant E : Three spots were obtained with solvent system C. The substituents of the upper, lower and middle spots are 2-ethylhexyl, isopropyl, and mixed alkyl of 2-ethylhexyl and isopropyl respectively. In the infrared spectra of this antioxidant, P-O-C absorption by secondary alkyl appears strongly.

Antioxidant F and EP hydraulic oil B : 1,3-dimethylbutyl.

Antioxidant G : Three spots were obtained with solvent system C. The substituents of the upper, lower and middle spots are 1,3-dimethylbutyl, isopropyl, and mixed alkyl of 1,3-dimethylbutyl and isopropyl respectively.

Antioxidant H : Alkylphenyl of lower carbon number than *p*-*tert*-octylphenyl.

Antioxidant I : *p*-*sec*-nonylphenyl.

4 Conclusion

(1) The solvent system of cresyldiphenyl phosphate — 90/10 isooctane-*n*-cetane is most suitable for the separation and identification of zinc dialkyldithiophosphates. The solvent system of liquid paraffin—*isopropyl alcohol* is applicable to zinc dialkyldithiophosphates having long chain alkyl groups.

When it is necessary to distinguish the type of the alkyl group, the solvent systems of polyoxyethylene octylphenyl ether (E. O. 10 mol) —*n*-heptane and chlorinated paraffin—*isopropyl alcohol* are useful.

(2) Zinc diaryldithiophosphates can be distinguished from zinc dialkyldithiophosphates by the solvent system of chlorinated paraffin—*isopropyl alcohol* and identified by the solvent system of cresyldiphenyl phosphate—90/10 isooctane-*n*-cetane or liquid paraffin—*isopropyl alcohol*.

(3) Zinc dithiophosphates in lubricating oils can be analysed by partition paper chromatography after concentrating them by silica gel adsorption chromatography.

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