Journal of Petroleum
Science and Technology

Research Note

An Investigation of Antioxidant Properties of Zinc and Molybdenum Dithiocarbamates in Hydrocarbons

Marzieh Shekarriz

Chemical, Polymeric and Petrochemical Technology Research Division, Faculty of Research and Development in Downstream Petroleum Industry, Research Institute of Petroleum Industry (RIPI), Tehran, Iran

ABSTRACT

The oxidation and degradation of hydrocarbons at high temperature and pressure in the presence of oxygen is one of the common oil product problems. There are many antioxidants to prevent or inhibit oxidation processes; molybdenum and zinc dithiocarbamates are known as powerful antioxidants. In this paper, the oxidation inhibition time of cumene has been investigated using zinc and molybdenum dithiocarbamate substituted with different alkyl groups as antioxidants and azobisisobutyronitrile (AIBN) as the initiator. The best result obtained for molybdenum dibutyldithiocarbamate was about 210 min, while zinc dialkyldithiophosphate (ZDDP), a well known commercial antioxidant, showed an oxidation inhibition time of about 14 min under the same conditions. It was shown that antioxidancy properties decreased with increasing the chain length of the substituted alkyl groups. This can be explained by the fact that alkyl groups participate in the oxidation process and thus increasing the alkyl chain length reduces antioxidancy effect. The synergism effect of molybdenum dibenzyl dithiocarbamate on ZDDP was also investigated and the oxidation inhibition time of about 110 min was obtained, which was greater than that of any individual antioxidant.

Keywords: Antioxidants, Molybdenum Dithiocarbamate, Zinc Dithiocarbamate, Alkyl Group, Lubricants

INTRODUCTION

Most petroleum products such as lubricants, engine oils, polymers, and fuels are oxidized in the presence of oxygen and metals (from metal surface), especially under severe application conditions such as high temperature and pressure; this reaction is called autoxidation. Hydrocarbon autoxidation is a free radical chain reaction and produces the corresponding peroxides or hydroperoxides in the propagation step. Alcohols, organic acids, ketones, and aldehydes are obtained in the termination step [1].

Antioxidants are used to inhibit oxidation reaction, and they react with free radicals to form stable species and prevent the degradation process. They can act as chain breaking by radical scavenging or peroxide destroying [2]. The first group inhibits oxidation by reacting with chain propagating free radicals to form stable molecules, and is known as primary antioxidants. The second group or peroxide destroying antioxidants are known as secondary antioxidants and act by specifically decomposing peroxide radicals. In some cases, antioxidants can be regenerated as part of this

***Corresponding author**
Marzieh Shekarriz
Email: shekarriz@ripi.ir
Tel: +98 21 4825 5058
Fax: +98 21 4473 9752

Article history
Received: April 25, 2015
Received in revised form: August 17, 2015
Accepted: August 19, 2015
Available online: October 20, 2016

process. Examples of primary antioxidants are hindered phenols and secondary arylamines such as alkylated diphenylamines. Phosphorous and a variety of sulfur compounds such as dithiophosphates or dithiocarbamates fall into the secondary antioxidant category [3].

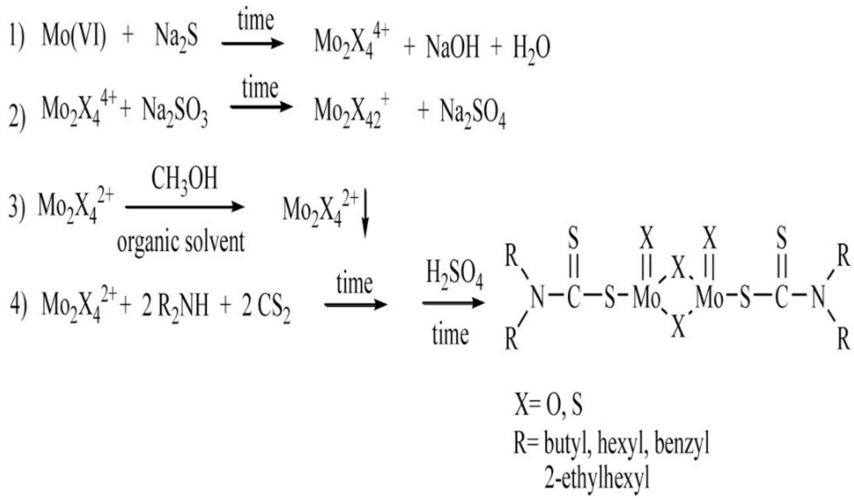
Engine oils are one of the most important lubricants because vast markets and modern automobiles need more stable and high performance lubricants. Therefore, additive packages containing antioxidants, antiwear compounds, detergents, and dispersants are used for improving the performance of engine oils. Life time of engine oils has been an attractive area of research due to the environmental and economic aspects. Several efficient antioxidants have been developed for engine oils such as hindered phenolic compounds [4], metal dialkyldithiophosphate [1, 2], metal dithiocarbamate [5, 6], and borate esters [7, 8].

Zinc and molybdenum dithiocarbamate (ZnDTC and MoDTC) are known as multifunctional lubricant additives used as antiwear, antioxidant, anticorrosion, and extreme pressure additives [9]. There are some methods for the preparation of these materials. Synthesis routes for zinc and molybdenum dialkyldithiocarbamate are shown in Schemes 1 and 2 respectively [10-12].

$$2\,R_2NH \;+\; 2CS_2 \longrightarrow 2R_2NCSSNa \xrightarrow{ZnCL_2} \left(R_2NCSS\right)_2 Zn$$

R= n-butyl, hexyl, cyclohexyl, 2-ethylhexyl, benzyl

Scheme 1: Synthesis of zinc dialkyldithiocarbamate (ZnDTC).



Scheme 2: Synthesis of molybdenum dialkyldithiocarbamate (MoDTC).

In this work, we report our study on the antioxidant characteristics and measurement of the oxidation inhibition time of zinc and molybdenum dithiocarbamates containing different alkyl groups. These antioxidants are then compared with zinc dialkyldithiophosphate and the synergism effect of MoDTC and ZDDP is investigated.

EXPERIMENTAL PROCEDURES

All reagents and solvents were purchased from Merck Chemical Company and used without further purification. Zinc and molybdenum dithiocarbamates were synthesized according to the procedures reported in the literature [10, 11].

Zinc Dithiocarbamates: To a solution of 0.1 mole of dialkylamine in a mixture of water and hexane, 5 ml of NaOH was added. Then, 0.11 moles of CS_2 was slowly added during 2 hrs at room temperature; 0.05 mole of zinc chloride was subsequently added at 40°C. The product was then separated, washed, and dried.

Molybdenum Dithiocarbamate: A mixture of 0.02 mole of molybdenum trioxide and 0.03 mole of sodium sulfide in 5 ml of water was prepared at 40°C. Then, 1 gr of Na_2SO_3 was added and the temperature was raised to 60°C, followed by the addition of 8 ml of ethanol and 0.02 mole of dialkylamine. 0.02 mole of CS_2 was subsequently added during 15 min, and then 0.01 mole of H_2SO_4 was added slowly. When the additions were completed, the reaction mixture was heated at 60°C for 4 hrs the product was separated and washed with water and ethanol.

Oxidation Test: The oxidation tests were carried out according to the reports [7, 13] as follows:

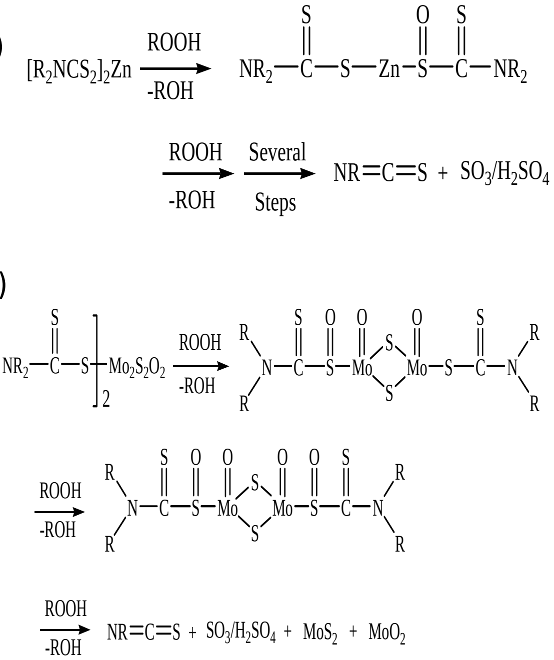
In a jacketed rector, a 0.0005 M solution of ZnDTC and a 0.0005 M solution of MoDTC in cumene were placed while the temperature was set to 60°C by circulating warm water through the reactor jacket. Then, 0.2 gr of azobisisobutyronitrile was added, and after vacuuming the reactor (removing air) oxygen gas inlet, the pressure was set to 1 atm (1 atm absolute). The reduction in oxygen pressure was measured by a barometer.

RESULTS AND DISCUSSION

Hydrocarbons and lubricants are oxidized to organic fatty compounds such as organic acids, alcohols, aldehydes, and ketones in the presence of oxygen at high temperatures. These compounds can form high molecular weight oil and insoluble polymeric materials (gum). For this reason, it is necessary to add antioxidants to lubricants to prevent the formation of such compounds, which increase the viscosity. As previously stated, zinc and molybdenum dithiocarbamates are secondary antioxidants, and they reduce the alkyl hydroperoxides in the radical chain to alcohols by oxidizing themselves. The oxidation mechanisms of ZnDTC and MoDTC are shown in scheme 3.

a)

b)



Scheme 3: Possible oxidation mechanisms; a) ZnDTC and b) MoDTC.

In this work, a test method was used involving the measurement of the oxidation rate of cumene containing an initiator such as azobisisobutyronitrile as a suitable system [7, 13]. Cumene is selected as a hydrocarbon solvent because it has alkyl and aryl groups for studying the oxidation process. The oxidation reaction is readily initiated at 60°C in the presence of oxygen.

The effects of ZnDTC and MoDTC on the oxidation of cumene are shown in Figures 1 and 2. These results clearly show that metal dithiocarbamates can act as powerful antioxidants. Cumene is oxidized without any oxidation inhibition time (time delay of hydrocarbon oxidation is called oxidation inhibition time) in the absence of antioxidants. The oxidation inhibition time was about 14 min in the presence of ZDDP (Figure 3), while that of ZnDTC with different alkyl groups varied from 50 min to 105 min. The same trend was observed for the oxidation inhibition time of MoDTC from 60 min to 210 min.

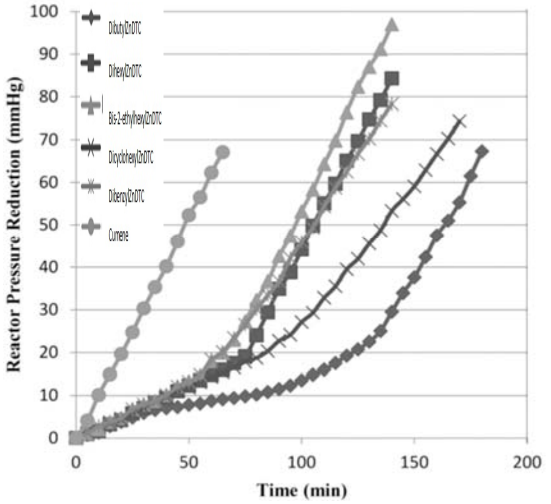


Figure 1: Effect of ZnDTC's (0.0005 M) on the oxidation of cumene

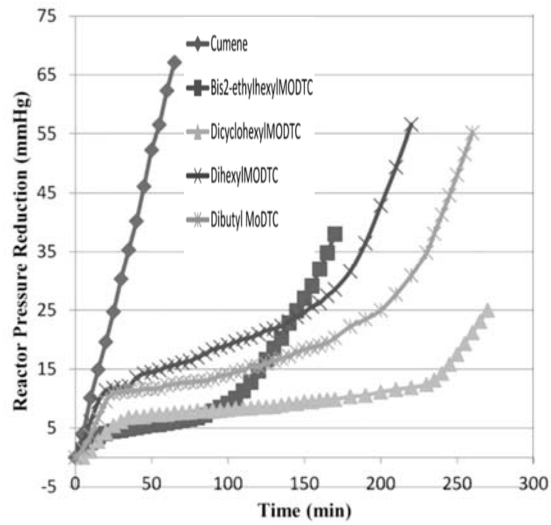


Figure 2: Effect of MoDTC's (0.0005 M) on the oxidation of cumene.

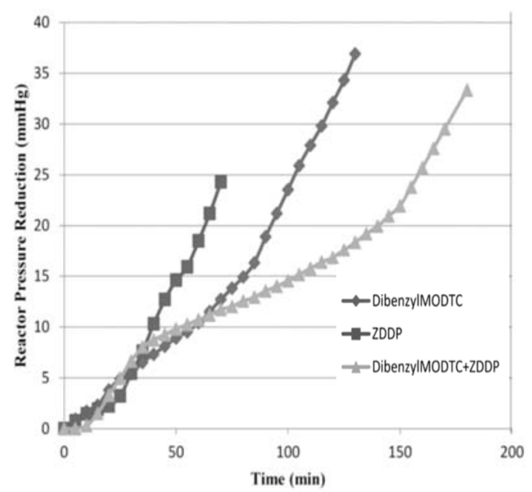


Figure 3: Synergism effect of MoDTC and ZDDP.

The synergism effect of MoDTC (oxidation inhibition time 60 min) on ZDDP (oxidation inhibition time 14 min) was also investigated and the oxidation inhibition time of about 110 min was obtained, which was greater than that of any individual antioxidant (Figure 3).

Table 1 shows the oxidation inhibition time results of ZnDTC's and MoDTC's.

Table 1: Oxidation inhibition time of ZnDTC and MoDTC.

Entry	Sample	Oxidation inhibition time (min)
1	Cumene without antioxidant	0
2	Zn dialkyldithiophosphate (ZDDP)	14
3	Zn Dibutyldithiocarbamate	105
4	Zn dicyclohexyldithiocarbamate	60
5	Zn dihexyldithiocarbamate	58
6	Zn bis (2-ethylhexyl)dithiocarbamate	50
7	Zn dibenzyldithiocarbamate	51
8	Mo Dibutyldithiocarbamate	210
9	Mo dicyclohexyldithiocarbamate	175
10	Mo dihexyldithiocarbamate	130
11	Mo bis (2-ethylhexyl)dithiocarbamate	110
12	Mo dibenzyldithiocarbamate	60
13	Mo dibenzylDTC + ZDDP	110

As shown in Table 1, the length of the alkyl chain is inversely proportional with the antioxidancy effect of the antioxidant although the solubility of the antioxidant in the oil increases as chain length increases. This can be explained by the fact that alkyl groups participate in the oxidation, and thus increasing the alkyl chain length reduces the antioxidancy effect. Thus dibenzyl group, which forms a highly stable radical, gives the lowest oxidation inhibition time since the higher stability of the radical formed brings about a lower antioxidancy effect.

CONCLUSIONS

In this study, it was shown that zinc and molybdenum dithiocarbamates are excellent antioxidants for hydrocarbons and lubricants such as engine oil in comparison with well-known commercial antioxidants (ZDDP). It was also shown that by increasing carbon atoms in alkyl groups, the solubility of dithiocarbamate in the lubricant increased, but antioxidant characteristics decreased. Molybdenum dibutyldithiocarbamate showed the best antioxidancy and the oxidation inhibition time was about 210 min. The synergism effect of the combined molybdenum dibenzyldithiocarbamate and ZDDP was also observed. Molybdenum dibenzyldithiocarbamate and ZDDP showed an oxidation inhibition time of 60 min and 14 min respectively, while the combined sample showed a higher oxidation inhibition time (110 min).

REFERENCES

[1] Rudnick L. R., *Lubricant Additives: Chemistry and Applications*, 2nd ed., USA, CRC press, Taylor & Francis Group, **2009**, 18-29.

[2] Ahmed N. S. and Nasar A. M., "Lubricating oil Additives,"http://www.cdn.intechopen.com/pdfs-wm/21936.pdf, Dec. **2015**.

[3] Canter N., "Use of Antioxidants in Automotive Lubricants," *Academic Journal*, **2012,** *64*, 9-12.

[4] Kumar R., Yang S., Kumar V., and Cholli A. L., "Nitrogen and Hindered Phenol Containing Dual Functional Macromolecular Antioxidants: Synthesis, Performances And Applications," US Patent, US 8080689 B2, Nov. 17, **2011**.

[5] Aguilar G. A., Cheng F. S., and Chase K. J., "Zinc Dithiocarbamate Lubricating Oil Additives," US Patent, US 20120258896 A1, Oct. 11, **2012**.

[6] Shah F., Glavatskih S., and Antzutkin O. N., "Novel Alkylborate–dithiocarbamate Lubricant Additives: Synthesis and Tribophysical Characterization," *Tribology Letter*, **2012,** *45*, 67-78.

[7] Shekarriz M., Ghanbari B., Taghipoor S., Khalili A. A., et al., "Synthesis and Antioxidant Characteristics of Borate Esters Used in Lubricating Oil," *Asian Journal of Chemistry*, **2010**, *22*, 3646-3652.

[8] Li J., Li Z, Ren T., Zeng X., et al., "Hydrolytic Stability and Tribological Properties of N-Containing Heterocyclic Borate Esters as Lubricant Additives in Rapeseed Oil," *Tribology International*, **2014**, *73*, 101-107.

[9] Parenago O. P., Vipper A. B., and Kuzmina G. N., "Zinc and Molybdenum Dithiocarbamates Antioxidant Additives," *Lubrication Science*, **2001**, *13*, 113-124.

[10] Schubart R. and Engels H. W., "Process for the Preparation of Zinc Dithiocarbamate," US Patent, US 2001/0039339, Oct. 6, **2001**.

[11] Iso K., Yokouchi A., Koizumi H., and Naka M., "Grease Composition for Rolling Bearing," US Patent, US 6352961 B1, **2002**.

[12] Tanaka N., Fukushima A., Tatsumi Y., Morita K., et al., "Process for Producing Molybdenum Oxysulfide Dithiocarbamate," US Patent, US 5631213, May 20, **1997**.

[13] Burn A. J., "The Mechanism of the Antioxidant Action of Zinc Dialkyldithiophosphates," *Tetrahedron*, **1966,** *22*, 2153-2161.