

Synergistic antioxidation of organic molybdenum complex with dithiocarbamate antioxidant evaluated by differential scanning calorimetry and thin film micro oxidation test

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Abstract

An oil-soluble sulfur- and phosphorus-free organic molybdenum complex (MC) was synthesized. The antioxidation properties of MC- and methylene bis(di-*n*-butyldithiocarbamate) (V 7723)-containing poly- α -olefin (PAO)-derived lubricants were evaluated by differential scanning calorimetry (DSC) and modified penn state micro-oxidation test (PMOT). DSC test measures incipient oxidation temperature (OT) and oxidation induction time (IT) of the lubricant at high temperatures and the oxidation stability of oil weight loss is measured by PMOT test. DSC test shows that OT and IT of V 7723-containing PAO were improved significantly by MC addition. PMOT test indicates that when combining with V 7723 antioxidants, MC can also effectively reduce the increase in weight loss of PAO. These results suggest that the MC shows a good oxidative synergism with V 7723 antioxidant. In addition, FTIR results from PMOT test confirm that addition of MC can significantly enhance the oxidation induction time of oils and inhibit formation of oxidation products containing carbonyl bonds or hydroxyl group. The proposed mechanism of the inhibition involves a synergy between MC and V 7723.

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1. Introduction

Organic species in mineral oils and lubricants are subject to deterioration by oxidation, especially at high temperatures and in the presence of air or metal [1]. Such deterioration often leads to buildup of insoluble deposits or sludge and viscosity increase during use [2]. In order to avoid the problems, lubricants need to possess superior oxidation stability.

Undesired roles of phosphorus and sulfur in engine oils will result in the decrease of emission system life by fouling catalytic exhaust converters and poisoning the catalyst [3–5].

Moreover, to meet the latest technical, economical and environmental requirements the lowest possible level of sulfur and phosphorus containing additive packages has to be used in the formulation of advanced engine oils [6,7]. In order to achieve these increasing demands developing new type of sulfur- and phosphorus-free organic molybdenum compounds (SPFOMCs) are desirable for advanced engine oils. However, absence of phosphorus and sulfur will reduce oxidation resistance of oils, so it is important to study synergistic effects on antioxidation properties between different additives.

Recent works show that the combination of SPFOMCs and alkylated diphenylamines can exhibit good oxidation and deposit inhibition at higher temperature [8–11]. Moreover, SPFOMCs were also reported to have good synergic effect with sulfur-containing additives such as zinc dialkyldithiophosphate (ZDTP), 1,3,4-thiadizole and dithiocarbamates compounds

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[12–14]. However, evaluation on synergistic antioxidation property of SPFOMCs with ashless antioxidant dialkyldithiocarbamate is rarely available to literatures.

For the investigation of oil oxidation stability, a large number of laboratory tests have been used to evaluate physical and chemical degradation of lubricants, mainly including thin film tests such as pressurized differential scanning calorimetry (PDSC), differential scanning calorimetry (DSC), or penn state microoxidation test (PMO) and bulk oil oxidation tests such as rotary bomb oxidation test (RBOT) or turbine oil stability test (TOST), etc. Thereto, thin film tests can alleviate the problem of oxygen diffusion and in some respects may more closely simulate the oxidation of lubricants under boundary lubrication conditions, moreover, these methods are simple, less time-consuming and have good relation with oxidation reactions of oils.

Many works have shown that DSC is an effective way to evaluate the oxidation stability of base oils and antioxidants [15–21]. DSC applications are run either in an isothermal or a programmed temperature mode, and it has been used to measure either inhibition time (isothermal) or the onset temperature (temperature ramping) of lubricant oxidation. In DSC test, oil samples were placed in aluminum pan, in order to investigate catalytic effect of Fe on oils, it can be supplied by penn state microoxidation test (PMO). PMO can not only evaluate thermo-oxidative stability of lubricants, but also provide details about the quantity and chemical nature of degradation products by analytical technologies such as gel permeation chromatography (GPC), FTIR and GC/MS, etc. [22–27].

In the present study, we synthesized a sulfur- and phosphorus-free molybdenum complex (MC) and investigated its synergic antioxidation properties with methylene bis(di-*n*-butyldithiocarbamate) (V 7723) by differential scanning calorimetry (DSC) and Modified Penn State Micro-Oxidation Test (PMOT) along with FTIR analysis.

2. Experimental

2.1. Test basestock and additives

The base fluids used in the present study are poly- α -olefin (PAO) synthetic lubricant with viscosity 6.0 centistokes at 100 °C. Antioxidant methylene bis(di-*n*-butyldithiocarbamate) (V 7723) and metal deactivator 1-[di(4-octylphenyl)amino-methyl]tolutriazole (V 887) are commercially purchased from R.T. Vanderbilt company.

Organic molybdenum complex (MC) Organic molybdenum complex (MC) was synthesized via two-step reactions. In the first step, a 250 mL of three-necked round flask with a condenser was charged with 47.5 g (0.05 mol) of soybean oil and 9.8 g (0.09 mol) of diethanolamine. Then, the flask was heated to ca. 135 °C in an oil bath and magnetically stirred at the temperature for 2.5 h. In the second step, 2.0 g of molybdenum oxide and 60 mL toluene were added to the reaction mixture and refluxed for 2.5 h. After reaction, water was removed from the reaction mixture by distillation. The water-free reaction mixture was filtrated to remove inorganic species, affording brown liquid as

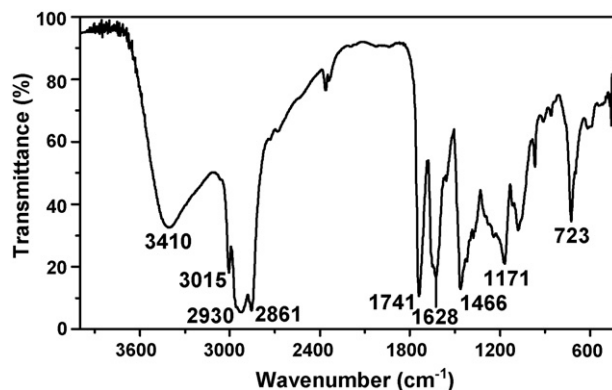
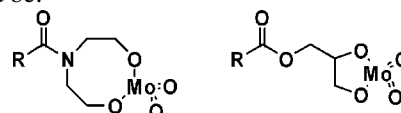


Fig. 1. FTIR spectrum of MC.

filtration. According to FTIR analysis as shown in Fig. 1 and Table 1, we presumed the structure of product MC in the brown liquid could be:



wherein R represents a fatty oily residue.

All the additive concentrations are expressed in weight percentage.

2.2. Standard procedure for DSC test

All the DSC experiments were carried out on a Perkin-Elmer 7 series thermal analysis system by heating a thin film of oil sample in an open aluminum pan under pure oxygen and thereby detecting the exotherm corresponding to the onset of rapid and accelerated oxidation. Oxidation onset temperature (OT) and oxidation induction time (IT) were measured in exothermic and isothermal modes, respectively. Higher OT and longer IT are indicative of improved oxidative stability. In this test, two replicate DSC analyses were made for each sample, and relative experimental error was 1% for OT and 5–8% for IT.

Sample weight, initial temperature and highly pure oxygen flow rate are 1.00 ± 0.05 mg, 150 °C and 60 mL min^{-1} , respectively. The onset temperature and induction periods from the isothermal experiments were obtained by extrapolation of the front edge of the exothermic peak to the baseline.

Table 1
Group assignment of MC

WN (cm^{-1})	Assignment
3410	O–H stretch
3015	Alkene C–H stretch
2930	C–H asymmetrical stretch
2861	C–H symmetrical stretch
1741	Ester C=O
1628	Amide carbonyl band
1466	C–H band
1161	Secondary amide C–N band
723	$-(\text{CH}_2)_n-$ rocking (n not less than 3)

WN denotes wavenumber.

2.3. Modified penn state micro-oxidation test (PMOT)

PMOT was used to measure the oxidative stability and deposit forming tendencies of lubricants under high temperature thin-film oxidation conditions. In this modification a thin-film of PAO lubricant (approximately 60 μL) is accurately weighed onto a carbon steel coupon and heated in an impinger beaker at 220 $^{\circ}\text{C}$ exposed to atmosphere. Test times are 40, 60, 80, 100 and 120 min. At the end of the test period the coupon is removed from the impinger tube, cooled and weighed to determine percent weight loss (also termed volatile loss), then the oxidized samples are diluted by petroleum ether for FTIR analysis. Higher weight loss indicates high volatility due to evaporation and low stability of the oil. These evaluations were performed in duplicate and the results averaged.

2.4. FTIR analysis

Oxidized oil samples were analyzed using a WQF-301 FTIR equipped with a TGS cooled detector and KBr beam splitter. Wavelengths were scanned in the range 400–4000 cm^{-1} , with a resolution of 4.0 cm^{-1} and 32 scans. The oxidation of the oil samples was quantified by calculating the area of the spectral band around 1720 cm^{-1} , measured from 1650 to 1850 cm^{-1} . This band is characteristic of the carbonyl bonds (C=O) present in the majority of the oxidation products, such as carboxylic acid, ketone, aldehyde, ester and lacton or organic carbonate. Data were acquired and processed using Origin software by integration. This technique is acknowledged as a satisfactory measure of the level of oil degradation, since the carbonyl band is not found in the spectrum of fresh oil [22,23,28–34].

In this study, in order to eliminate the influence of samples volume and cell thickness variances, the area of carbonyl band index (CBI) was introduced to provide quantitative results from the infrared spectra, which was obtained under the same experimental conditions by dividing the area of the carbonyl band around 1650–1850 cm^{-1} by the area of basic band (CH_3 stretching vibration around 3000 cm^{-1}).

3. Results

3.1. DSC test

As Figs. 2 and 3 demonstrate, in the presence of PAO and 1.0% V 7723, OT and IT are almost identical to PAO containing 4.0% MC under the experimental error, which suggests antioxidant V 7723 and MC alone in PAO do not possess better antioxidation property at higher temperature. When V 7723 was combined with MC at different proportions in PAO, OT can be increased from 218.2 to 250.2 $^{\circ}\text{C}$ and IT can be improved 12.5–40.9 min comparing to MC alone. Therefore, the significant improvement in OT or IT of oils shows that MC can exhibit good antioxidation synergism with dithiocarbamate antioxidant.

3.2. PMOT test

The data from DSC indicate that PAO containing V 7723 was oxidized easily at 200 $^{\circ}\text{C}$. In the PMOT test, carbon steel

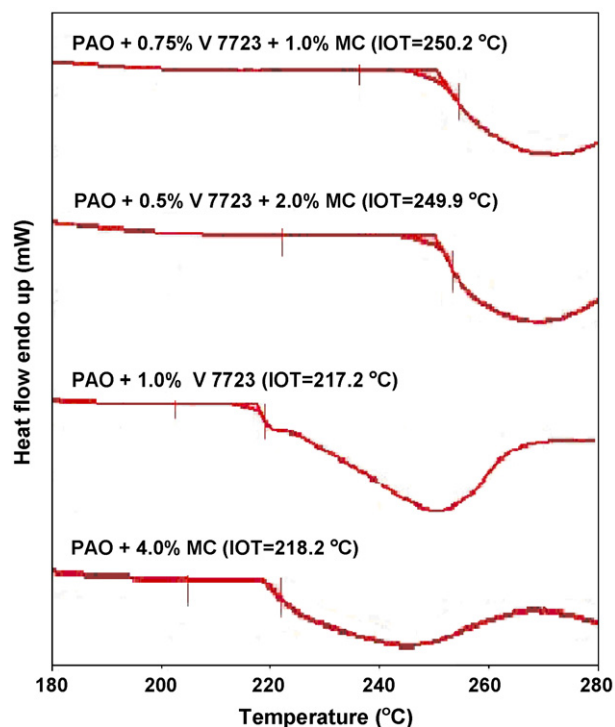


Fig. 2. Temperature programmed DSC test PAO oxidation in the presence of V 7723 with and without MC at 10 $^{\circ}\text{C min}^{-1}$.

coupon used can accelerate oxidation of oil as catalyst. In order to observe synergism of V 7723 with MC clearly, corrosion inhibitor V 887 was mixed with V 7723, which not only prevents catalytic oxidation from ions of iron, but also improve antioxidation property slightly [35].

Usually, less weight loss means that a lubricant maintains better resistance to internal oxidative degradation under high temperatures. The PMOT evaluation of PAO oil containing 0.5% V 7723 and 0.5% V 887 with and without 1.0% MC was illustrated in Fig. 4. The results indicate that adding MC significantly reduced oil weight loss of the PAO oil containing V 7723 and V 887. In other words, the complex can improve effectively oxidation stability of oils.

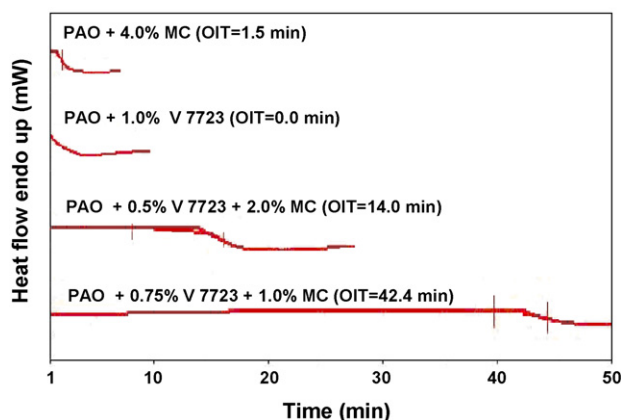


Fig. 3. Isothermal DSC test of PAO oxidation in the presence of V 7723 with and without MC at 200 $^{\circ}\text{C}$.

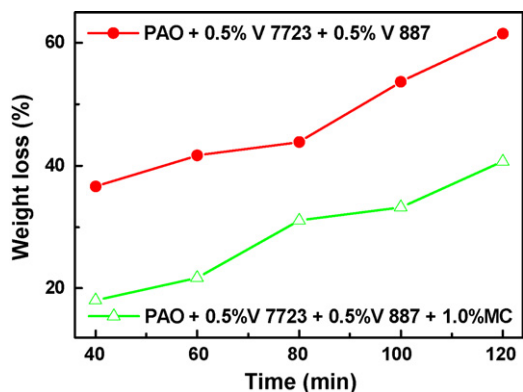


Fig. 4. Time profile of weight loss for PAO containing V 7723 and V 887 with and without MC.

3.3. FTIR analysis

Similar results were found in FTIR study from PMOT test. Figs. 5 and 6 show FTIR spectra of PAO containing 0.5% V 7723 and 0.5% V 887 with and without 1.0% MC at different times of oxidation in PMOT test. In Fig. 5, with increase of oxidation times, the area of the carbonyl band becomes wider and deeper, indicating an increasing level of degradation and also a greater variety of oxidation products. Moreover, hydroxyl groups are detected to an appreciable level after 60 min oxidation, which suggests that a great number of carboxylic acid were formed in oxidized oils. In Fig. 6, there are almost not carbonyl peak occurred in FTIR before 100 min yet, and weak carbonyl peak was only detected in FTIR at 120 min with few hydroxyl group. These observations confirm that addition of MC can significantly enhance the oxidation induction time of oils.

In addition, the plots of the CBI of the oils against time are shown in Fig. 7. It is also seen that lower CBI values are obtained with addition of MC comparing to oil containing V 7723 and V 887, which are agree well with the results from DSC and the weight loss form PMOT. Therefore, CBI is an effective index

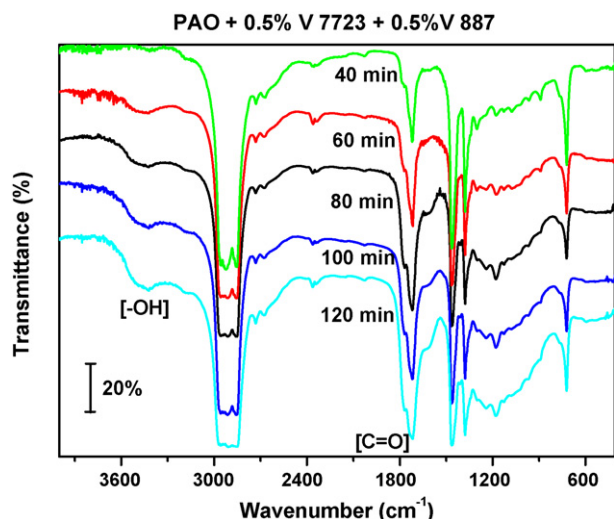


Fig. 5. FTIR spectra of oil samples containing V 7723 and V 887 at different times of oxidation in PMOT test.

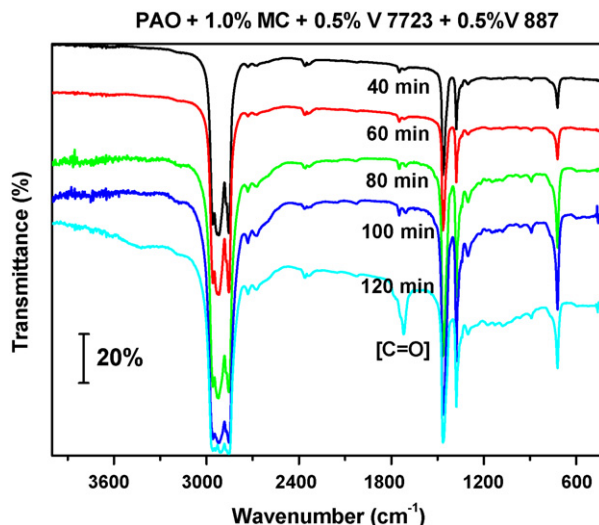


Fig. 6. FTIR spectra of oil samples containing V 7723, V 887 and MC at different times of oxidation in PMOT test.

to evaluate antioxidation properties of oils containing different additives.

4. Discussion

Scant literature information is available to explain the antioxidative synergism of SPFOMCs with antioxidants. Four possible mechanisms can be considered. The first one is that MC directs the base oil to form oxidation products other than acid or sludge without change in oxidation rate, but data on the isothermal DSC test clearly indicate that the oxidation rate was greatly reduced by MC addition. In the second one, MC may form free radicals and interfere with autoxidation, but it did not exhibit antioxidation in PAO lubricant, which did not agree with this proposal. The third one was proposed by Piccourt et al. [36] that the molybdenum compounds can coordinate with the N atoms of succinimide additives and prevent the molecule from chemical decomposition due to steric effects, so we suppose that MC may form a satisfactorily stable chemical bond with N or S atoms of V 7723 by the coordination effect, consequently

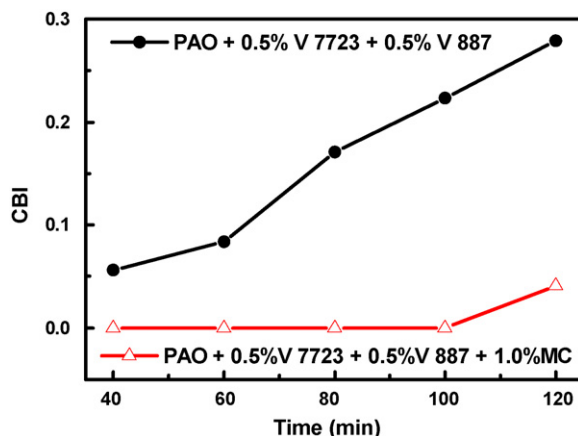


Fig. 7. Time profile of CBI for PAO containing V 7723 and V 887 with and without MC.

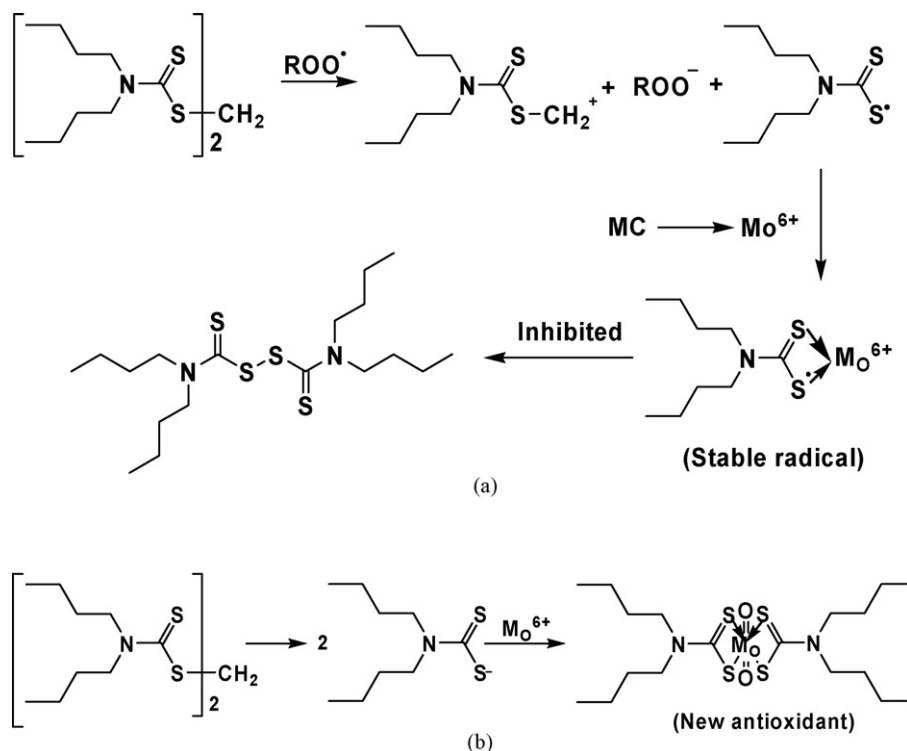


Fig. 8. Oxidation inhibiting process of antioxidant V 7723 in the presence of MC; (a) formation of stable radical; (b) formation of new antioxidant.

it will be much less sensitive against oxidation and has thermal effects than original materials. For instance, molybdenum of MC may coordinate with $(C_4H_9)_2NSCS^{\bullet}$ produced from V 7723 to form an intermediate radical, which will be more stable than original radical, and can inhibit interreaction of original radical, so that its efficiency to scavenge radicals was improved effectively (see in Fig. 8(a)). Finally, molybdenum dialkyldithiocarbamate (MoDDC) is widely used as good antioxidant in lubricants [37,38], the authors suppose that MC can exchange with V 7723 to form a new antioxidant with similar structures of MoDDC, which may exhibit good antioxidation properties (see in Fig. 8(b)). Therefore, we propose that MC can improve effectiveness of V 7723 antioxidant, which were contribute to stable intermediates exerting a shielding effect and formation of a new antioxidant similar to MoDDC.

However, the pattern and structure of the coordination of molybdenum with the N or S atoms of V 7723 antioxidant and whether new antioxidant was formed are not clear. A great deal of work is still required to evidence these hypotheses.

5. Conclusions

- (1) In the isothermal DSC oxidation test, MC shows synergic antioxidation with V 7723 in the PAO synthetic lubricant. When combining with V 7723 and V 887, MC can effectively reduce the weight loss of PAO oil and oxidation products produced in PMOT test.
- (2) The oil weight loss and CBI values are good indexes for evaluating the antioxidative effects of different additives in lubricants.

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