lubricants

Article

Impact of Fatty Triamine on Friction Reduction Performance of MoDTC Lubrication Additive

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Abstract: The impact of a fatty triamine (Triameen YT) additive was investigated on the friction performance and stability of molybdenum dithiocarbamate (MoDTC) in the formulations containing polyalphaolefin synthetic base oil (PAO) and zinc dialkyldithiophosphate (ZDDP). Triamine has no significant effect when mixed with MoDTC and ZDDP, but it improves the performance of MoDTC alone. However, in the MoDTC—Triamine—PAO solutions, a chemical reaction easily occurred and a reddish precipitate was formed upon storage. According to IR, XPS, TEM, and XAS characterizations, this precipitate is poorly crystalline layered alkylammonium oxothiomolybdate. Formation of the precipitate impaired the tribological performance by decreasing the number of active species delivered at the sliding contact interface. However, low friction coefficients were recovered by redispersion of the precipitate in PAO.

Keywords: organic additives; tribochemistry; molybdenum-based additives; electron microscopy; EXAFS

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1. Introduction

Friction modifiers (FM) are applied in the lubrication formulations to lower friction in automotive engines, and as a consequence, to prolong the engine's lifecycle, and to reduce energy consumption and CO_2 emissions [1]. Colloidal MoS_2 suspensions were first patented in 1939 as FMs, for their promising friction performance [2]. However, these colloidal suspensions were poorly stable in the hydrocarbon lubricant base. To overcome the poor dispersibility of MoS_2, oil-soluble molybdenum-based FMs were proposed [3–5]. The main molybdenum-based FMs currently used in lubrication are molybdenum dialkyldithiophosphate (MoDTP) and dialkyldithiocarbamate (MoDTC, Figure 1). These compounds are known to lower the friction coefficient (FCo) towards the range of 0.05–0.08 [6,7]. In the previous work, a synergistic effect was reported for a lubrication system composed of amide-molybdate and anti-wear zinc dialkyldithiophosphate (ZDDP) in the presence of a fatty triamine. Indeed, stabilizing the formulation over time, the addition of a fatty triamine allowed a further decrease of the friction coefficient down to 0.02 [8]. In combination with ZDDP, amines demonstrated improved friction [9,10]. In the paper by Lundgren et al., MoDTC was considered to be a booster, added to a set of amines, which were regarded as the main friction modifiers [11]. In another study, when combined with ZDDP, MoDTC showed decreased friction, but significantly increased wear [12]. However, the physical origin of the friction modification as well as the nature of chemical interactions between the additives still remains unclear.

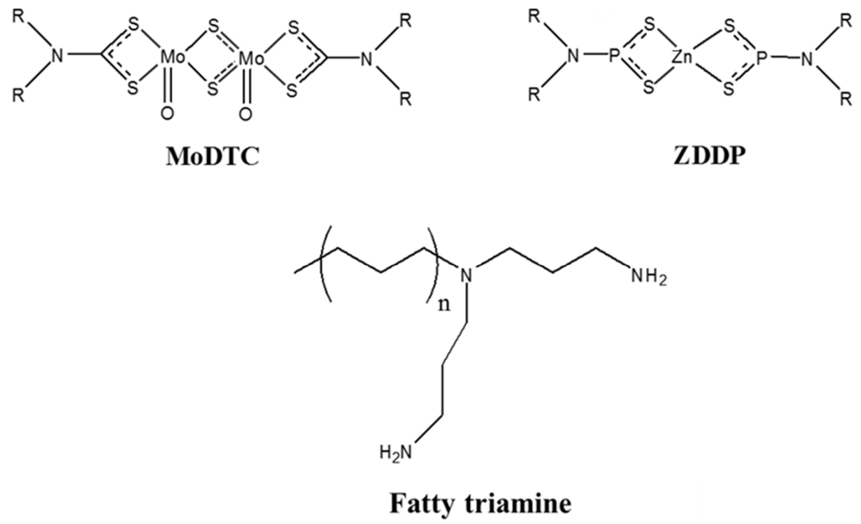


Figure 1. The chemical formula of MoDTC, ZDDP, and Triameen YT (further called also "fatty triamine" or "triamine").

The aim of this work is to investigate the impact of a fatty triamine, Triameen YT on the stability and friction performance of well-known MoDTC FM. To this aim, several additive combinations were tested, including MoDTC alone and MoDTC in the presence of ZDDP and/or fatty triamine. The products of chemical interactions in these mixtures have been identified using several physical and chemical techniques.

2. Methods

2.1. Additives and Lubricants

Lubricant formulations were prepared by blending MoDTC friction modifier from Vanderbilt, ZDDP anti-wear additive from Lubrizol, and fatty triamine N,N-bis(3-aminopropyl) alkylamine from AkzoNobel (Figure 1). The formulations were prepared by dissolving MoDTC alone or in combination with ZDDP and/or Triameen YT, in a synthetic Poly-Alpha-Olefin (PAO4) base oil having a dynamic viscosity of about 4.9×10^{-3} Pa.s. The additives contents were 400 ppm of Mo, 1% wt. of ZDDP, and 0.5% wt. of Triameen YT.

2.2. Tribological Experiments

The tribological tests were carried out on a linear reciprocating ball-on-flat tribometer. An AISI 52100 steel ball on AISI 52100 steel flat configuration was used. The surface roughness varied between 5 and 10 nm, and the hardness and biaxial Young modulus were 9 GPa and 210 GPa, respectively. Mild/severe conditions of sinusoidal motion were applied to generate tribofilms. The maximum sliding speed in the center of the track was $0.1\ \text{m}\cdot\text{s}^{-1}$, the maximum initial Hertzian contact pressure was 500 MPa. The tests were performed at 80 °C and 110 °C, for 1 h duration. For these sliding conditions, the thickness of the lubricant film at the maximum speed was around 10 nm ($\lambda \sim 1$). To remove surface contaminants before the tribological test both ball and flat were ultrasonically cleaned in heptane. For each sliding cycle, an average friction coefficient (FCo) was calculated from 1000 instantaneous FCo measurements. Each tribological test was reproduced four times.

2.3. Characterizations

X-ray photoelectron spectroscopy (XPS) analyses of the flat specimens were carried out on a ULVAC-PHI Versa Probe II spectrometer with a monochromatized Al Kα X-ray source at 1486.6 eV. The size of the X-ray spot was 50 μm and the energy scale was calibrated using C 1s signal from adventitious aliphatics, placing the binding energy (BE) at 284.8 eV. A survey spectrum on a wide range of 1200 eV was recorded at first, in order to identify all chemical elements. Then the individual photopeaks were scanned over a smaller range of

15–25 eV. Fitting and quantification of the XPS peaks were carried out using PHI multipack software and Shirley Wagner sensitivity factors. Prior to XPS analyses of the tribofilms the samples were cleaned in heptane to remove the residual lubricant.

Attenuated Total Reflectance Infrared spectra (ATR-IR) were recorded using an Agilent Cary 630 FTIR spectrometer (Agilent Technologies, Santa Clara, CA, USA).

Transmission electron microscopy (TEM) was performed on a JEOL 2010 device with 200 kV accelerating voltage. The samples were dispersed in heptane by ultrasound and then the suspension was dropped onto a holey carbon copper grid. The images were analyzed using Digital Micrograph Gatan™ software.

X-ray absorption spectra (XAS) were obtained at the BM30b (CRG-FAME) beamline of the ESRF synchrotron [13]. The Mo K-edge spectra were measured in the transmission mode, using a monochromator a Si(220) crystal. For the spectra alignment, the first inflection of the MoK edge of the Mo foil reference was placed at 20,000.0 eV. The data treatment was carried out using FEFF [14] and VIPER [15] software. Extended X-ray Absorption Fine Structure (EXAFS) spectra were fitted in both R and k spaces, using as fitting variables coordination numbers (CN), interatomic distances (R), distance variance parameter (σ^2), and energy shift (ΔE_0). The $S_0{}^2$ parameter was put at 0.8.

3. Results and Discussion

3.1. Friction Reduction Performances of MoDTC-Based Lubricant Formulations

The effect of Triameen YT was investigated by testing different formulations in PAO at 80 and 110 °C, two temperatures representative of engines lubrication. The evolution of friction coefficient (FCo) vs. time is shown in Figures 2 and 3, respectively. The steady-state values of FCo are summarized in the Table 1. In agreement with previous studies [16], for both temperatures, the addition of MoDTC to base PAO4 oil decreases the FCo from 0.14 to 0.07 (Table 1). The addition of ZDDP to the MoDTC-PAO4 mixture leads to a slight further decrease in FCo to 0.06 ± 0.01, in agreement with the literature [17,18]. For the MoDTC+Triameen YT binary composition, the FCo value decreased to 0.05. However, in order to simulate a more prolonged use, the MoDTC+Triameen YT formulation was pre-heated for 12 h at 80 °C before the friction test, and the boosting effect of the fatty amine was lost. At 80 °C unstable curves and a higher FCo value of 0.07 were obtained (Figure 2). At the same time, we noticed that a reddish precipitate was formed on the bottom of the flask after pre-heating for 12 h at 80 °C (Figure 4). However, if the test was conducted at 110 °C then low and stable FCo of the pre-heated MoDTC+Triameen YT was reached again (FCo = 0.05). Finally, the ternary formulation made of MoDTC+ZDDP+ Triameen YT showed a higher Fco (0.10–0.09). Overall, our experiments reveal that when Triameen YT is added in a binary mixture with MoDTC, a low value of FCo is rapidly reached, indicating a synergistic effect. However, this boosting effect of the fatty amine appears fragile and might be easily destroyed by some chemical interaction in the binary system. Indeed, after heating or after the addition of a third component such as ZDDP, the boosting effect disappears. Our results are in qualitative agreement with the work by Lundgren et al. [11].

Table 1. Steady-state values of FCo obtained for different lubricant formulations at 80 and 110 °C.

Formulation	FCo at 80 °C	FCo at 110 °C
PAO 4	0.14	-
MoDTC	0.07	0.07
MoDTC+ZDDP	0.06	0.06
MoDTC+Triameen YT	0.05	0.05
MoDTC+Triameen YT pre-heated *	0.07	0.05
MoDTC+Triameen YT +ZDDP	0.10	0.09
MoDTC+Triameen YT pre-heated+ZDDP **	0.07	0.07

* MoDTC+Triameen YT formulation was pre-heated for 12 h at 80 °C before the test. ** MoDTC+Triameen YT formulation was pre-heated for 12 h at 80 °C before introducing ZDDP at room temperature, before the test.

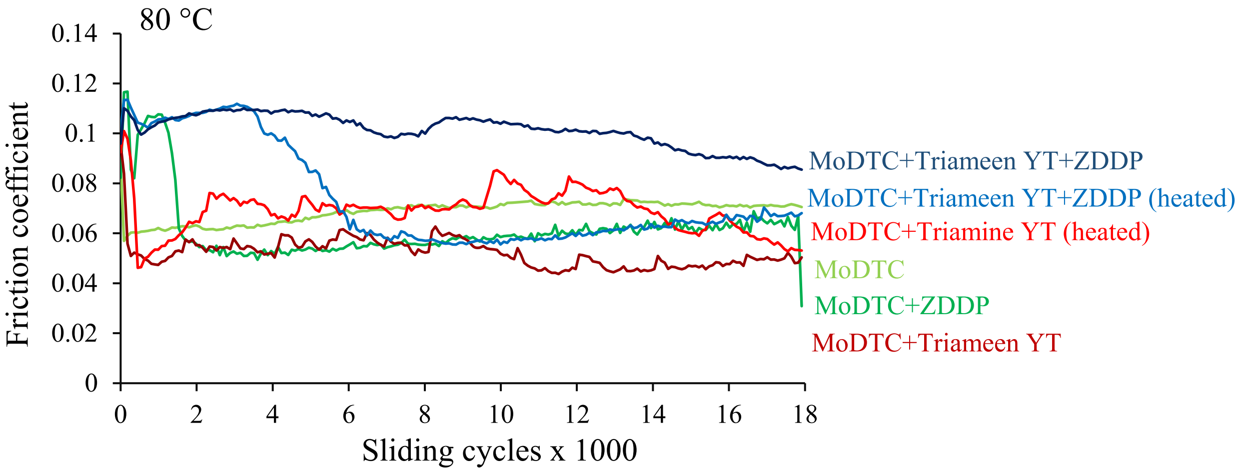


Figure 2. Evolution of FCo vs. sliding cycles at 80 °C for the formulations listed in Table 1.

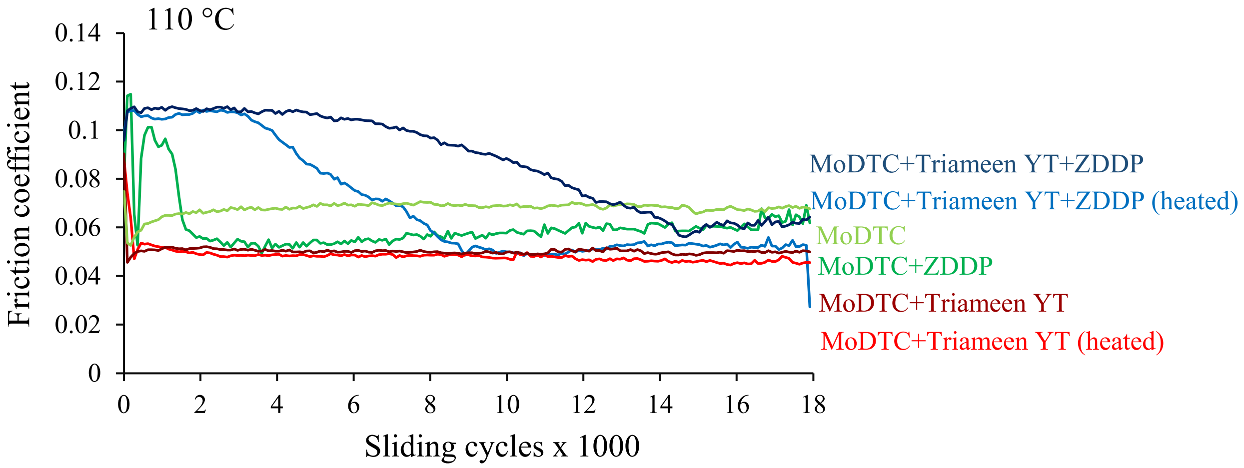


Figure 3. Evolution of FCo vs. sliding cycles at 110 °C for the formulations listed in Table 1.

3.2. Stability of MoDTC-Based Lubricant Formulations

The observed complexity and non-additivity of the tribological behavior suggest complex chemical interactions between the components. Most importantly, it appears that during the storage, Triameen YT reacts with MoDTC and this interaction decreases the tribological performance. The visual appearance of the MoDTC-based formulations (Figure 4a) indicates that they are all stable, except the MoDTC+Triameen YT one. This one rapidly formed a reddish precipitate (after only 48 h of storage at room temperature). To estimate the tribological properties of this precipitate, it was separated from the rest of the liquid and then re-dispersed by sonication for 30 min in the PAO4, without any other additive (Figure 4b). The resulting turbid suspension was then tested at 80 and 110 °C (Figure 5).

For the redispersed precipitate, the high friction coefficient was obtained at 80 °C (FCo = 0.09). However, at 110 °C, the FCo decreases to a value close to that provided by the fresh MoDTC+Triamine YT formulation (FCo = 0.05). Therefore, we suppose that the precipitate contains both triamine and MoDTC moieties in some bounded form and can deliver them during the tribological test performed at a sufficiently high temperature. Nevertheless, we can notice the formation of precipitate upon storage strongly impairs the tribological performance as it withdraws both MoDTC and Triameen YT from the liquid phase. Due to the potential interest of this precipitate, further study of its chemical nature has been undertaken.

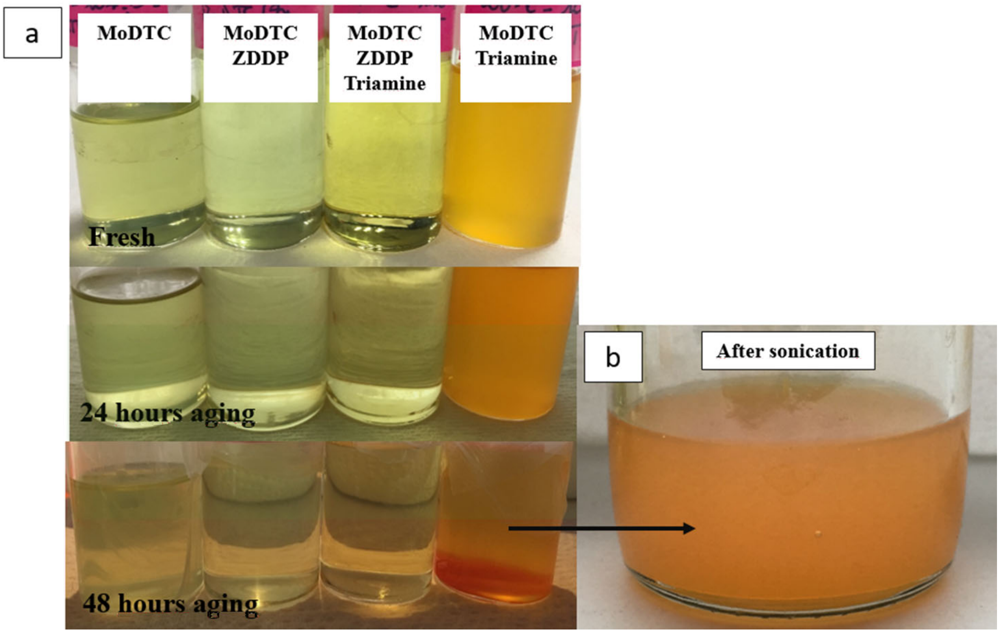


Figure 4. Pictures of MoDTC-based lubricant formulations in PAO4 base oil made of: (**a**) MoDTC, MoDTC+ZDDP, MoDTC+ZDDP+ Triameen YT, MoDTC+Triameen YT, and (**b**) MoDTC+Triameen YT reddish precipitate redispersed in PAO by sonication for 30 min.

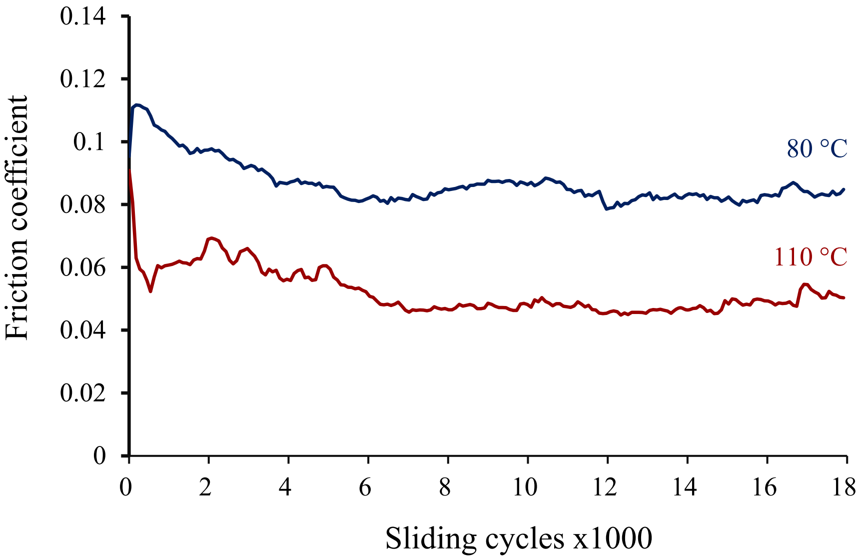


Figure 5. Friction coefficient vs. sliding cycles obtained with the redispersed reddish precipitate in PAO at 80 °C and 110 °C.

3.3. Chemical Nature of the Precipitate Formed from MoDTC and Triameen YT

3.3.1. IR Spectroscopy Analysis

The MoDTC+Triameen YT precipitate was collected, washed with heptane, and dried. It was first characterized by IR spectroscopy and compared to the triamine YT spectrum. The two spectra bear considerable similarities (Figure 6). For both triamine YT and reddish precipitate, aliphatics C-H vibrations are observed between 2800 and 2920 and between 1380 and 1525 cm^{-1}. Amine N-H vibrations are located at circa 1600 and 700 cm^{-1} (NH_2 bending modes). C-N absorption bands are observed between 1050 and 1200 cm^{-1} [19]. According to Fringeli et al., [20] the C-N bond stretching mode in organic amines, located around 914 cm^{-1} splits in three bands for an alkyl chain having more than 4 carbon atoms. The band at 720 cm^{-1} corresponds to the rocking mode of the CH_2 group for a number of carbon higher than five. Indeed, these are common features, a novel group of vibrations appearing on the precipitate, coming from different modes of Mo-O vibrations in the oxothiomolybates, with intense lines at 667, 932, and 982 cm^{-1} [21]. As Mo-S bonds are less polar than Mo-O ones, they are not visible in the IR spectrum. Moreover, a band at 1525 cm^{-1} appeared, which can be attributed to N-H bending in the R_3NH^+ anion, with a frequency strongly dependent on Van der Waals interactions in the system [22], but considerably overlapping with the individual MoDTC band [23]. Therefore, the IR-spectra attest that the precipitate is composed of both molybdenum- and nitrogen-containing fragments coming from both MoDTC and triamine YT, and present probably as protonated alkylammonium cation and a molybdenum-containing anion, perhaps an oxothiomolybdate.

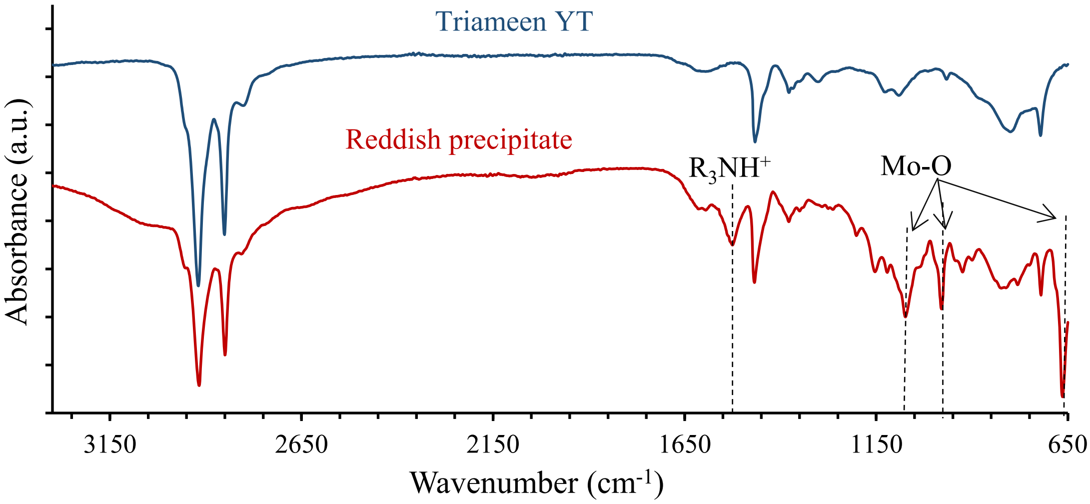


Figure 6. Attenuated Total Reflectance Infrared (ATR-IR) spectra of the reddish precipitate and Triameen YT.

3.3.2. XPS Spectroscopy Analysis

The surface of the solid reddish precipitate was then analyzed by XPS. The results are shown in Figure 7 for Mo3d, S2p, and O1s regions. Mo3d and S2p XPS spectra were fitted with two different Mo and S oxidation states. Mo3d and S2p peaks located respectively at 230.6 eV and 161.7 can be assigned to thiomolybdate $[MoS_4]^{2-}$ or oxothiomolybdate $[MoO_xS_y]^{2-}$ species [24,25]. A Mo3d peak located at 232.0 eV, accompanied by an O1s contribution at 530.5 eV corresponding to molybdenum (VI) oxide species [26,27]. The last S2p component at 168.1 eV is attributed to sulfate species that always appear under aerobic conditions in the molybdenum sulfide materials [28,29]. Overall, the XPS spectra suggest that the precipitate contains molybdenum in an oxosulfide environment.

3.3.3. TEM/EDS Analysis

The reddish solid was then analyzed by TEM/EDS. Several zones of the TEM grid were studied. Amorphous and shapeless particles of hundreds nm scale size were observed in all instances. In most cases, lamellar structure is hardly seen (Figure 8). However, in rare zones, clearer crystalline structure was observed with versatile but always large inter-reticular distances from 2.6 to 5.7 nm (Figure 9).

The composition, however, is homogeneous, i.e., the same species are present but the degree of the material crystallinity varies. The atomic S/Mo ratio for this lamellar compound measured from EDS analysis is close to with mean value of 3.98 and a standard deviation of 0.14. Therefore, according to IR, XPS, and TEM/EDS analyses, the reddish solid seems to be an alkylammonium thiomolybdate-like compound.

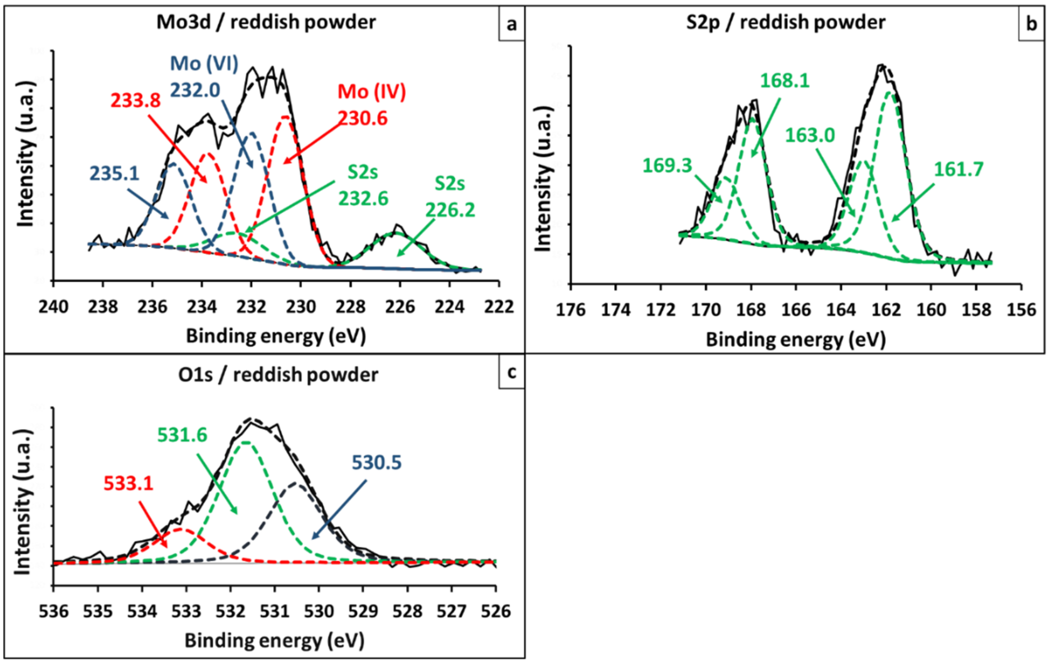


Figure 7. XPS spectra of the reddish precipitate: (**a**) Mo 3d, (**b**) S 2p, and (**c**) O1s signal.

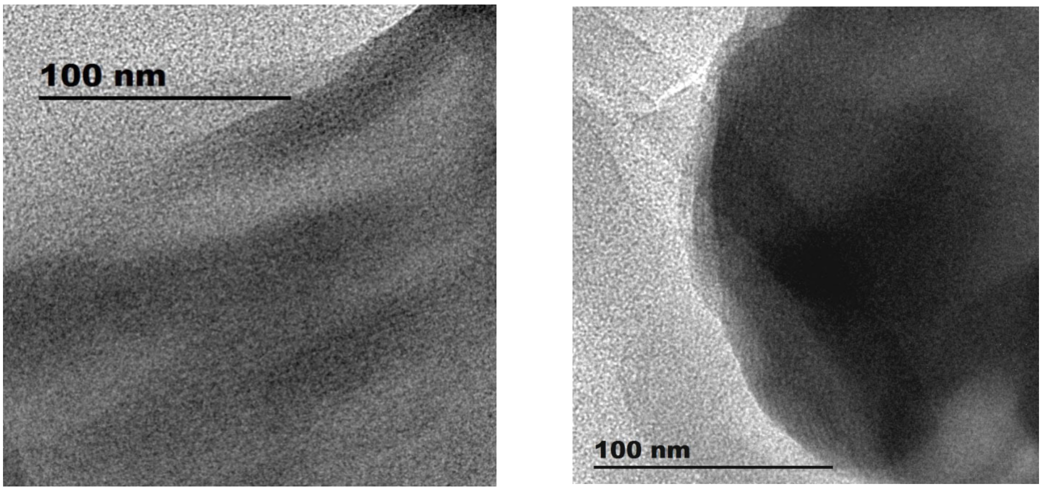
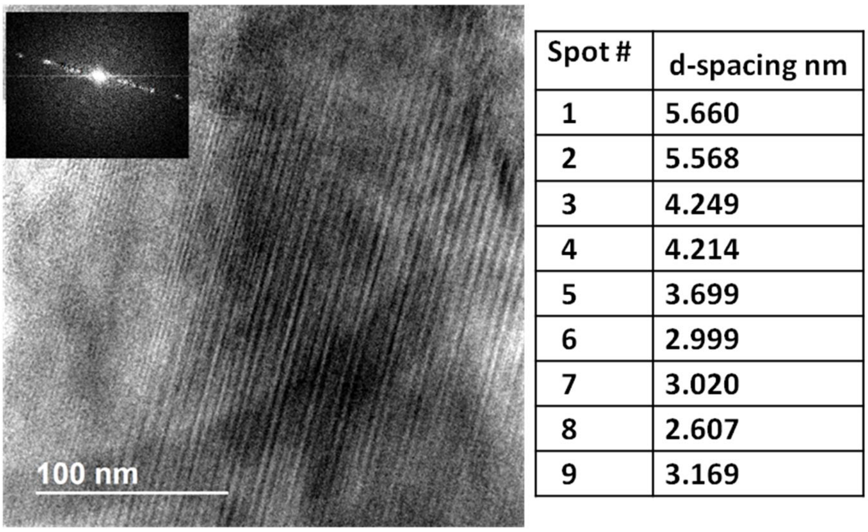


Figure 8. TEM pictures of the reddish solid precipitated from the mixture of MoDTC+Triameen YT in PAO4. The stacks of curved layers can barely be distinguished within mostly amorphous matter.

Such layered structures are typical for alkylammonium thiomolybdates, for example, cetylammonium thiomolybdate [30]. Large interlayer distances could be naturally explained by the large size of the triamine molecule and the multitude of ways the flexible aliphatic chains of alkylammonium cations could be packed between the layers of thiomolybdate anions.

3.3.4. XAS Analysis

To deeper understand the reactivity of the “reddish precipitate” it seemed necessary to go further into its structural characterization. Indeed, it remains unclear what is molybdenum coordination and whether the MoDTC structural unit is destroyed or if the “reddish precipitate” is just an adduct reversibly formed between the triamine and MoDTC. Hard X-ray absorption spectroscopy is well suited to investigate coordination in such ill-defined crystalline structures. It has been previously applied to analyze the evolution of P, S, and Mo species in the tribofilms [31].



Spot #	d-spacing nm
1	5.660
2	5.568
3	4.249
4	4.214
5	3.699
6	2.999
7	3.020
8	2.607
9	3.169

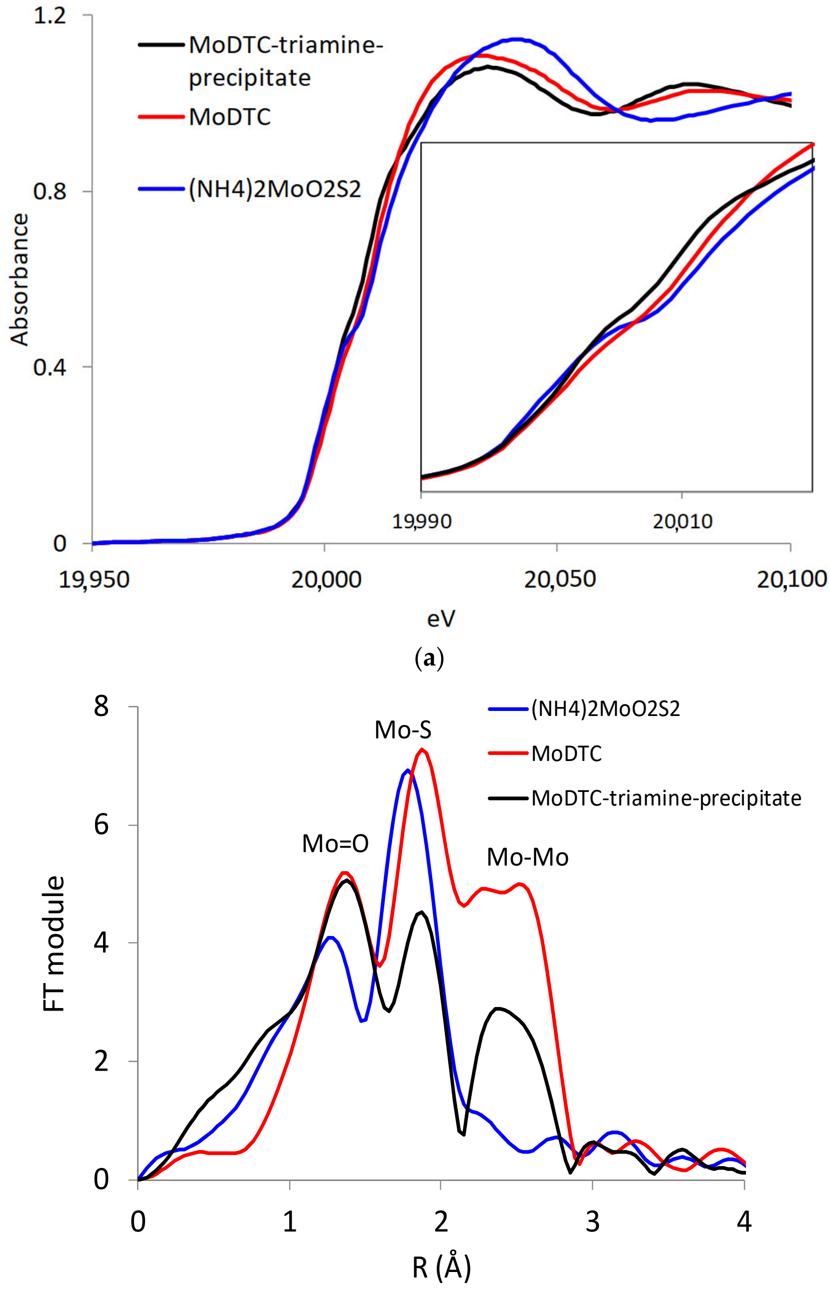
Figure 9. TEM image and numerical diffraction (inset) of the reddish precipitate. The table in the right panel summarizes the inter-reticular distances corresponding to the diffraction spots.

XAS spectra of the starting MoDTC, reddish precipitate, and ammonium oxothiomolybdate $(NH_4)_2MoO_2S_2$ (used as a reference containing both Mo-O and Mo-S bonds) are shown in Figure 10. The XANES spectra (Figure 10a) of the three compounds show slight differences between the main jump position and the pre-edge feature intensity. The similarities observed in the spectra, mainly the presence of characteristic features at about 20,008 eV, suggest non-centrosymmetric coordination of the Mo atom in all three samples. This feature merged with the main jump was previously attributed to the 1s → 4d transition and to the ligand p- orbitals mixing with the 4d orbitals of molybdenum [32,33]. The intensity of this transition decreases with the increasing amount of S in the molybdenum coordination sphere. Previous observations showed that this feature is more intense for Mo=O than for Mo=S groups [34]. XANES spectra suggest a decrease of the relative oxygen content in the sequence $(NH_4)_2MoO_2S_2$ > MoDTC ~ precipitate. The energy of the main jump slightly changes in the sequence $(NH_4)_2MoO_2S_2$ > MoDTC ~ precipitate in agreement with the sequence of the pre-edge intensity.

The results of EXAFS fitting for three spectra presented in Figure 10b are given in Table 2. The ammonium oxothiomolybdate reference shows the expected short Mo=O (1.76 Å) and Mo=S (2.22 Å) bonds. The EXAFS spectrum of MoDTC shows a pronounced Mo=O peak, Mo-S one, and the heavy neighbor (Mo-Mo) at 2.81 Å. In the MoDTC, similar to ammonium oxothiomolybdate double Mo=O bonds (1.78 Å) but longer (single) Mo-S bonds are present, in agreement with the chemical structure (Figure 1).

Table 2. Mo K edge EXAFS fitting parameters.

Shell	CN	R(Å)	σ^2(Å^2)	ΔE_0
		$(NH_4)_2MoO_2S_2$		
O	2	1.76(3)	0.0035(5)	0.1(5)
S	2	2.22(2)	0.0050(6)	0.1(5)
		MoDTC		
O	0.9(2)	1.78(2)	0.004(1)	0.1(5)
S	3.9(5)	2.41(2)	0.008(2)	0.1(5)
Mo	1.0(2)	2.81(2)	0.007(2)	0.1(5)
		Reddish MoDTC+ triamine precipitate		
O	1.0(3)	1.75(6)	0.006(2)	−0.4(5)
S	3.2(6)	2.32(6)	0.009(4)	−0.4(5)
Mo	0.4(3)	2.81(5)	0.008(5)	−0.4(5)



(**a**)

(**b**)

Figure 10. XANES (**a**) and FT EXAFS (**b**) spectra at Mo K edge for the samples of MoDTC, "reddish precipitate" and ammonium oxothiomolybdate $(NH_4)_2MoO_2S_2$ (used as reference).

In the reddish precipitate, the coordination of molybdenum is substantially different from the initial MoDTC, as follows from the comparison of FT spectra and fitting results (Figure 10b). In the reddish precipitate, the Mo=O bond is obviously preserved, but the CN values are decreased for both the Mo-S and Mo-Mo bonds. Moreover, in the reddish precipitate, the Mo-S bond is shorter than in MoDTC. This suggests a partial breaking of the Mo-S-Mo bonds in the MoDTC dimer, probably occurring due to nucleophilic attack by an amine, leading to monomeric oxothiomolybdate species.

It can therefore be supposed, that MoDTC reaction with triamine YT leads to the formation of an ionic compound (alkylammonium oxothiomolybdate), which, because of the increased charge separation is less soluble in the base oil than the more covalent MoDTC molecule.

From the above, it appears that improved friction reduction performance observed for the binary combination MoDTC-triamine is related to their interaction leading to the formation of alkylammonium oxothiomolybdate species. The interaction between MoDTC and triamine starts immediately, as indicates color change toward a red-orange shade, which occurs just upon mixing (Figure 4a). Such species are sparingly soluble in oil, but for some time they could be preserved in the (metastable) solution due to the high viscosity of the PAO4 solvent and low nucleation rate. This MoDTC-triamine interaction is obviously favorable for the lubricating properties as far as no bulky solid precipitation occurs. However, even in the latter case, good performance could be recovered by ultrasound redispersion. There are few patents, mostly from the last century, reporting on thiomolybdates solubilization and their interesting friction reduction performances [35–39]. The origin of their effectiveness could be due to the presence of molybdenum in the already sulfurized state which easily decomposes to form MoS_2 under shearing conditions. However, precipitation of oil-insoluble alkylammonium oxothiomolybdate observed in the binary mixture MoDTC-triamine deteriorated the lubricant performance, probably by decreasing the number of active species delivered at the sliding contact interface.

Remarkably, the addition of the third component ZDDP prevents the precipitation between MoDTC and triamine, but it also deteriorates the lubricant performance (Table 1). In the MoDTC-based ternary formulations, there was no change of color upon mixing (Figure 4). It can be supposed that ZDDP interacts preferentially as a Lewis acid with basic triamine and therefore prevents it from the interaction with MoDTC. The chemical nature of a compound (or adduct) formed between thiamine and ZDDP remains beyond the scope of this study and could be studied in the future. However, it seems obvious that ZDDP-triamine interaction in the presence of MoDTC is not favorable for the tribological properties in boundary lubrication conditions.

Several studies have shown the impact of friction modifiers containing amine functionality on ZDDP behavior. Thus, Dawczyk et al. studied the influence of ethomeens—(ethoxylated alkylamine organic friction modifiers) on the pre-formed ZDDP tribofilms [40]. They found that as a function of the amine structure (the number of ethoxy groups), there is a balance between ethomeen ability to reduce friction and its harmful effect on the ZDDP tribofilm. Direct investigations were also reported on the tribofilm formation rate and friction reduction performance of ZDDP-containing oils using blends, containing amine and ZDDP additives. Eriksson et al. have shown that both a primary amine and a tertiary ethomeen inhibited ZDDP tribofilm formation, confirming the surface adsorption competition between them [10]. Note that direct comparison is difficult, because ethomeens, while having an amino group in the structure, are chemically different from the fatty amines due to the presence of ethoxy groups. Lundgren et al. also studied the impact of three different fatty amines on ZDDP film formation and friction with and without MoDTC [11]. They found that amines reduced the effect of ZDDP, in line with the hypothesis that their acid-base interaction is deleterious for tribofilm formation.

4. Conclusions

This work investigates the chemical interaction of fatty triamine Triameen YT with MoDTC and its impact on the PAO formulation's friction performances and stability. The addition of triamine does not reduce the FCo of binary MoDTC+ZDDP formulation in severe boundary lubrication conditions, but it reduces FCo if mixed with MoDTC alone. However, despite this synergy, PAO solutions containing MoDTC and triamine are unstable. Solid precipitate is formed in the binary formulations, which appear to be alkylammonium oxothiomolybdate compound. Formation of this solid is deleterious for the lubrication performance at 80 °C, but at 110 °C the formulations recover their interesting FCo reduction performances, probably due to partial redissolution of the precipitate. A booster effect of Triameen YT on the MoDTC performance has been recovered after separation and ultrasound-assisted redispersion of the precipitate in PAO. This result suggests the possible efficiency of alkylammonium oxothiomolybdate species as friction modifiers.

Furthermore, efforts might be directed toward the characterization of tribofilm properties obtained from these formulations formed on different substrates such as stainless steel or DLC. Tribochemical interactions of the materials' surfaces with lubricant additives are crucial for the genesis of efficient anti-wear and friction-reducing films in boundary lubricated systems. Our current knowledge of the tribochemistry processes is mostly limited to the post-mortem characterizations of the tribofilms in ambient conditions. In future studies, *in operando* analysis of tribofilms (XAS, Raman.) would provide additional valuable insights.

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