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Transition metal dithiophosphates as antioxidant additives for engine oils

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Abstract

Currently, diaryl- and dialkyldithiophosphates of zinc, molybdenum and rarely barium are widely used as antioxidant and anti-wear additives for engine oils, while little attention has been paid to studies of dithiophosphates of other metals in the scientific literature. This article will consider transition metal dithiophosphates (copper and cobalt), the methods of their synthesis, and the antioxidant properties estimated by the HTCO (high-temperature catalytic oxidation) method (through polymer degradation and refractive index). The antioxidant properties of these compounds are compared with those of zinc dithiophosphate. The antioxidant efficacy of transition metal dithiophosphates (copper and cobalt) in extremely low concentrations has been shown. Special attention is paid to this topic not only to enhance existing characteristics but also to find innovative solutions to improve the efficiency of motor oils in modern operating conditions using transition metal dithiophosphates.

1. Introduction

The issue of oxidation resistance of lubricants has been on the agenda since the beginning of their use. The study of the mechanism of hydrocarbon oxidation made it possible to understand that the natural oxidation inhibitors contained in lubricating oils have various functional groups in their structure, including sulphur, nitrogen or phosphorus [1]. Thus, whole classes of compounds have been developed, which are currently successfully used as antioxidant additives in lubricating oils for various purposes (engine, transmission, turbine, etc.).

One of the most common compounds today is zinc dialkyldithiophosphate. Additives of this type have antioxidant, anti-corrosive and anti-wear properties, and with the appropriate structure, they can also serve as depressants and demulsifiers. Dialkyldithiophosphate-type antioxidants start to decompose at temperatures up to 150 °C [2,3]. During the transition to higher temperatures, the effect of antioxidants weakens, apparently due to their thermal decomposition.

There is a sufficient amount of information in the literature [4-7] on the effect of the structure of hydrocarbon radicals on the antioxidant and tribological properties of metal dialkyldithiophosphates. The effect of sulphur and phosphorus content on the properties of these additives has also been studied. Ultimately, the choice of components for the production of additives of this type is determined by the need for their complete dissolution in lubricating oils. The most common product today is an additive based on isobutyl and 2-ethylhexyl radicals [8,9].

The clearest understanding of the possibility of obtaining dialkyldithiophosphates of metals using cadmium compounds and lubricants based on them can be obtained from the work (USA Patent 3,232,873). The idea of using organocopper compounds has been investigated more than once. The first studies date back to the 1950s [10]. There are several proposed mechanisms of action of copper organic compounds. As discussed by Klaus et al. [11], organocopper compounds at concentrations from 100 to 200 ppm act as inhibitors of condensation polymerisation, at

concentrations from 200 to 2000 ppm they act as oxidation catalysts and at concentrations above 1000 – 2000 ppm they act as disruptors of hydroperoxide radicals.

The concentration limits of the various mechanisms of action of copper in polymerisation and oxidation reactions are not exact values. In the study by Brook and Matthews [12], paraffin oil was oxidised with oxygen at 150 °C in the presence of copper stearate. It was found that the maximum oxygen absorption was noticed at a copper concentration of 20 ppm. The articles by Black [13] and Colclough [14] describe the mechanism of action of organocopper compounds at high concentrations and explain some pulsations at the beginning of the oxidation process.

The exact mechanism of action of organocopper compounds in low concentrations could not be found, but two possible mechanisms of action were suggested by Klaus et al. [11]. The first is due to the deactivation of catalytic centres on the steel surface, and the second is due to the deactivation of iron ions entering the oil volume (possibly due to the formation of chelated copper-iron compounds in the volume). This paper describes an experiment showing that the second mechanism of polycondensation inhibition is quite possible.

Cobalt dithiophosphates are used as catalysts for the polymerisation of butadiene [15], and the study by Black [13] mentions the antioxidant properties of organic cobalt salts due to the formation of metal-hydroperoxide complexes. Currently, API group III base oils are becoming more widespread, in which the behaviour of transition metal dithiophosphates has not been studied at all. Thus, the purpose of this work is to study the effect of transition metal dialkyldithiophosphates on the antioxidant properties of API group III base oils.

2. Materials and methods

As part of the research, several metal dialkyldithiophosphates were synthesised in the Laboratory of Modern Functional Additives for Lubricants at Gubkin University in order to evaluate their performance in API group III base oils. Phosphorus pentasulfide, isobutyl and isooctyl alcohols were used as raw materials for the synthesis of additives. Copper(II) hydroxide, cobalt oxide (Co_3O_4) and zinc(II) oxide were used as metal donors. The conditions for the synthesis of all metal dithiophosphates were identical. At the first stage, dithiophosphoric acid was obtained (temperature = 50 °C, molar ratio of isobutanol : isooctanol = 3 : 1, time = 3 hours) and in the second stage (temperature 50 °C, time = 3 hours). Finally, we used three additives. The structural formulas of the obtained compounds are shown in Figure 1.

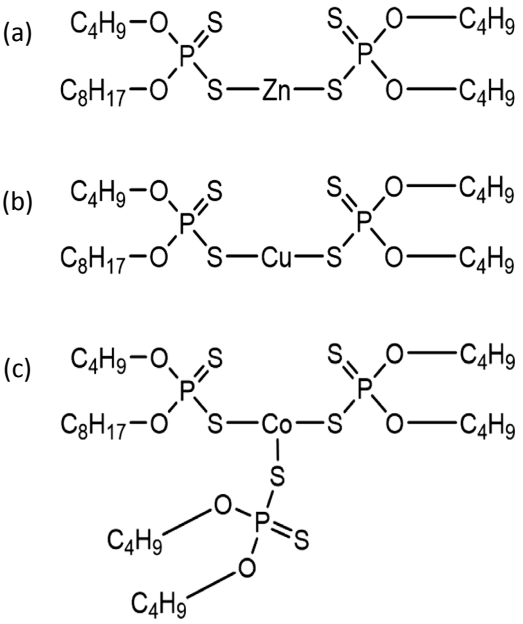

Figure 1. Structural formulas of synthesised additives: (a) zinc(II) dithiophosphate (ZnDTP), (b) copper(II) dithiophosphate (CuDTP) and (c) cobalt(II,III) dithiophosphate (CoDTP)

For each additive, the content of elements was determined according to ASTM D5185, as shown in Table 1.

Table 1. Content of elements in additives

Element	Content (calculated | found), wt. %		
	CuDTP	CoDTP	ZnDTP
S	21.26 | 21.32	22.91 | 22.97	21.22 | 21.36
P	10.30 | 10.22	11.10 | 11.23	10.28 | 10.40
Me	10.63 | 10.74	7.04 | 6.97	10.78 | 10.91

The VHVI-4 (technical specification 38.401-58-415-2014, produced by Tatneft LLC, Nizhnekamsk, Russia) hydrocracking oil was chosen as the base oil, and an engine oil additive package containing a depressor, polymer thickener, antioxidants and alkaline sulfonate was also used. The synthesised additives were introduced into the specified oil in various concentrations and then oxidised using the HTCO (high-temperature catalytic oxidation) method.

The additives were added to the reference oil in the calculated amount (by weight), then placed in a thermostat and kept at a temperature of 60 –

70 °C for one hour, stirring occasionally. At least 30 samples were tested during the study, the results of which are given below. It is worth noting that the initial values of the physicochemical properties of the samples may differ, since the amount of the thickening additive may vary slightly during the preparation of the model engine oil in the laboratory.

The HTCO is a method for determining the thermal and oxidative stability of lubricants on a special device, which is a bath in which metal cups with test samples are placed, and the sample is also reshaped with an aluminium pin at a frequency of 5000 rpm. The temperature of the coolant in the bath varies from room temperature to 250 °C. Metal rotating rods are lowered into glasses with oil samples, and then the samples are kept under selected conditions for a specified time. All tests were carried out at a temperature of 220 °C, which corresponds to the temperature in the area of the compression piston rings. Consequently, the test time varied. The following parameters were determined before and after oxidation: kinematic viscosity at 40 and 100 °C, viscosity index, acid number and refractive index at 20 °C.

The kinematic viscosity was measured as follows by the ISO 3104, using a Cannon miniAV-X capillary viscometer. The arithmetic mean value calculated from two definitions of kinematic viscosity according to the specified method was taken as the result of kinematic viscosity. All the values obtained are within the convergence range. The refractive index was measured as follows by the ASTM D1747, using the Mettler Toledo RM 40 refractometer. The acid number was measured using the ASTM D664 method for all test samples in order to determine the change in the acid number before and after the tests using the HTCO method.

3. Results and discussion

3.1 Copper dithiophosphate (CuDTP)

First series. The first decision was to investigate copper dithiophosphates for their antioxidant properties. The sample, which is a mixture of VHVI-4 and a package of additives for engine oil with the addition of CuDTP of various concentrations (from 10 to 2000 ppm), was evaluated using the HTCO method at a temperature of 220 °C for 1 hour. The antioxidant properties were evaluated by changes in kinematic viscosity and viscosity index. The results are presented in Table 2 and Figure 2.

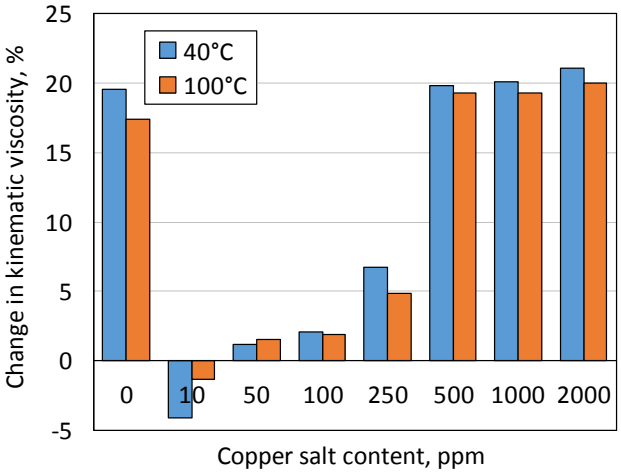

Figure 2. Change in kinematic viscosity after HTCO depending on the CuDTP content (first series)

As can be seen from Figure 2 and Table 2, the minimum change in kinematic viscosity is noticed in the concentration range of CuDTP from 10 to 100 ppm, from which it can be concluded that the maximum effectiveness of copper salts as antioxidant additives is precisely in this concentration range. An increase in the content of

Table 2. Results of the first series of CuDTP tests

Copper salt content, ppm	Kinematic viscosity at 40 °C, mm^2/s		Kinematic viscosity at 100 °C, mm^2/s		Viscosity index		Acid number, mg KOH/g	
	before	after	before	after	before	after	before	after
0	85.26	68.93	14.88	12.28	184	178	0.53	1.12
10	107.16	111.60	18.52	18.76	193	189	0.61	0.81
50	110.86	109.51	18.68	18.39	189	188	0.59	0.75
100	84.18	82.42	14.75	14.47	184	184	0.67	0.91
250	116.38	108.57	19.10	18.18	185	186	0.63	0.91
500	78.26	62.78	14.04	11.34	186	176	0.55	1.20
1000	97.53	77.91	16.96	13.69	190	181	0.49	1.14
2000	81.11	64.00	14.28	11.43	184	175	0.51	1.23

CuDTP of more than 100 ppm, on the contrary, catalyses oxidative processes in lubricating oil, which is highly undesirable in the conditions of engine oil operation.

Analysis of the acid numbers before and after oxidation in the first series allows us to conclude that the minimum increase in the acid number is also noticed in the range of 10 – 100 ppm. A further increase in the concentration of CuDTP leads to a significant increase in the acid number (i.e. oxidative degradation of lubricating oil occurs). In accordance with the recommendations mentioned by Levin and Mikhailov [16], the antioxidant properties of copper dithiophosphates were evaluated by polymer degradation. It was found that copper dithiophosphates exhibit the most significant antioxidant properties at concentrations from 10 to 100 ppm.

Second series. Due to the possible effects of other additives, in particular amine and phenolic antioxidants, on CuDTP, it was decided to test on VHVI-4 base oil without antioxidants using the HTCO method at a temperature of 220 °C for 4 hours. The results are shown in Tables 3 and 4.

Table 3. Results of the second series of CuDTP tests (base oil without antioxidants addition)

Time since the beginning of oxidation	Copper salt content, ppm			
	0		100	
	Kinematic viscosity at, mm^2/s			
	40 °C	100 °C	40 °C	100 °C
Before the test	83.69	14.84	83.69	14.84
After 1 hour	77.50	13.64	76.67	13.87
After 2 hours	35.40	6.27	33.91	6.08
After 3 hours	42.12	6.85	32.88	5.92
After 4 hours	56.50	8.14	46.72	7.34

The results of the second series of tests indicate that when using CuDTP in the amount of 100 ppm, and the HTCO method for 2 hours, no difference in viscosity and refractive index was noticed between the oil using CuDTP and without it. Further oxidation in the sample with CuDTP was slowed down. This may indicate the correctness of the mechanisms proposed by Klaus et al. [11], that at low concentrations, the copper is serving as a catalyst for the primary oxidation reactions, while acting as an inhibitor for the formation of high-molecular-weight products.

As for the refractive index, its insignificant increase when using the optimal concentration of CuDTP allows us to unequivocally conclude that there is no intensive destruction of hydrocarbon chains and their oxidation in the volume of lubricating oil.

3.2 Cobalt dithiophosphate (CoDTP)

First series. CoDTP was also synthesised and tested in two series: first in a mixture with an additive package (first series of tests) and then without (second series of tests). The test conditions of the first series, according to the HTCO method, were a temperature of 220 °C for 1.5 hours. The test results are shown in Table 5 and Figure 3. The longer test time with CoDTP is explained by the fact that it was assumed to have a mechanism of action different from CuDTP and similar to that of ZnDTP (CuDTP is a metal deactivator and CoDTP is a classical hydroperoxide decomposer).

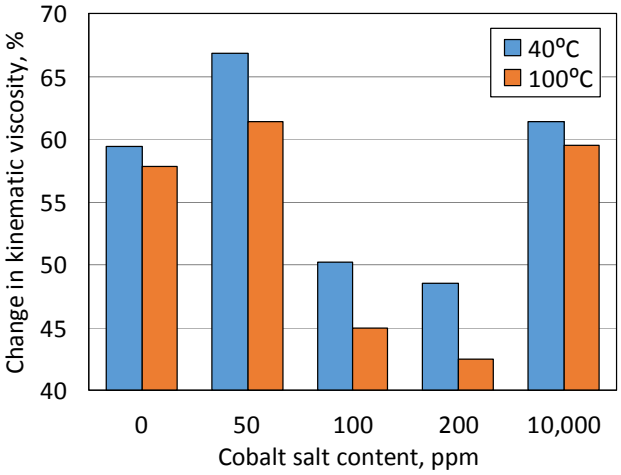

Figure 3. Change in kinematic viscosity after HTCO depending on the CoDTP content (first series)

Table 4. Results of the second series of CuDTP tests (base oil without antioxidants addition)

Copper salt content, ppm	Refractive index					Refractive index change after 4 hours	Acid number after 4 hours, mg KOH/g
	Time, hours						
	0	1	2	3	4		
0	1.4641	1.4641	1.4645	1.4647	1.4662	0.0021	4
100	1.4641	1.4641	1.4644	1.4645	1.4649	0.0008	1.5

Table 5. Results of the first series of CoDTP tests

Cobalt salt content, ppm	Kinematic viscosity at 40 °C, mm^2/s		Kinematic viscosity at 100 °C, mm^2/s		Viscosity index		Acid number, mg KOH/g	
	before	after	before	after	before	after	before	after
0	94.79	35.71	15.92	6.44	180	134	0.56	1.45
50	94.92	31.53	15.72	6.07	177	143	0.62	1.57
100	94.71	47.19	16.07	8.84	182	170	0.58	1.31
200	95.01	48.90	15.97	9.18	180	173	0.51	1.22
10.000	97.07	40.42	16.72	7.84	187	169	0.49	1.37

It is worth noting that large amounts of CoDTP (in wt. %) were tested in this series, since the effectiveness of these additives in low concentrations is known, but there is no information on the introduction of CoDTP in high concentrations. Among the studied concentrations of cobalt salts, the maximum efficiency is shown for 100 and 200 ppm, based on the minimum change in kinematic viscosity (Figure 3 and Table 5). Analysis of the acid numbers before and after oxidation also shows that the minimum increase in the acid number is noticed for 100 and 200 ppm, which is probably due to the formation of metal complexes with hydroperoxides, which limit the access of free radicals.

According to the results of the first series of tests, it is clear that CoDTP reduces the destruction of the polymer thickener in concentrations from 100 ppm to concentrations of 1 wt. %.

Second series. According to the results (Table 6) of the second series of tests, it can be seen that at CoDTP concentrations of 50 ppm or more, base oil oxidation reactions slow down. The test conditions of the second series, according to the HTCO method, were a temperature of 220 °C for 2 hours.

A minimal change in the refractive index and a slight increase in the acid number when using cobalt salts shows the effectiveness of these additives as oxidation inhibitors, since they probably work in several directions at once as metal deactivators, binding ions of catalytically active metals, peroxide destroyers and radical scavengers. Based on the results obtained in Table 6, it can be concluded that in all concentrations, adding CoDTP is a justified and effective solution.

3.3 Zinc dithiophosphate (ZnDTP)

As a comparison sample, ZnDTP was tested in the first (1.5 hours, model engine oils) and second series (2 hours, base oil) of tests in various concentrations, and the results are shown in Tables 7 and 8 and Figure 4.

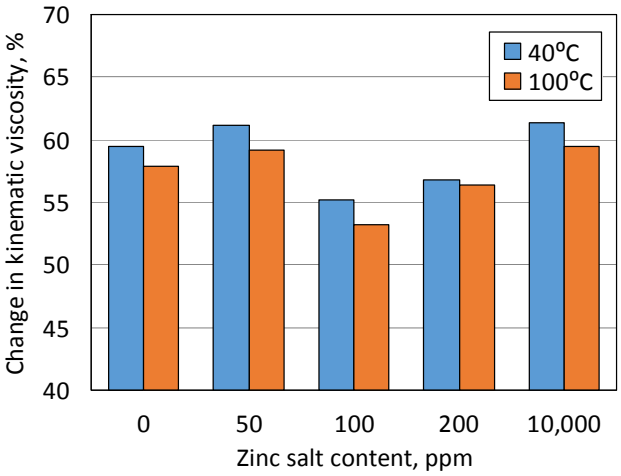

Figure 4. Change in kinematic viscosity after HTCO depending on the ZnDTP content (first series)

Table 6. Results of the second series of CoDTP tests (base oil without antioxidants addition)

Cobalt salt content, ppm	Refractive index				Refractive index change after 2 hours	Acid number, mg KOH/g	
	Time, hours						
	0	1	1.5	2		before	after
0	1.4673	1.4673	1.4684	1.4704	0.0031	0.02	2.32
50	1.4670	1.4670	1.4671	1.4670	0.0000	0.02	0.65
100	1.4669	1.4668	1.4669	1.4677	0.0008	0.04	0.79
250	1.4668	1.4667	1.4667	1.4675	0.0007	0.06	0.92
10.000	1.4675	1.4676	1.4677	1.4678	0.0003	0.12	0.85

Table 7. Results of the first series of ZnDTP tests

Zinc salt content, ppm	Kinematic viscosity at 40 °C, mm^2/s		Kinematic viscosity at 100 °C, mm^2/s		Viscosity index		Acid number, mg KOH/g	
	before	after	before	after	before	after	before	after
0	82.73	33.56	14.31	6.03	180	127	0.45	1.65
50	84.59	32.88	14.55	5.94	180	127	0.53	1.51
100	80.31	36.01	13.87	6.49	179	135	0.55	1.53
200	82.02	35.43	14.14	6.17	179	122	0.49	1.72
10.000	87.17	33.67	15.01	6.08	182	129	0.62	1.60

Table 8. Results of the second series of ZnDTP tests (base oil without antioxidants addition)

Zinc salt content, ppm	Refractive index				Refractive index change after 2 hours	Acid number, mg KOH/g	
	Time, hours						
	0	1	1.5	2		before	after
0	1.4667	1.4671	1.4676	1.4689	0.0022	0.02	2.01
50	1.4672	1.4676	1.4681	1.4696	0.0024	0.02	2.13
100	1.4672	1.4677	1.4683	1.4693	0.0022	0.02	2.07
250	1.4674	1.4679	1.4685	1.4697	0.0023	0.05	2.30
10.000	1.4677	1.4680	1.4682	1.4699	0.0022	0.09	2.11

According to the results of the first series of tests, it is clear that ZnDTP has no noticeable effect on the change in kinematic viscosity, since during oxidation (1.5 hours), the polymer thickener is completely destroyed (Table 7). There is also a significant increase in the acid number compared to other tested metals.

Tests conducted in the second series of experiments with zinc salts show an increase in the refractive index after oxidation, which leads to the conclusion that during the test, oxidative degradation of the oil occurs with the formation of dark oxidation products. According to the results of the second series of tests, it is clear that ZnDTP has no noticeable effect on the oxidation rate of the base oil (Table 8).

4. Conclusion

Based on the results of the study, several conclusions can be drawn.

Dialkyldithiophosphates of copper and cobalt have a noticeable effect on the inhibition of oxidation processes in extremely low concentrations, completely unusual for antioxidants in motor oils.

The possible mechanism of action given by Klaus et al., that at low concentrations, the copper is serving as a catalyst for the primary oxidation reactions, while acting as an inhibitor for the formation of high-molecular-weight products, may explain the results for low concentrations of dialkyldithiophosphates of copper and cobalt.

The antioxidant effect of cobalt dithiophosphate at high concentrations (up to 1 wt. %) can be explained within the framework of the traditional theory of the action of the second type of antioxidants, since apparently, cobalt dialkyldithiophosphate decomposes at higher temperatures compared to zinc dialkyldithiophosphates.

Zinc dialkyldithiophosphate does not exhibit antioxidant properties under experimental conditions, most likely due to rapid thermal decomposition.

The antioxidant properties exhibited by dialkyldithiophosphates of copper and cobalt are quite interesting and cannot be explained within the framework of the traditional theory of oxidation. Therefore, further study of their properties should be continued.

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