

금속 디알킬디티오인산염이 윤활유에 미치는 영향

文卓珍 · 權五寬*

고려대학교 공과대학 재료공학과

*한국과학기술연구소

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Effects of Metallic Dialkyldithiophosphates on Lubricating Oil

Tak Jin Moon and Oh Kwan Kwon*

Materials Science Department, Korea University, Seoul 132, Korea

*Korea Institute of Science and Technology, Seoul 131, Korea

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요 약. 금속 디알킬디티오인산염은 윤활유의 산화방지 및 내마모 첨가제로 널리 사용되고 있다. 특히 아연 DDTP가 윤활유 첨가제로서 가장 많이 사용되고 있다. 1차 및 2차 알킬기를 가진 아연, 납, 주석 및 코발트 디알킬디티오인산염을 각각 합성하였다. 합성된 각각의 금속 디알킬디티오인산염에 대하여 윤활유에서의 산화안정성, 열안정성, 금속부식성 및 내마모성을 실험검토하였다. 실험결과, 코발트 DDTP가 크롬합금강에 미치는 내마모성은 다른 화합물에 비하여 극히 우수하였으며 또한 코발트 DDTP는 일정온도 이상에서는 다갈색으로부터 청색으로 변하며 온도의 환원과 더불어 색상이 환원되는 특이한 색상의 온도 감도변화 성질이 있는 것을 알았다. 또한 모든 금속 디알킬디티오인산염은 일정 유효산 농도에 도달되어야만 윤활유의 산화 방지작용을 개시한다는 결과를 얻었다.

ABSTRACT. Metallic dialkyldithiophosphates are widely used in lubricating oils as antioxidant and antiwear agents. Zinc DDTP are used most frequently in lubricating oil. Zinc, lead, tin and cobalt DDTP were prepared with primary and secondary alkyl groups. The effects of oxidation, thermal stability, metal corrosion and antiwear of each metallic DDTP prepared were studied. Based on the results, cobalt DDTP has a significant effect of antiwear on chrome alloy steel comparing with the other metallic DDTP. Also cobalt DDTP has a characteristic property of thermal sensitivity in its color, which was shown by the color change from brown to blue over a certain temperature. Another phenomenon obtained was that all metallic DDTP initiates the effect of antioxidation at the time of reaching to a certain effective acid concentration in lubricating oil.

INTRODUCTION

Oxidation of mineral lubricating oil results in the formation of oil soluble and insoluble compounds. These materials give an adverse effect on the performance of lubricating oil. The use of antioxidant offers means of achieving desired oxidation stability. Among the most widely used additives, metal dithiophosphates (MDP) are the best known *anti*-oxidants, because they prevent the corrosive attack of oxidation products. The detailed mechanism of their action has been demonstrated in a number of studies¹⁻⁵. The effect of zinc dithiophosphate (ZDP) on lubricating oil has been investigated by Gallopoulos and Murphy⁶ and the performance of ZDP has been explained in terms of different alcohols by Larson⁷. The oxidation stability of base oil in terms of ZDP has been also demonstrated by Elliott *et al*⁸. and Denis *et al*⁹. There are other papers concerning the amounts of ZDP used and MDP of few metals^{6,10}.

However, the overall view of the effect of MDP on lubricating oil is still one of the targets to be studied further, and the work to be described in this paper concerns to the preparation of MDP using several alcohols for alkyl group and zinc, lead, tin, and cobalt as metal sources. The effect of MDP on lubricating oil is studied in terms of oxidation stability, metal corrosion stability, and antiwear property of the lubricating oil.

EXPERIMENTAL

Various dialkyldithiophosphoric acids(DDPA) were prepared by reacting 4 moles of isoamyl alcohol, *n*-hexyl alcohol, *n*-octyl alcohol, and di-*t*-amyl phenol with 1 mole of P₂S₅, respectively, at 90, 120°C for 40~90 minutes^{11,12}. The removal of trace H₂S formed in DDPA during the synthesis was attempted by using Al-Ca

mixture adsorbent. DDPA, then, were treated with KOH to make potassium salts and these salts were reacted with ZnCl₂, Pb(NO₃)₂, SnCl₂, and CoCl₂·6H₂O to make various metallic dialkyldithiophosphates (MDDP), respectively. MDDP, thus prepared, were purified by hexane extraction, and the purity of MDDP was examined by IR spectra of the compounds. Twelve samples of naphthenic oil were prepared by adding MDDP as shown in *Table 1* to see the effect of MDDP.

Strips of SAE 120 steel and copper were put in 300 ml of each sample, and the Indiana oxidation test was (JIS K 2514) performed at

Table 1. Twelve samples used in the experiment.

Sample No.	Base oil and additive used
0	Base Oil* + No additive
1	Base + 1 % Zn-ditert amylphenyl dithiophosphate
2	Base + 1 % Sn-dihexyl amylphenyl dithiophosphate
3	Base + 1 % Zn-dihexyl amylphenyl dithiophosphate
4	Base + 1 % Pb-dihexyl amylphenyl dithiophosphate
5	Base + 1 % Zn-dioctyl amylphenyl dithiophosphate
6	Base + 1 % Sn-dioctyl amylphenyl dithiophosphate
7	Base + 1 % Pb-dioctyl amylphenyl dithiophosphate
8	Base + 1 % Pb-diisoamyl amylphenyl dithiophosphate
9	Base + 1 % Sn-diisoamyl amylphenyl dithiophosphate
10	Base + 1 % Zn-diisoamyl amylphenyl dithiophosphate
11	Base + 1 % Co-diisoamyl amylphenyl dithiophosphate

* Viscosity=22.46cst @ 100°F, viscosity index = 39, total acid number=0.00 mg KOH/g sample, color (union)=1½(-), flash point=343 °F.

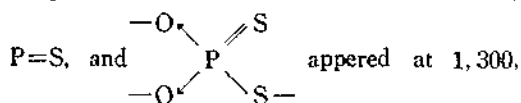
125°C by passing dry air at the rate of 10 l/hr for total of 96 hours. 50 ml of sample oil were taken after 24 hours of test, 50 ml of each fresh sample oil were refilled, and such procedure was made four times during the 96 hours of test, to see the oxidation stability, metal corrosion stability, and antiwear property of the base oil.

The degree of oxidation was determined by measuring changes in the viscosity (JIS K 2807), viscosity index (JIS K 2284) and acid number (JIS K 2502). Metal corrosion was checked by inspecting the metal strips, weight changes of the strips, and changes in oil color or sludge formation. Finally, the antiwear property was measured by a Shell fourball wear tester at 50 kg load and 1,200 rpm speed.

RESULTS AND DISCUSSION

In the synthesis of MDDP, the complete removal of trace H₂S gas is one of the awkward processes to be fulfilled. Blowing nitrogen gas into DDPA can not remove H₂S gas completely, and therefore Al-Ca mixture adsorbent was used in this experiment. From the IR spectra of thus synthesized MDDP and by a wet analytical method of tracing H₂S, no impurities such as trace H₂S were found and the physical states of

MDDP were as shown in Table 2. (Note: Strong IR absorption band was found at 2,900~3,000 cm⁻¹ due to the stretching of CH₃- and -CH₂- in the alkyl group. Deformation band of symmetrical and asymmetrical C-CH₃ was found at 1,380~1,370 and 1,450±20 cm⁻¹, respectively. Absorption due to O-PO-C, -P-O-C (aliphatic carbon of more than four atoms),



appeared at 1,300, 1,000~1,010, 665 and 750~880 cm⁻¹, respectively. Absorption bands at 2,500~2,700 cm⁻¹ due to S-H of a free acid and 500~400 cm⁻¹ due to -S-S-, which might forms if the DDPA is dimerized above 80°C in air, were not observed from the IR charts we obtained.)

The degree of oxidation of oil was evaluated by measuring the changes in viscosity and viscosity index of the oil before and after the oxidation test, and the results are shown in Table 3. The original base oil of no additives, sample #0, showed an increase in viscosity and decrease in viscosity index from 39 to 0 as oxidation proceeded. However, all other samples showed an increased ratio of 1 in viscosity, except sample #6, and almost no change in

Table 2. The Physical states of MDDP.

MDDP	Physical state at room temp.	Color	Yield, wt. %
Zn-dihexyl DP	Viscous liquid	Yellow-white	95.3
Pb-dihexyl DP	Viscous liquid	Pale yellow	95.1
Sn-dihexyl DP	Viscous liquid	Red-yellow	95.8
Zn-diisoamyl DP	Viscous liquid	Pale yellow	95.1
Pb-dioctyl DP	Trans. crystal	Pale brown	95.7
Sn-dioctyl DP	Viscous liquid	Red-yellow	95.7
Zn-dioctyl DP	Viscous liquid	Yellow-white	95.7
Pb-dioctyl DP	Trans. crystal	Yellow-white	95.2
Sn-dioctyl DP	Viscous liquid	Yellow	95.7
Co-diisoamyl DP	Crystal	Dark brown	95.7
Zn-di <i>i-t</i> -amylphenyl DP	Viscous liquid	Yellow	93.4

Table 3. Viscosity and VI changes after the oxidation test*.

Samples	Temp. (°F)	Viscosity, cst					Ratio in increasing viscosity	Viscosity index		Sludge formation (g/l)
		Oxid. hr.						Before Oxid.	After 96hr.	
		0	24	48	72	96				
# 0	100	22.46	24.75	28.05	30.87	34.46	1.534	39	below 0	5.2
	210	3.81	3.99	4.16	4.28	4.52	1.186			
# 1	100	21.05	22.62	23.02	23.02	23.14	1.090	28	86	None
	210	3.61	3.72	4.01	4.07	4.18	1.150			
# 2	100	21.87	22.16	22.38	22.67	23.12	1.057	53	60	12.0
	210	3.83	3.83	3.83	3.89	4.00	1.044			
# 3	100	19.76	19.23	18.76	18.92	19.13	0.968	45	below 0	2.0
	210	3.57	3.47	3.36	3.26	3.26	0.913			
# 4	100	21.98	22.15	22.33	22.21	22.09	1.005	61	70	None
	210	3.89	3.89	4.01	3.95	3.95	1.015			
# 5	100	22.63	22.63	22.66	22.94	23.00	1.016	34	38	None
	210	3.80	3.81	3.87	3.86	3.86	1.015			
# 6	100	21.76	25.19	29.88	34.57	40.42	1.857	47	130	2.5
	210	3.78	4.29	5.32	5.95	6.64	1.756			
# 7	100	18.71	18.81	18.87	18.81	18.81	1.005	25	23	None
	210	3.71	3.25	3.31	3.36	3.36	1.000			
# 8	100	18.39	18.39	18.49	18.49	18.60	1.011	11	6	None
	210	3.26	3.26	3.26	3.26	3.26	1.000			
# 9	100	21.75	21.86	22.27	22.33	22.50	1.034	74	88	8.4
	210	3.95	3.95	4.07	4.07	4.13	1.045			
# 10	100	22.42	22.46	22.51	22.88	22.93	1.023	40	43	None
	210	3.82	3.83	3.86	3.87	3.88	1.018			
# 11	100	21.82	22.09	22.38	22.44	22.44	1.028	73	71	None
	210	3.95	3.89	3.81	3.95	4.00	1.012			

* Oxidation temp. $125 \pm 0.5^\circ\text{C}$, Air supply 10 l/hr.

viscosity index, except sample #3. It is interesting to note that samples #2, #6, and #9 (tin salts) and sample #11 (cobalt salt) showed not only a good oxidation stability but also a good viscosity index and oiliness improvement. Tin salts, compared to cobalt salt, formed larger amounts of sludge and showed larger change in viscosity index. This result is expected from the oxidation of tin, $\text{Sn}^{2+} \rightarrow \text{Sn}^{4+}$, giving larger molecular weight product, while the oxidation of cobalt, $\text{Co}^{2+} \rightarrow \text{Co}^{3+}$, above 150°C is reduced to CO^{2+} as temperature reduced, since Co^{2+} is much more stable than Co^{3+} . Samples #1, #3, #5, and #10 (zinc salts) and samples #4, #7,

and #9 (lead salts) had no sludge formation as shown in the table. Reviewing the table, the effect of alkyl group on the sludge formation was found to be in the order of octyl < isoamyl < hexyl (no special trend was observed), and branched chain showed less sludge formation than straight chain.

The changes in acid number for all the samples were plotted against the oxidation time as shown in Figs. 1, 2 and 3. The increase in acid number for samples #1 to #11 was much less than that for sample #0, the base oil with no additive. The antioxidation effect of alkyl group was found to be in the order of octyl < isoamyl

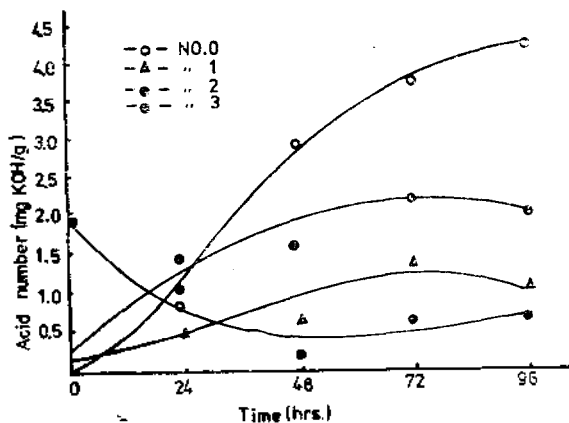


Fig. 1. Change in acid number for samples #0, #1, #2, and #3.

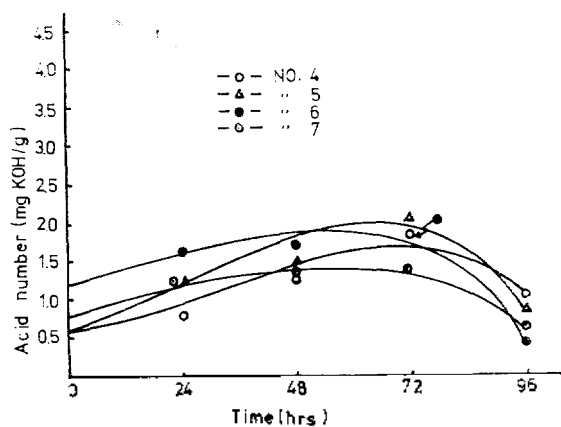


Fig. 2. Change in acid number for samples #4, #5, #6, and #7.

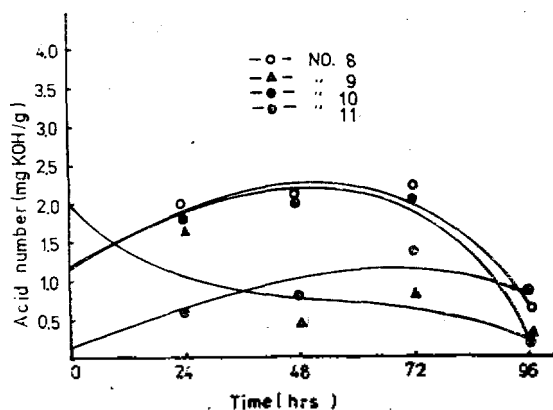


Fig. 3. Change in acid number for samples #8, #9, #10, and #11.

hexyl, and the order was coincided with the sludge formation order as described previously. It is interesting to note that the acidity of samples of zinc, lead, and cobalt salts reached to maximum of around 2 and then decreased as the oxidation time increased. For samples of tin salt such maximum in acidity was not observed, but the acidity decreased from the acid number of around 2 also. Therefore, the effective anti-oxidation started from the point where the effective acid concentration reached to around 2 mg KOH per gram of sample.

Metal corrosion was checked by measuring the weight change in steel and copper strips after the oxidation test of samples, and the results are shown in Table 4, as well as the color change of samples. No steel corrosion for all samples except samples #0 and #9 was observed, but a little copper corrosion was observed due to the decomposition products of additive (such as H_2S or SO_2) and base oil (such as oxy acid). No corrosion of both steel and copper was observed for samples #5 and #10 of zinc salt. Sample color, in general, changed to darker color as the oxidation proceeded as shown in the table.

Antiwear property of sample oils was compared before and after the oxidation test subjecting samples to the Shell four-ball tester for 10 minutes, and the results are shown in Table 5. Good antiwear property was observed for all samples, and sample #11 of cobalt salt showed an excellent antiwear property. The change in wear scar diameter for all samples before and after the test was found to be very small, providing a stable structure of additives. Since the antiwear property is relate to P-S and P-S bonds in the structure of the compound, better property can be obtained as the amounts of sulfur in the compound increase, and this fact was found by comparing the property of

Table 4. Metal corrosion test and color change.

Samples	Metals		Oils	
	Weight increased, %		Union color change	
	Steel	Copper	Before Tesst	After 96 hr.
# 0	0.0104	0.0000	11/2(-)	5
# 1	0.0000	0.1369	2(-)	<8
# 2	0.0000	0.2508	2(-)	31/2
# 3	0.0000	0.5689	11/2(-)	41/2
# 4	0.0000	0.0373	2(-)	41/2
# 5	0.0000	0.0000	11/2(-)	3(-)
# 6	0.0000	0.2422	2	4
# 7	0.0000	0.0105	11/2(-)	4(-)
# 8	0.0000	0.0018	2(-)	4
# 9	0.0757	0.0211	21/2	4
#10	0.0000	0.0000	11/2(-)	3
#11	0.0000	0.1470	31/2	3(-)

Table 5. Wear scar diameter of samples*.

Samples	Wear scar dia., mm	
	Before oxidation	After oxidation
# 0	1.919	2.044
# 1	1.881	0.985
# 2	0.546	0.981
# 3	0.671	0.545
# 4	0.875	0.936
# 5	0.701	0.736
# 6	0.543	1.036
# 7	0.043	1.040
# 8	0.895	0.973
# 9	0.999	0.971
#10	0.620	0.747
#11	0.443	0.449

* Load 50 kg, temp. $75 \pm 3^\circ\text{C}$, speed 1,200 rpm, time 10 mins.

samples #3 and #5 with that of sample #10 of zinc salt.

CONCLUSIONS

In the synthesis of MDDP, it was found that the purification was the most important factor to the usefulness of the compounds. All the

additives were found to be useful as antioxidants and wear reducers, and zinc and cobalt compounds showed much better property than the other compounds. Cobalt compound showed not only a good property in antioxidation and antiwear, but a good viscosity index improving property. In the zinc compound, octyl and isoamyl substituted compounds were found to be good antioxidant, EP additive, anticorrosion additive, and sludge preventive.

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