A Facile and Effective Method to Improve the Dispersibility of WS₂ Nanosheets in PAO8 for the Tribological Performances

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Abstract: The sedimentation of WS2 nanosheets in PAO8 is resolved by a facile method with the immobilization function of 1-methyl-2, 4-bis (N-octadecylurea) benzene (MOB), and tribological performance and mechanism of the composite lubricant are systematically investigated. Compared with blank PAO8, the composite lubricants have better tribological performance, which is attributed to the synergistic effect of WS2 and MOB. The immobilization function of MOB because of the network structure prevents the agglomeration and sedimentation of WS2 nanosheets. The boundary films, including tribochemical reaction film and physical absorbing film are formed on the surfaces of the friction pair during the friction process.

Dear editor,

Here we would like to submit our enclosed original research article entitled “**A Facile and Effective Method to Improve the Dispersibility of WS₂ Nanosheets in PAO8 for the Tribological Performances**”, which we would like to be considered for publication in **Tribology International**.

The authors: *Ruochong Zhang, Dan Qiao, Xuqing Liu, Zhiguang Guo, Meirong Cai, Lei Shi*

In the present paper, a facile and novel method has been proposed to resolve the agglomeration problem of WS₂ nanosheets in the PAO8 by utilizing the immobilization function of 1-methyl-2, 4-bis (N-octadecylurea) benzene (MOB). The results show that the excellent tribological performances are attributed to the synergistic effect of WS₂ nanosheets and MOB. The immobilization function of MOB promotes WS₂ nanosheets to disperse uniformly in PAO8 and reach the full potential in lubricating properties. The boundary lubricating film, containing tribochemical film and physical absorbing film are formed to avoid the direct contact of friction pair. The combined actions of WS₂ nanosheets and MOB give the contribution to the admirable lubricating properties of the composite lubricant.

We confirm that this manuscript has not been published elsewhere and is not under consideration by another journal. All authors have approved the manuscript and agree with submission to Tribology International. The study was supported by a grant from the National Natural Science Foundation of China (51405477, 51675512). The authors have no conflicts of interest to declare.

We look forward to hearing from you at your earliest convenience.

Sincerely yours,

Lei Shi

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Dear Editor,

1. The work described here has not been submitted elsewhere for publication, and all the authors listed have approved the manuscript that is enclosed.
2. I have read and have abided by the statement of ethical standards for manuscripts submitted to Tribology International.

Thanks very much for your attention to our paper.

Sincerely Yours,

Lei Shi

Highlights

- The good dispersibility of nanomaterial in base oil was obtained by a facile and effective method.
- The immobilization function of MOB on WS₂ nanosheets in base oil is proved.
- The synergistic effect of WS₂ nanosheets and MOB on lubricating performance is demonstrated in the paper.
- The lubrication mechanisms of the composite lubricant, containing immobilization function of MOB and formation of boundary film were investigated systematically.

Dear Prof. Weimin Liu,

Thanks very much for your email regarding our manuscript again (Ms. Ref. No.: TRIBINT-D-17-00970). We should show our appreciations to you again for your consideration for our manuscript. As for this question proposed by the reviewers and editor, we have carefully checked the whole manuscript again and changed the manuscript according to the referee's comments. Meanwhile, we have further polished the English throughout the manuscript. Some data has been supplemented and perfected to complete the manuscript. The manuscript with and without the revised track are both provided.

Yours sincerely,

Lei Shi

Detailed responses to the comments made by the Editor are listed as follows:

Reviewer #2:

1) **What is the real composition of these boundary layers resulting from the physical absorption and tribochemical lubrication?**

Thanks very much for your question. According to the data of XPS and Raman spectra analysis (Fig.11 and 12, Table 2), not only could MOB and WS₂ nanosheets as additives in PAO8 complicate tribochemical reactions occur, leading to a surface protective film composed of sulphur oxides, organic sulfides, nitrogen oxide, nitrates and iron oxides on the lubricated metal surface, but physical adsorption film of WS₂ nanosheets also formed. This boundary protective layer benefits friction reduction and anti-wear performances.

Fig. 11 XPS spectra of S2p, N1s, O1s, C1s of MOB, WS₂ and the worn scars lubricated by the different lubricants.

Fig. 12 Raman spectra of the wear scars lubricated by (a) PAO8 and (b) PAO8-1% MOB-1% WS₂.

Table 2. Identification of peaks of Raman spectra about wear scars lubricated by PAO8 and PAO8-1% MOB-1% WS₂ under frequency ramp test.

PAO8		PAO8-1% MOB-1% WS ₂	
Frequency/cm ⁻¹	Corresponding compounds	Frequency/cm ⁻¹	Corresponding compounds
210	α -Fe ₂ O ₃ [46-47]	217, 184, 500	α -Fe ₂ O ₃ [46-47]
273	α -Fe ₂ O ₃ [46-47]	350, 417	WS ₂ [28]
386	γ -FeOOH [46, 48]	398	S-C-C deformation vibration [50]
482	α -FeOOH [46]	565	Fe-N-O binding vibration [49]
586	α -Fe ₂ O ₃ , Fe-C-O [46-47, 49]	596	Fe-NO stretching vibration [49]
645	Fe ₃ O ₄ [46]	654	S-CH ₂ stretching vibration [50]
1300	γ -FeOOH [46, 48]	1290	C-N stretching vibration of Aromatic amine [18]
1340	Carbonization [44-45]	1410	N = N stretching vibration of the azo compound conjugated to the aromatic ring [18]
1575	Carbonization [44-45]	1503	NH in-plane bending vibration [51]
--	--	1340, 1575	Carbonization [44-45]

2) What is the reason that these boundary layers are remaining stable for the best performance?

Thanks very much for your question. There are several reasons for the boundary layers to remain stable for the best performance: first, the immobilization performance of MOB promotes the dispersibility of WS₂ nanosheets in PAO8; second, WS₂ nanosheets immobilized in the network of MOB are gradually released on the friction surface, so PAO8-MOB-WS₂ presents the better long-term lubricating performance than PAO8-MOB and PAO8-WS₂; third, the active elements in MOB molecules and WS₂ nanosheets easily react with steel surfaces to produce the stable tribochemical reaction film; finally, the layer structure of WS₂ help WS₂ to form the stable and long-term effective physical absorption film on the surfaces of the friction pairs.

3) Some figures such as 3a, 3b, 4 and even 8 and 9 are not necessary in the manuscript and can be deleted from the proposed manuscript and the corresponding description as to be adopted accordingly.

Thanks very much for your suggestion. In the present work, the excellent

dispersibility and stability of WS₂ nanosheets in PAO8 is obtained and proved by the digital picture in Figure 3. And Figure 8 could demonstrate morphology of wear scars, helping to further understand the tribological process and lubricating mechanism. Therefore, we consider the Figure 3 and Figure 8 are too necessary to delete in the work. According to the suggestion, Figure 4 and Figure 9 were deleted and the corresponding description was adjusted.

Reviewer #3:

- 1) Introduction part must be rewrite taking care of language and completeness of sentences.

Thanks very much for your suggestion. We have rewritten the introduction according to your opinions. We hope that this introduction can satisfy the request.

- 2) Authors didn't provide the testing standards which they have been used in their studies.

Thanks very much for your suggestion. We think the testing standards you mentioned are that of friction tests. The testing conditions chosen in the present work are according to the previous researches and our experimental experience rather than testing standard. The details could be obtained according to following reference:

- (1) Yu QL, Fan MJ, Li DM, Song ZH, Cai MR, Zhou F and Liu WM. Thermoreversible gel lubricants through universal supramolecular assembly of a nonionic surfactant in a variety of base lubricating liquids. ACS Appl Mater Inter 2014; 6: 15783-94.
- (2) Huang GW, Yu QL, Ma ZF, Cai MR and Liu WM. Probing the lubricating mechanism of oil-soluble ionic liquids additives. Tribol Int 2017; 107: 152-62.
- (3) Han Yunyan, Qiao Dan, Guo Yuexia and Feng Dapeng. Tribological performance and mechanism of phosphonate ionic liquids as additives in two hydrocarbon oils. Tribol 2017; 37:27-34.

- 3) Authors have used to demonstrate the stability of nanofluids only by sedimentation. Besides this, authors have to use UV-Visible spectroscopy to strengthen their statement.

Thanks very much for your suggestion. The stabilities of PAO8-1% WS₂ and PAO8-1% MOB-1% WS₂ were demonstrated by UV-Visible spectroscopy in Fig. 4 in the manuscript and the paper has been modified as “The transmittance of PAO8-1% WS₂ and PAO8-1% MOB-1% WS₂ were investigated by UV-Visible spectroscopy in Fig. 4 to further record the stability of the both lubricants. It shows that the transmittance values of the two lubricants are zero for homogeneous dispersion of WS₂ nanosheets in PAO8 oil at the beginning of the test. However, the transmittance value of PAO8-1% WS₂ increases to about 30% after 24 h standing and 60% after 48 h standing, showing the apparent agglomeration and sedimentation tendency. The transmittance value of PAO8-1% WS₂ reaches to nearly 80% after 9 days while that of PAO8-1% MOB-1% WS₂ maintains 0 during the whole process. The results combining that of the above sedimentation experience in Fig. 3 both indicate the excellent stability of gel lubricant.”

Fig. 4 The transmittance of (a) PAO-1% WS₂ and (b) PAO8-1% MOB-1% WS₂ recorded by UV-Visible spectroscopy with the evolution of time.

4) The manuscript needs some data in commercial formulations (like 5W30, 10W40) to demonstrate their true potentials.

Thanks very much for your suggestion. Some relevant data have been provided in the Fig. 9 in the manuscript and the paper has been modified as “Figure 9a and 9b show the picture of 5W30-1% MOB and 5W30-1% MOB-1% WS₂, which indicating the excellent gelation ability of MOB in PAO8 and PAO8 with WS₂ nanosheets. The tribological performances of MOB and WS₂ nanosheets in 5W30 were replenished in Fig. 9c and 9d of the manuscript to illustrate the potential applications of the both additives in the commercial oil. It shows that the COF and wear volume values of 5W30 decrease after the addition of 1% MOB and 1% WS₂. The wear volume value of 5W30-1% MOB-1% WS₂ ($2 \times 10^5 \mu\text{m}^3$) is lower than that of 5W30 ($2.5 \times 10^5 \mu\text{m}^3$), indicating this additive can improve anti-wear property of the commercial full formula lubricant. Combined the COF curve in Figure 9d, the running-in period of 5W30 is alleviated when MOB and WS₂ added, showing the certain lubricating advantages of 5W30-1% MOB-1% WS₂ than that of 5W30 commercial oil.”

Fig. 9 The picture of (a) 5W30-1% MOB and (b) 5W30-1% MOB-1% WS₂ lubricants; (c) Mean COF and wear volume of 5W30, 5W30-1% MOB, 5W30-1% WS₂ and 5W30-1% MOB-1% WS₂ (d) real-time COF of 5W30 and 5W30-1% MOB-1% WS₂.

5) The survey XPS scan of the lubricated sample must be provided.

Thanks very much for your suggestion. The survey XPS scans of different lubricants are provided in the follow Figure 2. The peak of S element is hardly to detect in the

survey spectra for the little content on the wear scar surfaces. However the fine spectra showing in the manuscript are fully demonstrated the existence of S element and the tribochemical reaction of WS_2 . The corresponding contents of the manuscript are not revised.

Figure 1. The survey XPS scan of different lubricants

Reviewer #4:

- 1) p.2, l. 9: now is "van der waals" - should be "van der Waals"

Thanks very much for your reminder. The mistake has been corrected in the revised manuscript.

- 2) p.5, l.15: please provide clearly, how many repetitions had tribological tests and what statistical function (e.g. standard deviation, confidence intervals) was applied for mean values calculating (e.g. Fig. 5 - COF and wear volume)

Thanks very much for your question. In the present work, three repetitive measurements were performed for each tribological process and the standard deviation was used for mean values calculating. The representative repetitive tests are showed in the following Figure 2.

Figure 2 The repetitive tribological tests of (a) PAO8, (b) PAO8-1% MOB, (c) PAO8-1% WS₂, (d) PAO8-1%MOB-1% WS₂.

- 3) authors should present more detailed information concerning the way of wear volume calculation

Thanks very much for your suggestion. The wear volume in the present work is directly calculated by the software of MicroXAM-3D noncontact surface mapping profiler without further processing.

- 4) Fig. 5a - description - I suppose that the unit of wear volume should be cubic micro-meters

Thanks very much for your reminder. The mistake has been corrected in the revised manuscript.

- 5) Fig. 6 - why only extreme cases were investigated (PAO8 and PAO8-1% MOB-1% WS₂)?

Thanks very much for your question. We have adjusted the orders of Figure 6, 7 and 8 for the better organized article structure. The main purpose of the present work was effectively making full use of the merits of MOB and WS₂ nanosheets to enhance the tribological performance of PAO8. And the synergistic effect of both additives in PAO8 had been investigated, showing that PAO8-1% MOB-1% WS₂ possess better friction-reducing and anti-wear performance than PAO8-1% MOB, PAO8-1% WS₂ and PAO8. Then the systematic tribological performances of PAO8 and PAO8-1% MOB-1% WS₂ were investigated to further evaluate the improvement of lubricating properties.

- 6) Fig. 6 - how to explain the decrease and stabilization of the COF value in the case

PAO8? (Even under increasing load - Fig. 6d). We have no here any AW/EP additives which can be activated by temperature (as a consequence of increasing frequency or load).

Thanks very much for your question. As you can see from Fig. 6 in the revised manuscript, the mean COF of the PAO8 lubricant is about 0.2, and the test condition has little influence on the value of COF. These indicate that PAO8 has a stable tribological property. In the initial friction stage in Fig. 8 in the revised manuscript, PAO8 may form boundary lubricating film and the curve shape was stable for the initial 200-300 s. Then the boundary film might be worn away and could not complement rapidly probably because of low absorption strength of PAO8, the COF suddenly increased to 0.5-0.6, and afterward stabilized at the value equal to 0.2 after the running-in period for the re-formation of boundary lubrication film. And the phenomenon has been demonstrated in many researches. The details could be obtained according to following reference:

- (1) Yu QL, Fan MJ, Li DM, Song ZH, Cai MR, Zhou F and Liu WM. Thermoreversible gel lubricants through universal supramolecular assembly of a nonionic surfactant in a variety of base lubricating liquids. ACS Appl Mater Inter 2014; 6: 15783-94.
 - (2) Huang GW, Yu QL, Ma ZF, Cai MR and Liu WM. Probing the lubricating mechanism of oil-soluble ionic liquids additives. Tribol Int 2017; 107: 152-62.
- 7) p.10, 1.54/55: in my opinion is rather conjecture - there is no clear evidence of this reaction

Thanks very much for your suggestion. The tribochemical reactions of WS₂ nanosheets were inferred by the XPS spectra of S2p and Raman spectra. It shows that when lubricated by PAO8-1%WS₂ and PAO8-1%MOB-1%WS₂, the peak of S2p was shifted from 163.6 eV and 162.6 eV to 170.8 eV and 168.7 eV, which means that the active element sulfur in WS₂ involves in a tribochemical reaction during the friction process. Combined the O1s peak at 531.6 eV, C1s peak at 285.6 eV and the new peaks at 168.7 eV and 170.8 eV of S2p, the sulphur oxides and organic sulfides are deduced to be produced when lubricated by PAO8-1% MOB-1% WS₂ according to the references [30-37] in the manuscript. What's more, the Raman spectra analysis also indicates that the complicated tribochemical reaction occurred during the friction process. The results are showed in the Table 3 of the manuscript.

Fig. 11 XPS spectra of S2p, N1s, O1s, C1s of MOB, WS₂ and the worn scars lubricated by the different lubricants.

Table 2 Identification of peaks of Raman spectra about wear scars lubricated by PAO8 and PAO8-1% MOB-1% WS₂ under frequency ramp test

PAO8		PAO8-1% MOB-1% WS ₂	
Frequency/cm ⁻¹	Corresponding compounds	Frequency/cm ⁻¹	Corresponding compounds
210	α -Fe ₂ O ₃ [46-47]	217, 184, 500	α -Fe ₂ O ₃ [46-47]
273	α -Fe ₂ O ₃ [46-47]	350, 417	WS ₂ [28]
386	γ -FeOOH [46, 48]	398	S-C-C deformation vibration [50]
482	α -FeOOH [46]	565	Fe-N-O binding vibration [49]
586	α -Fe ₂ O ₃ , Fe-C-O [46-47, 49]	596	Fe-NO stretching vibration [49]
645	Fe ₃ O ₄ [46]	654	S-CH ₂ stretching vibration [50]
1300	γ -FeOOH [46, 48]	1290	C-N stretching vibration of Aromatic amine [18]
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			aromatic ring [18]
1575	Carbonization [44-45]	1503	NH in-plane bending vibration [51]
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36. Wang YR, Yu QL, Cai MR, Shi L, Zhou F and Liu WM. Synergy of lithium salt and non-ionic surfactant for significantly improved tribological properties of water-based fluids. *Tribol Int* 2017;113:58-64.
37. <http://srdata.nist.gov/xps/>

A Facile and Effective Method to Improve the Dispersibility of WS₂ Nanosheets in PAO8 for the Tribological Performances

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ABSTRACT

The sedimentation of WS₂ nanosheets in PAO8 is resolved by a facile method with the immobilization function of 1-methyl-2, 4-bis (N-octadecylurea) benzene (MOB), and tribological performances and mechanism of the composite lubricant are systematically investigated. Compared with blank PAO8, the composite lubricants have excellent tribological performance, which is attributed to the synergistic effect of WS₂ and MOB. The immobilization function of MOB because of the network structure prevents the agglomeration and sedimentation of WS₂ nanosheets. The boundary films, including tribochemical reaction film and physical absorbing film are formed on the surfaces of the friction pair during the friction process.

Keywords: dispersibility, WS₂ nanosheets, tribological performance, lubricating mechanism

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1. Introduction

Some layer materials, such as graphene, MoS₂ and WS₂, are generally used as the additives of solid and fluid lubricants because of the lower tangential resistance deriving from the van der Waals force among interlayer [1]. And WS₂ nanoparticles as the additive in oil and grease show excellent tribological performance under the severe condition. It was found that a small amount of fullerene-like WS₂ nanoparticles (IF-WS₂) added into the oil can alleviate the friction-coefficient and wear-volume remarkably as well as improve the load-bearing capacity of the friction pair [2]. Joly-Pottuz investigated the tribological performance of IF-WS₂ as additive in oil under boundary lubrication and several theories were proposed to explain the friction reducing properties. The dramatic lubrication performance of WS₂ is due to the easy slide among the interlayers and the formation of the transfer film on the surface of friction pair [3]. Rapoport proposed the excellent tribological performances of IF-WS₂ are attributed to the third body material transfer, which is the mixture of oil, WS₂ and wear debris [4].

On the strength of thermodynamic argument, Tolman presented that the surface energy could decrease with the decrease of the particle size [5]. And the large surface energy of nanoparticle leads to the agglomeration of particle [6]. The lubricating properties of nano materials would be affected by the agglomeration tendency of nanoparticles, leading to the higher value of friction coefficient and surface worn of friction pairs [7]. At present, three major methods have been applied to improve the dispersibility of nano materials and give full play to their potential: stirring, ultrasonic treatment and chemical modification [8-9]. Moshkovith' study showed that the agglomeration of IF-WS₂ nanoparticle had a dramatic effect on the friction and stirring was an effective method to enhance the dispersibility IF-WS₂ nanoparticles [10]. In fact, it is very difficult to use the continuous stirring and ultrasonic in the lubricating system of moving parts during the practical application. Jiang et al. studied that the ultrathin WS₂ nanosheets modified by oleylamine as the additive in poly alpha olefin (PAO6), presented the good dispersion stability during 6 months and the

admirable lubricating performance over the wide temperature range [11]. However, the strict reaction conditions with high temperature (500 °C) and inert environment (Ar) restrict the broad application.

According to the previous report, the low molecular weight organic gelator (LMWG) as the additive can effectively trap the base oil to improve the tribological performance and prevent the leakage of lubricant [12]. 1-methyl-2, 4-bis (N-octadecylurea) benzene (MOB) as LMWG with ureido (NH-CO-NH) shows the stronger capacity for gelating the solvent with the comparatively low content [13] and excellent tribological performance due to containing the active element N in ureido [14]. Utilizing the quick gelation ability of MOB, the nano materials in base oil are trapped in the network of MOB before the agglomeration and sedimentation, obtaining the good dispersibility in base oil. However, few have been reported on the incorporation of LMWG and nanoparticles in base oil. In the present work, PAO8 oil with the addition of WS₂ nanosheets was immobilized by MOB under a facile condition and the tribological properties and wear mechanisms of the MOB and WS₂ as the additive in PAO8 were investigated.

2. Experimental Section

2.1 Materials

Toluene-2, 4-diisocyanate (TDI) was purchased from Shanghai Sanyou Chemical Reagent Co. Ltd. Octadecylamine (OA) was purchased from Tianjin Guangfu Fine Chemical Research Institute. Absolute ethanol was purchased from Rionlon Bohua (Tianjin) Pharmaceutical & Chemical Co. Ltd. WS₂ nanosheets were purchased from Huajing Powdery Material Science&Technological Co. Ltd. PAO8 was synthesized according to the previous report [15]. All the other chemicals used in the work were of AR grade and the deionized water was used in all the experiment.

2.2 Preparation of MOB

MOB was synthesized according to previous research [16]. Briefly, 1.7 g (10 mmol) TDI with 100 mL toluene was added to toluene solvent with 5.4 g (20 mmol) OA under the ice bath condition. Toluene was removed by distillation under reduced pressure after stirring the system for half an hour. The product was refluxed with

absolute ethanol for half an hour to remove the remaining reactants. This procedure was repeated several times and the white product was dried 12 h in vacuum oven at 50 °C after filtrating.

2.3 Preparation of xerogel

The xerogel was prepared according to previous report [16]. Chlorobenzene with 3% MOB was heated and stirred to form transparent solution and then slowly cooled to the room temperature (RT). The xerogel of chlorobenzene gel was formed in freeze dryer after removing the chlorobenzene in the network of MOB.

2.4 Preparation of lubricant

The **system of** PAO8 with MOB or WS₂ is denoted as PAO8-MOB or PAO8-WS₂ and PAO8 with both MOB and WS₂ nanosheets is written as PAO8-MOB-WS₂. The percentage content mentioned in this paper refers to the mass concentration.

PAO8-MOB-WS₂: WS₂ nanosheets were dispersed in PAO8 at a given concentration by stirring for 1 h and ultrasonic treatment for 15 min in a sample vessal. A given certain content of MOB were immediately added and dissolved into PAO8 with WS₂ nanosheets by heating and stirring at 140 °C for 5 min and then the gel lubricants were formed in several minutes when mixed solution were slowly cooled to the RT. In order to achieve the long-term stability of PAO8-MOB-WS₂, the concentration of MOB was chosen as 1% although the minimum gelator content of MOB for PAO8-WS₂ is 0.5%

PAO8-WS₂: WS₂ nanosheets were dispersed in PAO8 at a given concentration by stirring for 1 h and ultrasonic treatment for 15 min in a sample vessal. It is used immediately after ultrasonic to keep the dispersibility and stability of WS₂ nanosheets in oil.

PAO8-MOB: A given content of MOB were added into PAO8 to dissolved in base oil by heating and stirring at 140 °C for 5 min and then gel lubricants were formed in several minutes when mixed solution were slowly cooled to the RT.

2.5 Characteristics

The structure of MOB was confirmed by Nicolet iS10 FTIR spectrometer and

LabRAM HR Evolution Raman. The morphology of MOB xerogel and purchased WS₂ nanosheets were recorded by Field emission scanning electron microscopy (FESEM, JEOL JSM-6701F). The structure of WS₂ was investigated by Raman and X'PERT PRO XRD. The stabilities of PAO8-1% WS₂ and PAO8-1% MOB-1% WS₂ were studied by Agilent Technologies Cary 60 UV-Visible spectroscopy and sedimentation test. ~~STA 449 C Jupiter simultaneous TG-DSC was used to investigate the thermal property of composite lubricant from 25 °C to 800 °C with 10 °C min⁻¹ of the temperature ramp under air.~~

2.6 Tribological test

The tribological performance of lubricant was evaluated by Optimol SRV-IV oscillating reciprocating friction and wear tester. The common test condition is: Frequency = 25 Hz; Load = 200 N; Amplitude = 1 mm; Temperature = 20 °C; Time = 30 min. The changes of test conditions would be referred to the legends of figures. Three repetitive measurements were performed for each tribological process. And the standard deviation was used as the error bar in this work.

The corresponding wear volumes and morphologies of wear scars were recorded by MicroXAM-3D noncontact surface mapping profiler and JEOL JSM-5600LV scanning electron microscope (SEM) (JEOL, Japan), respectively. Then the lubricating mechanism was speculated according to the results of Raman and X-ray photoelectron spectroscopy (XPS) of worn scars on the steel disks

The morphology and structure of the worn debris were analysed by FEI Tecnai F300 high-resolution transmission electron microscope (HRTEM) to speculate the change of lubricant. The preparation process of the TEM sample is as follows:

The lubricant with debris was together dispersed into petroleum ether after friction test. The copper grid covered with thin carbon film was gently immersed into the dispersion liquid to promote the adhesion of the wear debris to the surface of carbon film. The grid was then lifted off and purged with petroleum ether more than ten times to remove the residual oil on the surface.

3. Result and Discussion

3.1 Structure of MOB

FTIR and Raman were used to demonstrate the structure of MOB in the Figure 1a and 1b. The peaks of C-H stretching vibrations in alkyl group are shown at 2890 cm^{-1} both in IR and Raman. N-H and C=O stretching vibrations with the greater change of dipole moment show the quite distinct peaks at 3305 cm^{-1} and 1634 cm^{-1} respectively in FTIR. The specific analysis of every main peak is summarized in the Table 1, which demonstrates the structure of MOB. The morphology of MOB xerogel in Figure 1c shows the formation of the fibrous structure by the self-assembly. It was speculated that the PAO8 and WS_2 nanosheets can be trapped in the empty space, which was similar to the results of the previous report [16].

3.2 Morphology and structure of WS_2 nanosheets

The morphology of WS_2 nanosheets is testified by FESEM in the Figure 2a (magnification is 20000 $\times$) and 2b (magnification is 60000 $\times$). It shows the nanosheets with the thickness of nearly 10 nm agglomerate haphazardly, indicating the characteristic of nanosheets. The Raman spectra in Figure 2c demonstrates the presence of two strong peaks at 352 and 421 cm^{-1} , which correspond to the in-plane phonon mode (E_{2g}^1) and out-of-plane phonon mode (A_{1g}) modes, respectively [3, 28]. Figure 2d shows the XRD spectra of WS_2 nanosheets. The planes marked as (002), (100) and (110) correspond to the diffraction angles of 14.24°, 33.23° and 58.45°. The broad trend of some diffraction peaks indicates the small size of WS_2 nanosheets.

3.3 Stability of the gel lubricant

The sedimentation experiments of PAO8-1% MOB-1% WS_2 (Figure 3a) and PAO8-1% WS_2 (Figure 3b) were recorded by digital camera to demonstrate the stability and dispersity of gel lubricant. The homogeneous and stable system is presented by PAO8-1% MOB-1% WS_2 during the whole test period. The apparent sedimentation phenomenon emerge even after half a day in the PAO8-1% WS_2 system and the WS_2 is completely sedimentated and delaminated from PAO8 oil after 10 days. What's more, PAO8-1% MOB-1% WS_2 can maintain stability for more than 40 days. It indicates that the MOB can effectively prevent or alleviate the agglomeration and sedimentation of WS_2 nanosheet in oil. And it can be reasonably speculated that this method is universally applicable for many nanomaterial to solve the problem of

dispersity and stability.

The transmittance of PAO8-1% WS₂ and PAO8-1% MOB-1% WS₂ were investigated by UV-Visible spectroscopy in Figure 4 to further investigate the stability of the both lubricants. It shows that the transmittance values of the two lubricants are zero for homogeneous dispersion of WS₂ nanosheets in PAO8 oil at the beginning of the test. However, the transmittance value of PAO8-1% WS₂ increases to about 30% after 1 d standing and 60% after 2 d standing, indicating the apparent agglomeration and sedimentation tendency of WS₂ nanosheets. The transmittance value reaches to nearly 80% after 9 days while that of PAO8-1% MOB-1% WS₂ maintains 0 during the whole process. The results combining that of the above sedimentation experience both indicate the excellent stability of gel lubricants.

3.4 Thermal properties of gel lubricant

~~The thermal stabilities of PAO8, MOB, PAO8-1% MOB and PAO8-1% MOB-1% WS₂ were investigated respectively by TGA at air atmosphere in the Figure 4. And 30%, 50% and 70% of mass loss of each sample are summarized in the Table 2 for the convenient comparison. It shows that the temperatures of certain mass loss of PAO8 are slightly improved after adding 1% MOB compared to that of pure PAO8 and the temperature of PAO8-1% MOB-1% WS₂ system demonstrates more increase than that of the other two samples, which means that the addition of MOB and WS₂ could delay the degradation and improve the thermal stability of the lubricant system [28-29].~~

3.4 Tribological performances

3.4.1 The effect of concentration of WS₂ on the tribological performances

Figure 5 shows that the mean friction coefficient (COF), wear volume and real-time COF of PAO8-1% MOB with the different concentration of WS₂ **under the common lubricating condition**. It shows that the COF value of PAO8-1% MOB-0.1% WS₂ is more than 0.22 with the relatively large fluctuation in Figure 5a. When the content of WS₂ is increased to 0.5%, the mean value of COF decreases sharply compared to that of the PAO8-1% MOB-0.1% WS₂ and the time of stable stage of real-time COF value is extended from 6min to 13min in Figure 5b. It can be inferred that the more WS₂ can extend the lubrication lifetime of lubricant. The value of mean

COF decreases rapidly when the content of WS₂ increases to 1%, showing the low and stable real-time COF without the distinct fluctuation during the whole lubricating process. It demonstrates that PAO8-1% MOB-1% WS₂ can exert the excellent friction-reduced and anti-wear performance. The COF values of the composite lubricant stop decreasing when the concentration of WS₂ increases to 2%, which means the applying saturation of WS₂ nanosheets into PAO8 gel.

The wear volumes of each scar were investigated by the software of MicroXAM-3D noncontact surface mapping profiler showing in Figure 5a. The wear volume of the disk lubricated by PAO8-1% MOB-0.5% WS₂ decreases slightly compared to that of PAO8-1% MOB-0.1% WS₂ although the extended stable time appears in friction curve. With the similar tendency of COF, the wear volume of the steel disk reduced with the largest margin (decreased by 95.67%) when the content of WS₂ in PAO8-1% MOB increases to 1%. The results of COF and wear volume indicate the dramatically friction-reducing and anti-wear performance of PAO8-1% MOB-1% WS₂.

3.4.2 Synergistic effect of MOB and WS₂ nanosheets

The synergistic effects of MOB and WS₂ nanosheets on the lubricating performance in steel-steel contact were investigated by the tribological tests of PAO8, PAO8-1% MOB, PAO8-1% WS₂ and PAO8-1% MOB-1% WS₂ with the same steel blocks and steel balls in the Figure 6. It shows that the COF value of PAO8 is more than 0.24 with the relatively large fluctuation. The mean COF value with comparative minor standard deviation decreases after adding 1% MOB. Combining with the real-time COF in Figure 6b, it shows obviously that the COF value of pure PAO8 soar to more than 0.6 in running-in period at approximately 3 min and reaches the stable level at nearly 0.2 during the later lubricating stage. The stable COF value after the running-in period gradually decreases to 0.175 when lubricated by PAO8-1% MOB, which might be inferred that N elements in the gelator molecules act as the active element to react with the metal and form the tribochemical reaction film [14]. However, the friction curve of PAO8-1% MOB indicates that the tendency of the COF curve with the sharp peak of running-in period does not change. PAO8-1% WS₂

possesses the better tribological performance than PAO8-1% MOB. The COF value of PAO8-1% WS₂ decreases by the larger margin compared to that of blank PAO8 and the severe running-in period is avoid effectively, showing the longer stable time during nearly 20 min. However, the friction curve gradually increases during the later stage of friction process, which might be caused by the agglomeration and the absented supplement of WS₂ nanosheets. After adding 1% MOB and 1% WS₂ nanosheets, the COF value and wear volume decrease dramatically and the friction curve keeps a low and stable value during the whole lubrication process. The tendency of wear volume is consistent with that of COF. It might be ascribed to the synergistic effect of the MOB and WS₂ nanosheets. The MOB can restrict the WS₂ nanosheets in its network, which could effectively prevent the agglomerate of WS₂ and promote WS₂ to exert the lubricating performances.

The surface morphologies of wear scars of different lubricants were recorded by SEM and 3D noncontact surface mapping profiler in Figure 7. The wear scar lubricated by pure PAO8 shows the large area damages with many deep and big pits on the worn surface, which demonstrates the tribological mechanism of that is abrasive wear. When adding 1% MOB into PAO8, The debris exfoliated from surface is apparently smaller and less and the furrow is slighter as shown in the Figure 7b and 7b', indicating the alleviation of abrasive wear. The obviously reduced exfoliation in Figure 7c and 7c' demonstrates that WS₂ is the better anti-wear additive than MOB for PAO8. However, the furrow is consistent with the result of the corresponding COF, indicating the failure of lubricating film and the direct contact of a certain point on the friction pair. The wear scar lubricated by PAO8-1% MOB-1% WS₂ is nearly invisible in the Figure 7d and 7d', which fully confirmed the synergistic anti-wear effect of MOB and WS₂ nanosheets. The result is further proved by the 3D optical microscopic images shown in the Figure 7a''-d''. The maximum depth of wear scar lubricated by PAO8-1% MOB-1% WS₂ dramatically decreases than that of the other three lubricants.

3.4.3 The effect of frequency, temperature, time and load on the tribological performances

To investigate the friction-reducing performance of PAO8-1% MOB-1% WS₂ under the severe tribological condition, the effect of frequency, temperature, time and load on the COF of PAO8-1% MOB-1% WS₂ was studied in the Figure 8. The apparent running-in period and higher COF value are recorded when lubricated by PAO8 oil under the four lubricating conditions. The decrease and stabilization of the COF value might be due to the re-formation of the continuous steady boundary film after the running-in period. However, PAO8-1% MOB-1% WS₂ presents the low and stable COF value under the wide range of frequency and temperature. The steady value of COF during the 2 h test shown in the Figure 8c demonstrates the long-term effective friction-reducing ability of PAO8-1% MOB-1% WS₂. The load capacity of the friction pair lubricated by PAO8-1% MOB-1% WS₂ is further improved to 500N. The above results fully indicate the excellent lubrication performance of PAO8-1% MOB-1% WS₂ under the various tribological conditions.

3.4.4 Potential applications in commercial oil

Figure 9a and 9b show the pictures of 5W30-1% MOB and 5W30-1% MOB-1% WS₂ lubricants, which indicating the excellent gelation ability of MOB in PAO8 and PAO8 with WS₂ nanosheets. The tribological performances of MOB and WS₂ nanosheets in 5W30 were investigated in Figure 9c and 9d to illustrate the potential applications of the both additives in the commercial oil. It shows that the COF and wear volume values of 5W30 decrease after the addition of 1% MOB and 1% WS₂. The wear volume value of 5W30-1% MOB-1% WS₂ ($2 \times 10^5 \mu\text{m}^3$) is lower than that of 5W30 ($2.5 \times 10^5 \mu\text{m}^3$), indicating this additive can improve anti-wear property of the commercial full formula lubricant. Combined the COF curve in Figure 9b, the running-in period of 5W30 are alleviated when MOB and WS₂ added, showing the certain lubricating advantages of 5W30-1% MOB-1% WS₂ than 5W30 commercial oil.

3.5 Lubricating mechanism

The worn debris from the wear scars lubricated by PAO8-1% WS₂ (Figure 10a and 10b) and PAO8-1% MOB-1% WS₂ (Figure 10c and 10d) under the common lubricating condition were investigated by HRTEM. As shown in Figure 10a, besides

the obvious layer structure (part A) which might be due to the separation among interlamination during the friction process, the apparent agglomeration of WS₂ is also observed. The severe agglomerations seriously influence the inherent outstanding tribological properties of WS₂ during the whole friction test. WS₂ in PAO8-1% MOB do not show the obvious agglomeration like WS₂ in PAO8. Figure 10c shows a large piece of WS₂ with thin and translucence characteristics, indicating the separation of WS₂ lamellar structure with the low shear force. The layer structure of WS₂ (shown in part B) endows WS₂ with the excellent lubricating property. This result also demonstrates that MOB can promote the good dispersibility of WS₂ in PAO8. The EDX spectra in Figure 10b and 10d shows a little content of Fe and O, which could be the existence of Fe and/or iron oxide formed from the tribochemical reaction during the friction test. The iron oxide might absorb to the layer structure of WS₂ during friction process to avoid the abrasion of direct contact between the steel and ball and improve the lubricating and anti-wear performance [29].

XPS is an effective tool to investigate the chemical states of elements during the friction process. The spectra of S2p, N1s, O1s and C1s about MOB, WS₂ and wear scars lubricated by different lubricants were recorded by XPS (Figure 11). It shows that the S2p peak of wear scars lubricated by PAO8-1% WS₂ and PAO8-1% MOB-1% WS₂ is different from that of WS₂, which means that S element of WS₂ takes tribochemical reaction during the lubricating process and WS₂ absorbed on the surface of wear scar might be removed during the ultrasonic process before the XPS test. Combined the O1s peak at 531.6 eV, C1s peak at 285.6 eV and the new peak at 168.7 eV and 170.8 eV of S2p, the sulphur oxides or organic sulfides are deduced to be produced when lubricated by PAO8-1% MOB-1% WS₂ [30-37]. The N1s peak of MOB at 399.4 eV and 397.9 eV might be assigned to N-H [38-39] and N-C [40] respectively. The new peak at 397.3 eV and 400.5 eV of the wear scars lubricated by PAO8-1% MOB and PAO8-1% MOB-1% WS₂ could be attributed to nitrogen oxide or nitrates [41]. It also shows that the tribochemical reactions presented on the wear scar lubricated by the PAO8-1% MOB-1% WS₂ are combined that of PAO8-1% MOB and PAO8-1% WS₂. The O1s spectrum of wear scar lubricated by pure PAO8 at 530.0

and 532.0 eV can be referred to iron oxides (Fe_2O_3 and Fe_3O_4) [41]. The new peaks of wear scar lubricated by PAO8-1% MOB-1% WS_2 at 532.3 and 533.0 eV possibly correspondence with O-H and C-O respectively. The comparison of C1s spectra of wear scars lubricated by PAO8 and PAO8-1% MOB-1% WS_2 shows that the O-C-O, O=C-O and organic sulfide might produce after the addition of additive MOB and WS_2 [36, 39, 42-43]. It shows that the protective film formed by the tribochemical reaction can prevent the direct contact of the friction pair and play an important role in reducing friction and wear resistance.

The lubricating mechanism of the frequency ramp test was investigated by Raman spectra in the Figure 12 and the identification of peaks was concluded in Table 2. Figure 12 and Table 2 shows that the iron oxides, such as $\alpha\text{-Fe}_2\text{O}_3$, $\gamma\text{-FeOOH}$, $\alpha\text{-FeOOH}$ and Fe_3O_4 , are the main reaction product on wear scar lubricated by neat PAO8. Carbonization of PAO8 might occur for the presence of the peak at 1340 cm^{-1} and 1570 cm^{-1} . However, some different product might exist on the surface of wear scar lubricated by the PAO8-1% MOB-1% WS_2 . Besides the existence of WS_2 , iron oxide and carbonization of PAO8, some nitride and sulfide concluded in the Table 2 might be the new products of tribochemical reactions, which are conducive to the lubrication performance. It should be mentioned that the content of carbonization on the scar of the disk lubricated by PAO8-1% MOB-1% WS_2 reduces in the Raman spectra compared with that of the disk lubricated by PAO8, which is consistent with the previous results [44-45]. Therefore, the addition of MOB and WS_2 in PAO8 can decrease the carbonization as well as lower the COF value for the formation of physical absorbing film and tribochemical lubrication film.

The schematic diagram of the lubricating mechanisms of PAO8-1% MOB-1% WS_2 is shown in the Figure 13. There are several factors to improve the lubrication performance of PAO8 with the additive MOB and WS_2 nanosheets. The existence of MOB is conducive to the dispersibility of WS_2 , preventing the inhomogeneity of the additive because of the agglomeration of WS_2 . Meanwhile, MOB with the active element N in ureido has a certain friction-reducing and anti-wear properties because of the reaction with the friction pair and formation of nitride during the lubrication

process. The WS₂ nanosheet could exert the lubricating function layer by layer with the low shear force among the interlamination, which is also beneficial to the formation of the physical absorbing film on the surface of friction pairs. WS₂ nanosheets which are immobilized in the network of MOB are gradually released on the friction surface, so PAO8-MOB-WS₂ presents the better long-term lubricating performance than PAO8-MOB and PAO8-WS₂. And the big pieces of WS₂ could adsorb or wrap up the small wear particles exfoliated from the steel surface to decrease the abrasive wear of the friction pair. The boundary films, containing the physical absorbing film and tribochemical lubrication film are formed on the surface of the friction pair, which improves the friction-reducing and anti-wear properties of PAO8. Namely, MOB and WS₂ nanosheet have the synergistic effect on enhancing the tribological performance of PAO8.

4. Conclusion

A facile and novel method to resolve the agglomeration problem of nanomaterial in the base oil is proposed in the present work by utilizing the quick gelling ability of MOB gelator. ~~The addition of MOB and WS₂ nanosheet can slightly improve the thermal stability of PAO8.~~ The tribological tests show that PAO8-1% MOB-1% WS₂ has better lubricating and anti-wear performances than that of PAO8-1% MOB and PAO8-1% WS₂ lubricants, which demonstrates the synergistic lubrication effects between 1% MOB and 1% WS₂ nanosheets as the additives in PAO8. The immobilization function of MOB can effectively avoid the agglomeration of WS₂ and promote WS₂ nanosheets to exert the lubricating performance layer by layer. What's more, the tribochemical reaction which occurs in WS₂, MOB and the metal surface and the physical absorbing films recorded on the wear scars of steel disks can produce the strong protective film to prevent the direct contact of friction pair. The network structure of MOB gelator and the formation of boundary lubrication film play the important effects on the excellent tribological performance of PAO8 with the addition of WS₂ and MOB.

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Table captions

Table 1 Identification of the peaks of FTIR and Raman about MOB.

Table 2 Identification of the peaks of Raman spectra about wear scars lubricated by
PAO8 and PAO8-1% MOB-1% WS₂ under frequency ramp test.

Figure captions

Fig. 1 (a) FTIR, (b) Raman spectra and (c) xerogel morphology of MOB.

Fig. 2 (a) (b) Morphologies of WS₂ nanosheet with the different magnification. (c) Raman (d) XRD spectra of WS₂ nanosheets.

Fig. 3 Digital picture of (a) PAO8-1% MOB-1% WS₂ and (b) PAO8-1% WS₂ system in different time.

Fig. 4 The transmittance of (a) PAO-1% WS₂ and (b) PAO8-1% MOB-1% WS₂ recorded by UV-Visible spectroscopy of with the evolution of time.

Fig. 5 (a) Mean COF and wear volume (b) real-time COF of PAO8-1% MOB-WS₂.

Fig. 6 (a) Mean COF and wear volume (b) real-time COF of PAO8, PAO8-1% MOB, PAO8-1% WS₂ and PAO8-1% MOB-1% WS₂.

Fig. 7 SEM morphologies and 3D profile of worn scars on the steel disk lubricated by (a)(a')(a'') PAO8, (b)(b')(b'')PAO8-1% MOB, (c)(c')(c'')PAO8-1% WS₂ and (d)(d')(d'')PAO8-1% MOB-1% WS₂.

Fig. 8 Evolution of COF (a) with time during a frequency ramp test from 15 to 40 Hz (b) with time during a temperature ramp test from 20 to 120 °C (c) of long time testing (d) with time during a load ramp test from 100N to 500N for pure PAO8 and PAO8-1% MOB-1% WS₂.

Fig. 9 The picture of (a) 5W30-1% MOB and (b) 5W30-1% MOB-1% WS₂ lubricant; (c) Mean COF and wear volume of 5W30, 5W30-1% MOB, 5W30-1% WS₂ and 5W30-1% MOB-1% WS₂ (d) real-time COF of 5W30 and 5W30-1% MOB-1% WS₂.

Fig. 10 HRTEM micrographs and EDX elemental counts images of worn debris on the disk lubricated by (a) (b) PAO8-1% WS₂ and (c) (d) PAO8-1% MOB-1% WS₂.

Fig. 11 XPS spectra of S2p, N1s, O1s, C1s of MOB, WS₂ and the worn scars lubricated by the different lubricants.

Fig. 12 Raman spectra of the wear scars lubricated by (a) PAO8 and (b) PAO8-1% MOB-1% WS₂ under frequency ramp test.

Fig. 13 Lubricating mechanisms of PAO8-1% MOB-1% WS₂ on the steel/steel

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A Facile and Effective Method to Improve the Dispersibility of WS₂ Nanosheets in PAO8 for the Tribological Performances

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ABSTRACT

The sedimentation of WS₂ nanosheets in PAO8 is resolved by a facile method with the immobilization function of 1-methyl-2, 4-bis (N-octadecylurea) benzene (MOB), and tribological performances and mechanism of the composite lubricant are systematically investigated. Compared with blank PAO8, the composite lubricants have excellent tribological performance, which is attributed to the synergistic effect of WS₂ and MOB. The immobilization function of MOB because of the network structure prevents the agglomeration and sedimentation of WS₂ nanosheets. The boundary films, including tribochemical reaction film and physical absorbing film are formed on the surfaces of the friction pair during the friction process.

Keywords: dispersibility, WS₂ nanosheets, tribological performance, lubricating mechanism

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1. Introduction

Some layer materials, such as graphene, MoS₂ and WS₂, are generally used as the additives of solid and fluid lubricants because of the lower tangential resistance deriving from the van der Waals force among interlayer [1]. And WS₂ nanoparticles as the additive in oil and grease show excellent tribological performance under the severe condition. It was found that a small amount of fullerene-like WS₂ nanoparticles (IF-WS₂) added into the oil can alleviate the friction and wear remarkably as well as improve the load-bearing capacity of the friction pair [2]. Joly-Pottuz investigated the tribological performance of IF-WS₂ as additive in oil under boundary lubrication and several theories were proposed to explain the friction reducing properties. The dramatic lubrication performance of WS₂ is due to the easy slide among the interlayers and the formation of the transfer film on the surface of friction pair [3]. Rapoport proposed the excellent tribological performances of IF-WS₂ are attributed to the third body material transfer, which is the mixture of oil, WS₂ and wear debris [4].

On the strength of thermodynamic argument, Tolman presented that the surface energy could decrease with the decrease of the particle size [5]. And the large surface energy of nanoparticle leads to the agglomeration of particle [6]. The lubricating properties of nano materials would be affected by the agglomeration tendency of nanoparticles, leading to the higher value of friction coefficient and surface worn of friction pairs [7]. At present, three major methods have been applied to improve the dispersibility of nano materials: stirring, ultrasonic treatment and chemical modification [8-9]. Moshkovith' study showed that the agglomeration of IF-WS₂ nanoparticle had a dramatic effect on the friction and stirring was an effective method to enhance the dispersibility IF-WS₂ nanoparticles [10]. In fact, it is very difficult to use the continuous stirring and ultrasonic in the lubricating system of moving parts during the practical application. Jiang et al. studied that the ultrathin WS₂ nanosheets modified by oleylamine as the additive in poly alpha olefin (PAO6), presented the good dispersion stability during 6 months and the admirable lubricating performance over the wide temperature range [11]. However, the strict reaction conditions with

high temperature (500 °C) and inert environment (Ar) restrict the broad application.

According to the previous report, the low molecular weight organic gelator (LMWG) as the additive can effectively trap the base oil to improve the tribological performance and prevent the leakage of lubricant [12]. 1-methyl-2, 4-bis (N-octadecylurea) benzene (MOB) as LMWG with ureido (NH-CO-NH) shows the stronger capacity for gelating the solvent with the comparatively low content [13] and excellent tribological performance due to containing the active element N in ureido [14]. Utilizing the quick gelation ability of MOB, the nano materials in base oil are trapped in the network of MOB before the agglomeration and sedimentation, obtaining the good dispersibility in base oil. However, few have been reported on the incorporation of LMWG and nanoparticles in base oil. In the present work, PAO8 oil with the addition of WS₂ nanosheets was immobilized by MOB under a facile condition and the tribological properties and wear mechanisms of the MOB and WS₂ as the additive in PAO8 were investigated.

2. Experimental Section

2.1 Materials

Toluene-2, 4-diisocyanate (TDI) was purchased from Shanghai Sanyou Chemical Reagent Co. Ltd. Octadecylamine (OA) was purchased from Tianjin Guangfu Fine Chemical Research Institute. Absolute ethanol was purchased from Rionlon Bohua (Tianjin) Pharmaceutical & Chemical Co. Ltd. WS₂ nanosheets were purchased from Huajing Powdery Material Science&Technological Co. Ltd. PAO8 was synthesized according to the previous report [15]. All the other chemicals used in the work were of AR grade and the deionized water was used in all the experiment.

2.2 Preparation of MOB

MOB was synthesized according to previous research [16]. Briefly, 1.7 g (10 mmol) TDI with 100 mL toluene was added to toluene solvent with 5.4 g (20 mmol) OA under the ice bath condition. Toluene was removed by distillation under reduced pressure after stirring the system for half an hour. The product was refluxed with absolute ethanol for half an hour to remove the remaining reactants. This procedure was repeated several times and the white product was dried 12 h in vacuum oven at 50

°C after filtrating.

2.3 Preparation of xerogel

The xerogel was prepared according to previous report [16]. Chlorobenzene with 3% MOB was heated and stirred to form transparent solution and then slowly cooled to the room temperature (RT). The xerogel of chlorobenzene gel was formed in freeze dryer after removing the chlorobenzene in the network of MOB.

2.4 Preparation of lubricant

The system of PAO8 with MOB or WS₂ is denoted as PAO8-MOB or PAO8-WS₂ and PAO8 with both MOB and WS₂ nanosheets is written as PAO8-MOB-WS₂. The percentage content mentioned in this paper refers to the mass concentration.

PAO8-MOB-WS₂: WS₂ nanosheets were dispersed in PAO8 at a given concentration by stirring for 1 h and ultrasonic treatment for 15 min in a sample vessal. A given certain content of MOB were immediately added and dissolved into PAO8 with WS₂ nanosheets by heating and stirring at 140 °C for 5 min and then the gel lubricants were formed in several minutes when mixed solution were slowly cooled to the RT. In order to achieve the long-term stability of PAO8-MOB-WS₂, the concentration of MOB was chosen as 1% although the minimum gelator content of MOB for PAO8-WS₂ is 0.5%

PAO8-WS₂: WS₂ nanosheets were dispersed in PAO8 at a given concentration by stirring for 1 h and ultrasonic treatment for 15 min in a sample vessal. It is used immediately after ultrasonic to keep the dispersibility and stability of WS₂ nanosheets in oil.

PAO8-MOB: A given content of MOB were added into PAO8 to dissolved in base oil by heating and stirring at 140 °C for 5 min and then gel lubricants were formed in several minutes when mixed solution were slowly cooled to the RT.

2.5 Characteristics

The structure of MOB was confirmed by Nicolet iS10 FTIR spectrometer and LabRAM HR Evolution Raman. The morphology of MOB xerogel and purchased WS₂ nanosheets were recorded by Field emission scanning electron microscopy

(FESEM, JEOL JSM-6701F). The structure of WS₂ was investigated by Raman and X'PERT PRO XRD. The stabilities of PAO8-1% WS₂ and PAO8-1% MOB-1%WS₂ were studied by Agilent Technologies Cary 60 UV-Visible spectroscopy and sedimentation test.

2.6 Tribological test

The tribological performance of lubricant was evaluated by Optimol SRV-IV oscillating reciprocating friction and wear tester. The common test condition is: Frequency = 25 Hz; Load = 200 N; Amplitude = 1 mm; Temperature = 20 °C; Time = 30 min. The changes of test conditions would be referred to the legends of figures. Three repetitive measurements were performed for each tribological process. And the standard deviation was used as the error bar in this work.

The corresponding wear volumes and morphologies of wear scars were recorded by MicroXAM-3D noncontact surface mapping profiler and JEOL JSM-5600LV scanning electron microscope (SEM) (JEOL, Japan), respectively. Then the lubricating mechanism was speculated according to the results of Raman and X-ray photoelectron spectroscopy (XPS) of worn scars on the steel disks

The morphology and structure of the worn debris were analysed by FEI Tecnai F300 high-resolution transmission electron microscope (HRTEM) to speculate the change of lubricant. The preparation process of the TEM sample is as follows:

The lubricant with debris was together dispersed into petroleum ether after friction test. The copper grid covered with thin carbon film was gently immersed into the dispersion liquid to promote the adhesion of the wear debris to the surface of carbon film. The grid was then lifted off and purged with petroleum ether more than ten times to remove the residual oil on the surface.

3. Result and Discussion

3.1 Structure of MOB

FTIR and Raman were used to demonstrate the structure of MOB in the Figure 1a and 1b. The peaks of C-H stretching vibrations in alkyl group are shown at 2890 cm⁻¹ both in IR and Raman. N-H and C=O stretching vibrations with the greater change of dipole moment show the quite distinct peaks at 3305 cm⁻¹ and 1634 cm⁻¹

respectively in FTIR. The specific analysis of every main peak is summarized in the Table 1, which demonstrates the structure of MOB. The morphology of MOB xerogel in Figure 1c shows the formation of the fibrous structure by the self-assembly. It was speculated that the PAO8 and WS₂ nanosheets can be trapped in the empty space, which was similar to the results of the previous report [16].

3.2 Morphology and structure of WS₂ nanosheets

The morphology of WS₂ nanosheets is testified by FESEM in the Figure 2a (magnification is 20000×) and 2b (magnification is 60000×). It shows the nanosheets with the thickness of nearly 10 nm agglomerate haphazardly, indicating the characteristic of nanosheets. The Raman spectra in Figure 2c demonstrates the presence of two strong peaks at 352 and 421 cm⁻¹, which correspond to the in-plane phonon mode (E_{2g}¹) and out-of-plane phonon mode (A_{1g}) modes, respectively [3, 28]. Figure 2d shows the XRD spectra of WS₂ nanosheets. The planes marked as (002), (100) and (110) correspond to the diffraction angles of 14.24°, 33.23° and 58.45°. The broad trend of some diffraction peaks indicates the small size of WS₂ nanosheets.

3.3 Stability of the gel lubricant

The sedimentation experiments of PAO8-1% MOB-1% WS₂ (Figure 3a) and PAO8-1% WS₂ (Figure 3b) were recorded by digital camera to demonstrate the stability and dispersity of gel lubricant. The homogeneous and stable system is presented by PAO8-1% MOB-1% WS₂ during the whole test period. The apparent sedimentation phenomenon emerge even after half a day in the PAO8-1% WS₂ system and the WS₂ is completely sedimentated and delaminated from PAO8 oil after 10 days. What's more, PAO8-1% MOB-1% WS₂ can maintain stability for more than 40 days. It indicates that the MOB can effectively prevent or alleviate the agglomeration and sedimentation of WS₂ nanosheet in oil. And it can be reasonably speculated that this method is universally applicable for many nanomaterial to solve the problem of dispersity and stability.

The transmittance of PAO8-1% WS₂ and PAO8-1% MOB-1% WS₂ were investigated by UV-Visible spectroscopy in Figure 4 to further investigate the stability of the both lubricants. It shows that the transmittance values of the two lubricants are

zero for homogeneous dispersion of WS₂ nanosheets in PAO8 oil at the beginning of the test. However, the transmittance value of PAO8-1% WS₂ increases to about 30% after 1 d standing and 60% after 2 d standing, indicating the apparent agglomeration and sedimentation tendency of WS₂ nanosheets. The transmittance value reaches to nearly 80% after 9 days while that of PAO8-1% MOB-1% WS₂ maintains 0 during the whole process. The results combining that of the above sedimentation experience both indicate the excellent stability of gel lubricants.

3.4 Tribological performances

3.4.1 The effect of concentration of WS₂ on the tribological performances

Figure 5 shows that the mean friction coefficient (COF), wear volume and real-time COF of PAO8-1% MOB with the different concentration of WS₂ under the common lubricating condition. It shows that the COF value of PAO8-1% MOB-0.1% WS₂ is more than 0.22 with the relatively large fluctuation in Figure 5a. When the content of WS₂ is increased to 0.5%, the mean value of COF decreases sharply compared to that of the PAO8-1% MOB-0.1% WS₂ and the time of stable stage of real-time COF value is extended from 6min to 13min in Figure 5b. It can be inferred that the more WS₂ can extend the lubrication lifetime of lubricant. The value of mean COF decreases rapidly when the content of WS₂ increases to 1%, showing the low and stable real-time COF without the distinct fluctuation during the whole lubricating process. It demonstrates that PAO8-1% MOB-1% WS₂ can exert the excellent friction-reduced and anti-wear performance. The COF values of the composite lubricant stop decreasing when the concentration of WS₂ increases to 2%, which means the applying saturation of WS₂ nanosheets into PAO8 gel.

The wear volumes of each scar were investigated by the software of MicroXAM-3D noncontact surface mapping profiler showing in Figure 5a. The wear volume of the disk lubricated by PAO8-1% MOB-0.5% WS₂ decreases slightly compared to that of PAO8-1% MOB-0.1% WS₂ although the extended stable time appears in friction curve. With the similar tendency of COF, the wear volume of the steel disk reduced with the largest margin (decreased by 95.67%) when the content of WS₂ in PAO8-1% MOB increases to 1%. The results of COF and wear volume

1 indicate the dramatically friction-reducing and anti-wear performance of PAO8-1%
2 MOB-1% WS₂.
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4 3.4.2 Synergistic effect of MOB and WS₂ nanosheets 5

6 The synergistic effects of MOB and WS₂ nanosheets on the lubricating
7 performance in steel-steel contact were investigated by the tribological tests of PAO8,
8 PAO8-1% MOB, PAO8-1% WS₂ and PAO8-1% MOB-1% WS₂ with the same steel
9 blocks and steel balls in the Figure 6. It shows that the COF value of PAO8 is more
10 than 0.24 with the relatively large fluctuation. The mean COF value with comparative
11 minor standard deviation decreases after adding 1% MOB. Combining with the
12 real-time COF in Figure 6b, it shows obviously that the COF value of pure PAO8 soar
13 to more than 0.6 in running-in period at approximately 3 min and reaches the stable
14 level at nearly 0.2 during the later lubricating stage. The stable COF value after the
15 running-in period gradually decreases to 0.175 when lubricated by PAO8-1% MOB,
16 which might be inferred that N elements in the gelator molecules act as the active
17 element to react with the metal and form the tribochemical reaction film [14].
18 However, the friction curve of PAO8-1% MOB indicates that the tendency of the COF
19 curve with the sharp peak of running-in period does not change. PAO8-1% WS₂
20 possesses the better tribological performance than PAO8-1% MOB. The COF value of
21 PAO8-1% WS₂ decreases by the larger margin compared to that of blank PAO8 and
22 the severe running-in period is avoid effectively, showing the longer stable time
23 during nearly 20 min. However, the friction curve gradually increases during the later
24 stage of friction process, which might be caused by the agglomeration and the
25 absented supplement of WS₂ nanosheets. After adding 1% MOB and 1% WS₂
26 nanosheets, the COF value and wear volume decrease dramatically and the friction
27 curve keeps a low and stable value during the whole lubrication process. The
28 tendency of wear volume is consistent with that of COF. It might be ascribed to the
29 synergistic effect of the MOB and WS₂ nanosheets. The MOB can restrict the WS₂
30 nanosheets in its network, which could effectively prevent the agglomerate of WS₂
31 and promote WS₂ to exert the lubricating performances.
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60 The surface morphologies of wear scars of different lubricants were recorded by
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SEM and 3D noncontact surface mapping profiler in Figure 7. The wear scar lubricated by pure PAO8 shows the large area damages with many deep and big pits on the worn surface, which demonstrates the tribological mechanism of that is abrasive wear. When adding 1% MOB into PAO8, The debris exfoliated from surface is apparently smaller and less and the furrow is slighter as shown in the Figure 7b and 7b', indicating the alleviation of abrasive wear. The obviously reduced exfoliation in Figure 7c and 7c' demonstrates that WS₂ is the better anti-wear additive than MOB for PAO8. However, the furrow is consistent with the result of the corresponding COF, indicating the failure of lubricating film and the direct contact of a certain point on the friction pair. The wear scar lubricated by PAO8-1% MOB-1% WS₂ is nearly invisible in the Figure 7d and 7d', which fully confirmed the synergistic anti-wear effect of MOB and WS₂ nanosheets. The result is further proved by the 3D optical microscopic images shown in the Figure 7a''-d''. The maximum depth of wear scar lubricated by PAO8-1% MOB-1% WS₂ dramatically decreases than that of the other three lubricants.

3.4.3 The effect of frequency, temperature, time and load on the tribological performances

To investigate the friction-reducing performance of PAO8-1% MOB-1% WS₂ under the severe tribological condition, the effect of frequency, temperature, time and load on the COF of PAO8-1% MOB-1% WS₂ was studied in the Figure 8. The apparent running-in period and higher COF value are recorded when lubricated by PAO8 oil under the four lubricating conditions. The decrease and stabilization of the COF value might be due to the re-formation of the continuous steady boundary film after the running-in period. However, PAO8-1% MOB-1% WS₂ presents the low and stable COF value under the wide range of frequency and temperature. The steady value of COF during the 2 h test shown in the Figure 8c demonstrates the long-term effective friction-reducing ability of PAO8-1% MOB-1% WS₂. The load capacity of the friction pair lubricated by PAO8-1% MOB-1% WS₂ is further improved to 500N. The above results fully indicate the excellent lubrication performance of PAO8-1% MOB-1% WS₂ under the various tribological conditions.

3.4.4 Potential applications in commercial oil

Figure 9a and 9b show the pictures of 5W30-1% MOB and 5W30-1% MOB-1% WS₂ lubricants, which indicating the excellent gelation ability of MOB in PAO8 and PAO8 with WS₂ nanosheets. The tribological performances of MOB and WS₂ nanosheets in 5W30 were investigated in Figure 9c and 9d to illustrate the potential applications of the both additives in the commercial oil. It shows that the COF and wear volume values of 5W30 decrease after the addition of 1% MOB and 1% WS₂. The wear volume value of 5W30-1% MOB-1% WS₂ ($2 \times 10^5 \mu\text{m}^3$) is lower than that of 5W30 ($2.5 \times 10^5 \mu\text{m}^3$), indicating this additive can improve anti-wear property of the commercial full formula lubricant. Combined the COF curve in Figure 9b, the running-in period of 5W30 are alleviated when MOB and WS₂ added, showing the certain lubricating advantages of 5W30-1% MOB-1% WS₂ than 5W30 commercial oil.

3.5 Lubricating mechanism

The worn debris from the wear scars lubricated by PAO8-1% WS₂ (Figure 10a and 10b) and PAO8-1% MOB-1% WS₂ (Figure 10c and 10d) under the common lubricating condition were investigated by HRTEM. As shown in Figure 10a, besides the obvious layer structure (part A) which might be due to the separation among interlamination during the friction process, the apparent agglomeration of WS₂ is also observed. The severe agglomerations seriously influence the inherent outstanding tribological properties of WS₂ during the whole friction test. WS₂ in PAO8-1% MOB do not show the obvious agglomeration like WS₂ in PAO8. Figure 10c shows a large piece of WS₂ with thin and translucence characteristics, indicating the separation of WS₂ lamellar structure with the low shear force. The layer structure of WS₂ (shown in part B) endows WS₂ with the excellent lubricating property. This result also demonstrates that MOB can promote the good dispersibility of WS₂ in PAO8. The EDX spectra in Figure 10b and 10d shows a little content of Fe and O, which could be the existence of Fe and/or iron oxide formed from the tribochemical reaction during the friction test. The iron oxide might absorb to the layer structure of WS₂ during friction process to avoid the abrasion of direct contact between the steel and ball and

improve the lubricating and anti-wear performance [29].

XPS is an effective tool to investigate the chemical states of elements during the friction process. The spectra of S2p, N1s, O1s and C1s about MOB, WS₂ and wear scars lubricated by different lubricants were recorded by XPS (Figure 11). It shows that the S2p peak of wear scars lubricated by PAO8-1% WS₂ and PAO8-1% MOB-1% WS₂ is different from that of WS₂, which means that S element of WS₂ takes tribochemical reaction during the lubricating process and WS₂ absorbed on the surface of wear scar might be removed during the ultrasonic process before the XPS test. Combined the O1s peak at 531.6 eV, C1s peak at 285.6 eV and the new peak at 168.7 eV and 170.8 eV of S2p, the sulphur oxides or organic sulfides are deduced to be produced when lubricated by PAO8-1% MOB-1% WS₂ [30-37]. The N1s peak of MOB at 399.4 eV and 397.9 eV might be assigned to N-H [38-39] and N-C [40] respectively. The new peak at 397.3 eV and 400.5 eV of the wear scars lubricated by PAO8-1% MOB and PAO8-1% MOB-1% WS₂ could be attributed to nitrogen oxide or nitrates [41]. It also shows that the tribochemical reactions presented on the wear scar lubricated by the PAO8-1% MOB-1% WS₂ are combined that of PAO8-1% MOB and PAO8-1% WS₂. The O1s spectrum of wear scar lubricated by pure PAO8 at 530.0 and 532.0 eV can be referred to iron oxides (Fe₂O₃ and Fe₃O₄) [41]. The new peaks of wear scar lubricated by PAO8-1% MOB-1% WS₂ at 532.3 and 533.0 eV possibly correspondence with O-H and C-O respectively. The comparison of C1s spectra of wear scars lubricated by PAO8 and PAO8-1% MOB-1% WS₂ shows that the O-C-O, O=C-O and organic sulfide might produce after the addition of additive MOB and WS₂ [36, 39, 42-43]. It shows that the protective film formed by the tribochemical reaction can prevent the direct contact of the friction pair and play an important role in reducing friction and wear resistance.

The lubricating mechanism of the frequency ramp test was investigated by Raman spectra in the Figure 12 and the identification of peaks was concluded in Table 2. Figure 12 and Table 2 shows that the iron oxides, such as α -Fe₂O₃, γ -FeOOH, α -FeOOH and Fe₃O₄, are the main reaction product on wear scar lubricated by neat PAO8. Carbonization of PAO8 might occur for the presence of the peak at 1340 cm⁻¹

and 1570 cm^{-1} . However, some different product might exist on the surface of wear scar lubricated by the PAO8-1% MOB-1% WS_2 . Besides the existence of WS_2 , iron oxide and carbonization of PAO8, some nitride and sulfide concluded in the Table 2 might be the new products of tribochemical reactions, which are conducive to the lubrication performance. It should be mentioned that the content of carbonization on the scar of the disk lubricated by PAO8-1% MOB-1% WS_2 reduces in the Raman spectra compared with that of the disk lubricated by PAO8, which is consistent with the previous results [44-45]. Therefore, the addition of MOB and WS_2 in PAO8 can decrease the carbonization as well as lower the COF value for the formation of physical absorbing film and tribochemical lubrication film.

The schematic diagram of the lubricating mechanisms of PAO8-1% MOB-1% WS_2 is shown in the Figure 13. There are several factors to improve the lubrication performance of PAO8 with the additive MOB and WS_2 nanosheets. The existence of MOB is conducive to the dispersibility of WS_2 , preventing the inhomogeneity of the additive because of the agglomeration of WS_2 . Meanwhile, MOB with the active element N in ureido has a certain friction-reducing and anti-wear properties because of the reaction with the friction pair and formation of nitride during the lubrication process. The WS_2 nanosheet could exert the lubricating function layer by layer with the low shear force among the interlamination, which is also beneficial to the formation of the physical absorbing film on the surface of friction pairs. WS_2 nanosheets which are immobilization in the network of MOB are gradually released on the friction surface, so PAO8-MOB- WS_2 presents the better long-term lubricating performance than PAO8-MOB and PAO8- WS_2 . And the big pieces of WS_2 could adsorb or wrap up the small wear particles exfoliated from the steel surface to decrease the abrasive wear of the friction pair. The boundary films, containing the physical absorbing film and tribochemical lubrication film are formed on the surface of the friction pair, which improves the friction-reducing and anti-wear properties of PAO8. Namely, MOB and WS_2 nanosheet have the synergistic effect on enhancing the tribological performance of PAO8.

4. Conclusion

A facile and novel method to resolve the agglomeration problem of nanomaterial in the base oil is proposed in the present work by utilizing the quick gelling ability of MOB gelator. The tribological tests show that PAO8-1% MOB-1% WS₂ has better lubricating and anti-wear performances than that of PAO8-1% MOB and PAO8-1% WS₂ lubricants, which demonstrates the synergistic lubrication effects between 1% MOB and 1% WS₂ nanosheets as the additives in PAO8. The immobilization function of MOB can effectively avoid the agglomeration of WS₂ and promote WS₂ nanosheets to exert the lubricating performance layer by layer. What's more, the tribochemical reaction which occur in WS₂, MOB and the metal surface and the physical absorbing films recorded on the wear scars of steel disks can produce the strong protective film to prevent the direct contact of friction pair. The network structure of MOB gelator and the formation of boundary lubrication film play the important effects on the excellent tribological performance of PAO8 with the addition of WS₂ and MOB.

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Table captions

Table 1 Identification of the peaks of FTIR and Raman about MOB.

Table 2 Identification of the peaks of Raman spectra about wear scars lubricated by
PAO8 and PAO8-1% MOB-1% WS₂ under frequency ramp test.

Figure captions

Fig. 1 (a) FTIR, (b) Raman spectra and (c) xerogel morphology of MOB.

Fig. 2 (a) (b) Morphologies of WS₂ nanosheet with the different magnification. (c) Raman (d) XRD spectra of WS₂ nanosheets.

Fig. 3 Digital picture of (a) PAO8-1% MOB-1% WS₂ and (b) PAO8-1% WS₂ system in different time.

Fig. 4 The transmittance of (a) PAO-1% WS₂ and (b) PAO8-1% MOB-1% WS₂ recorded by UV-Visible spectroscopy of with the evolution of time.

Fig. 5 (a) Mean COF and wear volume (b) real-time COF of PAO8-1% MOB-WS₂.

Fig. 6 (a) Mean COF and wear volume (b) real-time COF of PAO8, PAO8-1% MOB, PAO8-1% WS₂ and PAO8-1% MOB-1% WS₂.

Fig. 7 SEM morphologies and 3D profile of worn scars on the steel disk lubricated by (a)(a')(a'') PAO8, (b)(b')(b'')PAO8-1% MOB, (c)(c')(c'')PAO8-1% WS₂ and (d)(d')(d'')PAO8-1% MOB-1% WS₂.

Fig. 8 Evolution of COF (a) with time during a frequency ramp test from 15 to 40 Hz (b) with time during a temperature ramp test from 20 to 120 °C (c) of long time testing (d) with time during a load ramp test from 100N to 500N for pure PAO8 and PAO8-1% MOB-1% WS₂.

Fig. 9 The picture of (a) 5W30-1% MOB and (b) 5W30-1% MOB-1% WS₂ lubricant; (c) Mean COF and wear volume of 5W30, 5W30-1% MOB, 5W30-1% WS₂ and 5W30-1% MOB-1% WS₂ (d) real-time COF of 5W30 and 5W30-1% MOB-1% WS₂.

Fig. 10 HRTEM micrographs and EDX elemental counts images of worn debris on the disk lubricated by (a) (b) PAO8-1% WS₂ and (c) (d) PAO8-1% MOB-1% WS₂.

Fig. 11 XPS spectra of S2p, N1s, O1s, C1s of MOB, WS₂ and the worn scars lubricated by the different lubricants.

Fig. 12 Raman spectra of the wear scars lubricated by (a) PAO8 and (b) PAO8-1% MOB-1% WS₂ under frequency ramp test.

Fig. 13 Lubricating mechanisms of PAO8-1% MOB-1% WS₂ on the steel/steel

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Table 1

Vibration mode	IR /cm ⁻¹	Raman /cm ⁻¹
N-H stretching vibration	3305 [17-18]	3320 [17]
C-H stretch modes in phenyl group	3119 [19]	3060 [17]
C=O stretch	1634 [17, 20]	1657 [17, 21]
C-C stretch in alkyl	1171 [22]	1132, 1057 [21]
CH ₂ deformation vibration	1467 [23]	1440 [21]
CH ₂ wagging	--	1292 [27]
CH ₂ symmetrical stretching vibration	3031 [22]	2850 [27]
CH ₃ symmetrical stretching vibration	2846 [22]	2884 [27]
CH ₂ unsymmetrical stretching vibration	2923 [24]	2927 [27]
CH ₃ symmetrical deformation vibration	1380 [25-26]	1380 [18]

Table 2

PAO8		PAO8-1% MOB-1% WS ₂	
Frequency/cm ⁻¹	Corresponding compounds	Frequency/cm ⁻¹	Corresponding compounds
210	α -Fe ₂ O ₃ [46-47]	217, 184, 500	α -Fe ₂ O ₃ [46-47]
273	α -Fe ₂ O ₃ [46-47]	350, 417	WS ₂ [28]
386	γ -FeOOH [46, 48]	398	S-C-C deformation vibration [50]
482	α -FeOOH [46]	565	Fe-N-O binding vibration [49]
586	α -Fe ₂ O ₃ , Fe-C-O [46-47, 49]	596	Fe-NO stretching vibration [49]
645	Fe ₃ O ₄ [46]	654	S-CH ₂ stretching vibration [50]
1300	γ -FeOOH [46, 48]	1290	C-N stretching vibration of Aromatic amine [18]
1340	Carbonization [44-45]	1410	N = N stretching vibration of the azo compound conjugated to the aromatic ring [18]
1575	Carbonization [44-45]	1503	NH in-plane bending vibration [51]
--	--	1340, 1575	Carbonization [44-45]