Research on the Characteristics of Greases of Nano - Modified MoS2 Additive on the Basis of CTAB

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Abstract: The effects of nano-MoS2 as additive and CTAB modified MOS2 as additive on the properties and mechanism of Lithium Grease were investigated. The maximum bite-free load (PB), sintering load (PD), cone penetration, Shear Stability, drop point and Steel Mesh separation of grease were tested according to the performance test standard of Grease Quality Index. The effects of nano-MoS2 and CTAB on the physical and chemical properties of lithium-based Grease were studied by comparing the physical and chemical data of three samples: lithium-based Grease without additives, lithium-based grease with nano-MoS2 and lithium-based grease with CTAB. The surface structure of nano-MoS2 modified by CTAB was analyzed by Scanning electron microscope method. The results showed that CTAB was uniformly adhered to the surface of nano-MoS2, and the surface energy of nano-MoS2 was decreased, it helps to disperse the grease more evenly and stably. The results show that CTAB can modify the surface of MOS2 and reduce the surface energy of MOS2, and the surface energy of MOS2 can be decreased by using Fourier infrared scanner. Combining the physical and chemical properties of the Lithium Grease with the SEM and Fourier infrared scanning data, the nano-MoS2 modified by CTAB as additive can improve the performance of lubricating grease better than nano-MoS2 without surface modification, and disperse in lubricating grease more evenly and stably, thus, the colloidal structure of the lubricating grease is more stable.

1.Introduction
Molybdic sulfide (MOS2) is a typical layered hexagonal metallic compound with a unique sandwich structure. It has the characteristics of typical graphene-like two-dimensional materials as well as lubrication, catalytic and electrochemical properties [1-3]. The surface effect, quantum size effect, volume effect and macroscopic quantum tunneling effect of nano-MOS2 particles make its anti-friction and anti-wear mechanism different from those of traditional loading additives. The major views include the views of deposition film, ball bearing, permeability and tribochemistry [4]. MOS2 is widely used as the extreme pressure (EP) anti-wear additive for lubricating grease, and the extreme pressure performance of nano-MOS2 is also widely studied by scholars. Cheng et al. [5] pointed out that nano-graphene can significantly improve the anti-wear and extreme pressure properties of lithium-based grease. Wang et al. [6] pointed out that nano-copper, as an additive, can significantly improve the anti-wear performance of lubricating grease and the formed nano-copper film can reduce the friction coefficient between friction pairs. Wo et al. [7] took nano-MOS2 as the additive of N46 machine grease for studying its tribological properties, pointing out that nano-MOS2 has better anti-wear performance than ordinary MOS2. The mechanism behind this is that nano-MOS2, compared...
to ordinary MOS₂, is more prone to frictional chemical reactions, during which a lubricating film rich in sulfur and molybdenum is formed, thereby improving the anti-wear performance. Wang et al. [8] studied the modification of nano-MOS₂ by lauramide propyl oxide amine, suggesting that the surface of nano-MOS₂ is modified to reduce the surface energy, so that MOS₂ can be better dispersed in the grease, leading to a more stable grease structure. In addition, Liu [9] pointed out that CTAB solution can reduce the charge on the surface of SiO₂. Cao et al. [10] pointed out that surface modified SiO₂, as a grease additive, can significantly improve the bearing capacity and anti-wear ability of the grease. Since nano-MOS₂ is separately added to lubricating grease, it tends to disperse unevenly and agglomerate in groups, thereby affecting the performance of lubricating grease. Many researchers are conducting in-depth research on related issues. In this paper, cetyltrimethylammonium bromide (CTAB) is used as a modifier to modify the surface of nano-MOS₂ so as to study the influence of nano-MOS₂ on the properties of grease and the related mechanism.

2. Experiment

2.1. Preparation of test materials and grease

Cetyl trimethyl ammonium bromide (CTAB) is a good cationic surface modifier. Its hydrophilic nitrogen atom carries a positive charge when it dissolves in water; therefore, CTAB has amphiphilic molecular structure composed of hydrophobic and hydrophilic bases. In the aqueous solution, CTAB could be dissociated into positively charged CTA⁺ and negatively charged Br⁻. The solid surface is uniformly adhered to by CTAB⁺ through physical or chemical adsorption to form an absorption layer with directional arrangement. MOS₂ have rich sulphur adsorption layer on its particle surface, which is negatively charged. After CTAB with cationic groups joins the system, MOS₂ particle surface will change its negativeness. This kind of amphiphilic molecule faces its polar groups to the solid, with hydrophilic groups exposed on the surface of solid with an absorption layer; therefore, this molecule is nicely compatible with polymers.[11]

In this paper, the base grease of Class II hydrogenated mineral grease 500N and 12-hydroxystearic acid are used as thickeners, anhydrous lithium hydroxide is the alkali, and analytically pure nano-MOS₂ and CTAB-modified nano-MOS₂ are used as additives to prepare three samples, including lithium-based grease, nano-MOS₂ lithium-based grease, CTAB-modified nano-MOS₂ lithium-based grease.

1) Proportion of raw material

| Raw material        | Mass (g) |
|---------------------|----------|
| 12-hydroxystearic acid | 100      |
| 500N base grease    | 865      |
| Anhydrous lithium hydroxide | 15      |
| Nano-MOS₂          | 20       |

2) Mix 2/3 base grease with 12-hydroxystearic acid; heat to 115°C to dissolve it completely.
3) Dissolve lithium hydroxide in warm water and stir until completely dissolved. After the reaction liquid is clear and transparent, slowly add lithium hydroxide.
4) Add lithium hydroxide and a large amount of foam is produced; speed up stirring; maintain the reaction temperature at about 115°C for 1 hour.
5) After the completion of reaction, raise the temperature to 150°C for dehydration. After that, take the sample for ph test.
6) Add the remaining base grease and nano-MOS₂ additive and stir evenly; quickly cool it down to about 60°C.
7) Place the sample on a triple-roller mill for grinding; take samples for testing. Prepare three kinds of different sample lubricating grease by using the same technique [12].
2.2. Analytical methods

2.2.1. Penetration
The penetration of the grease mainly reflects its consistency and hardness. The non-working penetration indicates the depth at which the standard cone drop from the specified height into the grease sample within 5 seconds under specified conditions when the grease is at 25℃. Working penetration means the depth of penetration of the standard cone into the grease after the sample has been used in the machine for 60 times. The penetration of 100,000 working times represents the penetration value after the grease has been used for 100,000 times in the kit. The difference between the above three reflects the hardness and stability of grease in the working environment. The test standard is GB/T269[13].

2.2.2. Dropping point
Dropping point refers to the temperature at which the grease is converted from solid to liquid. The dropping point shall be at least 40℃ higher than the operating temperature. If the operating temperature is higher than the dropping point, then the grease might leak. The dropping point is mainly determined by the base grease and the thickener, and is also affected by various additives. In the same base oil and thickener grease, the higher the drop point, the more stable the grease structure. The main test standards are GB/T 4929 and GB/T 3498 [14].

2.2.3. Grease separation by using steel mesh
The grease separation ability of the grease is closely related to the thickener and base grease. The grease precipitation within a certain extent is required for the grease application, and it also reflects the stability of the grease colloid. In the non-working state, the grease is kept by the thickener at the position where lubrication is needed; when the load is applied, the grease is released for lubrication. The ability of grease separation also reflects the ability of soap fiber structure to keep the grease as well as the stability of colloid structure. Therefore, the mass of separated grease is an important indicator characterizing the lubrication efficiency (implementation standard SH/T 0324) [15].

2.2.4. Four-ball experiment
The four-ball method is mainly used to test the bearing capacity of the grease. Put a certain amount of grease and three steel balls in the base grease cup. Then install another steel ball in the rotating shaft, which is just tangent to the three steel balls at the base. Set different speed, load and time to test the wear pattern of steel balls. The four-ball experiment is used to detect the PB value and PD value of the grease, mainly reflecting the grease load at which point the lubrication capacity fails and the maximum load that the grease could bear in the lubrication process. The implementation standard is GB/T 3142 [16].

2.2.5. Fourier infrared detector (FT-IR)
The infrared spectrum is generated due to the absorption of infrared light with a specific wavelength when the compound molecules vibrate. The wavelength of infrared light depends on the dynamic constant of the chemical bond and the reduced mass of the atoms connected at both ends, which is, on the structural characteristics of the substance. In the experiment, the original spectrogram is the interferogram of the light source, and the interferogram is calculated by adopting fast Fourier transform by using the computer, so as to obtain the spectrogram with the wavelength or wave number as the function. Therefore, the spectrogram is called Fourier transform spectrometer. The changes of functional groups before and after the addition of various additives to grease are characterized by using the infrared spectrometer. [17]

2.2.6. Scanning electron microscopy (SEM)
Scanning electron microscopy consists of three parts: vacuum system, electron beam system, and
imaging system. Its working principle is to use a bunch of extremely fine electron beam to scan the sample, on which surface the secondary electrons are stimulated. The number of secondary electrons and the angle of incidence are related to the surface structure of the sample. The secondary electrons are collected by using the probe body, where they are converted into light signals by the scintillator. Then, they are converted into electrical signals to control the strength of the electron beam on the screen and display the scanning images which are synchronous with electron beam by using the photoelectric multiplier and the amplifier. The image is three-dimensional, reflecting the surface structure of the sample. For the sample to emit secondary electrons from the surface, it is necessary to spray a layer of heavy metal particles on the sample after fixation and dehydration (the heavy metal would emit secondary electronic signals under the action of electron beams). SEM is used to characterize the surface of CTAB modified nano-MOS2 and the micro-structural change of lithium soap fibers after adding the additive.

3. Result discussion

3.1. Physical and chemical properties

Test the penetration, extended working penetration, dropping point, PB, PD and grease separation by using steel mesh on the three samples of lithium-based grease, including lithium-based grease without additive, lithium-based grease added with nano-MOS2 additive, and lithium-based grease added with CTAB-modified nano-MOS2 according to the implementation standards. The results are shown in Table 1.

| Table 1 Physical and chemical properties of three types of grease |
|----------------|----------------|----------------|----------------|----------------|
| Item                        | Lithium-based grease without additive | Lithium-based grease added with nano-MOS2 additive | Lithium-based grease added with CTAB-modified nano-MOS2 | Detection method |
| Appearance                  | White uniform ointment                  | Black uniform ointment                  | Black uniform ointment                  | Visual measurement |
| Working penetration (0.1mm) | 300                                      | 290                                      | 295                                      | GB/T 269         |
| Extended penetration (0.1mm)| 17                                       | 19                                       | 19                                       | GB/T 269         |
| Dropping point (℃)          | 155                                      | 165                                      | 195                                      | GB/T 3498        |
| PB/kg                       | 48                                       | 48                                       | 88                                       | GB/T 3142        |
| PD/kg                       | 200                                      | 200                                      | 315                                      | GB/T 3142        |
| Grease separation by using steel mesh (%) | 8.2                                      | 7.9                                      | 6.5                                      | SH/T 0324        |

From Table 1, it can be seen that nano-MOS2 additive has little impact on the denseness and grease generation capacity; however, the penetration difference is smaller after adding CTAB-modified MOS2, indicating that CTAB-modified MOS2 can be used as an additive to facilitate better distribution of the nano-MOS2. The comparison of dropping point performance shows that nano-MOS2 additive can improve the dropping point of lithium-based grease. The dropping point is higher after adding CTAB-modified nano-MOS2, indicating that the colloid structure of lithium-based soap fiber grease is more stable and can better fix free grease in the soap fiber frame. By comparing the PB and PD performance, it can be seen that nano-MOS2 additive can not improve the wear resistance and extreme pressure performance of lithium-based grease. The addition of modified MOS2 leads to better PB and PD performance, indicating that the CTAB modification reduces the surface energy of nano-MOS2, which makes its distribution more uniform and stable, thus achieving better lubrication performance. The comparison of grease separation by using steel mesh shows that MOS2 addition can help to reduce the amount of grease separation, while CTAB addition can reduce more, indicating that the lubricating grease is stronger in terms of grease fixation, and that the fiber structure of the grease is more firm.
The modified CTAB and MOS$_2$ can be combined together stably, and the positively charged surface of CTAB and the negative charges on MOS$_2$ surface can be attracted towards each other. The other side of the CTAB is non-polar end, which is similar to and compatible with the lubricating grease; therefore, the modified nano-MOS$_2$ can reduce surface energy and prevent aggregation. In this way, MOS$_2$ can also be dispersed evenly in the grease, thereby improving the anti-wear capacity, extreme pressure performance, and the colloid stability of the grease.

3.2. Infrared spectrum analysis

The characteristic peaks and changes of the groups of three samples are analyzed by using infrared spectroscopy. Xue et al. [17] investigated the application of infrared spectroscopy in grease and the relationship between group changes and absorption peaks. This paper explores the relationship between the physical and chemical properties of the three samples from the aspect of structural determinability. Fourier infrared analyzer is used to conduct infrared scanning with KBr as the carrier, and the scanning results are shown in Figures 1~3.
The grease has a stable colloidal soap fiber structure composed of the thickener, base grease, and additive. The grease used in this experiment is lithium soap-based, so the carbonyl (\(>\text{C}=\text{O}\)) delivers most obvious absorption in the conventional infrared frequency region of 650-4000 cm\(^{-1}\). The carbonyl of long-chain fatty acid is absorbed near 1700 cm\(^{-1}\). When the lithium ion and the hydrogen ion in fatty acid are exchanged, the absorption position of carbonyl moves in the direction of lower frequency. In Figure 1, the infrared characteristic peak of mineral grease is at 1337 cm\(^{-1}\) [18], and the characteristic peak at 1559 cm\(^{-1}\) in the lithium-based grease spectrum is the asymmetric O-Li absorption peak of lithium fatty acid, and that at 1455 cm\(^{-1}\) is the symmetrical O-Li absorption peak.
of lithium fatty acid. As can be seen from Figure 2, the MO-O characteristic peak of MOS2 additive is at 532 cm\(^{-1}\). In Figure 3, the C-N characteristic peak appears between 1020 cm\(^{-1}\) and 1360 cm\(^{-1}\), and the characteristic peak of MOS2 disappears at 532 cm\(^{-1}\), indicating that CTAB combines with MOS2 to generate a new absorption peak at 1810-1790 cm\(^{-1}\), which should belong to the characteristic absorption peak of N-H bending vibration. The characteristic peak disappears at 1400-700 cm\(^{-1}\), indicating that after CTAB modifies MOS2, a new characteristic peak of nano-MOS2 lithium-based grease appears, which further shows that MOS2 particles have new groups on the surface, and that the organic modifier successfully modifies MOS2 and reduce the overall surface energy. Lone pair electrons on the MOS2 particle surface can easily attract free cationic groups in the grease system. The negatively charged MOS2 particles bond with positively charged CTAB molecules, which wrap the MOS2 particles, thereby reducing the surface energy of nano-MOS2 to maintain structural stability and prevent aggregation.

### 3.3. Structural characteristics of grease

Pan et al. [19] adopted SEM with an effective magnification factor of 1×105 to observe the soap fiber structure of grease, as shown in Figure 4. Wang et al. [8] used electron microscope to observe the aggregation state of nano-MOS2 in the grease soap fiber structure, as shown in Figure 5.

![Fig. 4 The saponin structure of lithium-based resin](image1)

![Fig. 5 Lithium-based lipid structure after adding MOS2](image2)

![Fig. 6 CTAB modified nanometer MoS2 structure](image3)

The soap fiber structure of the grease is shown in Figure 4 and Figure 5. It can be seen from Figure 4 that the grease colloid is fibrous with a clear structure, and that between the soap fibers, there exists
the highly tangled network structure. In Figure 5, we can easily see the MOS2 layer and soap fiber structure (the white part is the structure of MOS2, and the black part is soap fiber structure), which indicates that MOS2 particles do not react with the thickener molecular, and that the MOS2 particles are in a free state. These particles tend to gather together with time, and then they settle and agglomerate, eventually affecting the performance of the grease. Figure 6 shows the picture of CTAB-modified MOS2 particles which is taken by using a electron microscope with a magnification factor of $8 \times 10^4$. As can be seen from Figure 6, the CTAB molecular is closely adhered to the MOS2 layer (gray part), and its non-polar carbon chains form an unsmooth external structure. Based on the above MOS2 morphology analysis, it can be seen that grease with CTAB components can facilitate the even distribution of MOS2 particles in lubricating grease. The space steric hindrance produced due to nonpolar groups of CTAB slows down the trend of attraction and aggregation of MOS2 particles. At the same time, CTAB and lithium soap interact with each other, stabilizing MOS2 in grease system and improving the dispersion stability of grease.

4. Conclusion

(1) Nano-MOS2 cannot significantly improve the extreme pressure and anti-wear performance of the grease when it is added alone. CTAB-modified nano-MOS2 can not only significantly increase the extreme pressure and anti-wear properties of the grease, but also reduce the value of grease separation, thereby making the colloid structure and the grease more stable.

(2) CTAB molecule is used as cationic surfactant for surface modification of nano-MOS2 molecule. CTAB surfactant attracts the negatively charged nano-MOS2 on the surface, and wraps MOS2 particles in the middle, while alkyl or methyl groups extend into the grease. A layer of CTAB molecule is coated on the MOS2 surface to reduce the surface energy. The polar end of CTAB molecule is combined with nano-MOS2, while the non-polar end can be stably dispersed in the grease.

(3) Before applying the nano-scale extreme pressure anti-wear additive in the grease, it is necessary to modify it and reduce its surface energy. In this way, the influence on grease performance due to the aggregation and precipitation of nano-particles can be prevented. Therefore, it can be seen that after CTAB modification, the lipophilicity of nano-MOS2 is significantly improved.

References

[1] HUANG. Two dimensional atomically thin MoS2 nanosheets and their sensing applications[J]. Nanoscale, 2015, 7(46): 19358.
[2] Anon. Synthetic approaches to the Molybdenum sulfide materials[J]. Retour AU Numéro, 2008, 40(25): 159-182.
[3] Anon. Facile synthesis and characterization of ultrathin MoS2 nanosheets[J]. Materials Letters, 2014, 130(5): 83-86.
[4] Wenshi Zhu. Progress and reflection on lubrication theory. J. Journal of Tribology, 2007,27(6)
[5] Cheng Jiaxing, Xie F, Li B. Anti-wear and anti-friction Properties of nano-graphite with different particle sizes in Lithium Grease J. Petrochemical applications, 2016,35(6): 5.
[6] Wang Xiaoli, Xu B S, Xu Y. tribological properties and mechanisms of copper nanoparticles as lubricating oil additives J. Journal of Tribology, 2007,27(3): 2-4
[7] W0 Hengzhou, Hu Xg, Chen Gang. tribological properties of nano-MOS2 under ring-block condition J. Lubrication and sealing, 2006(2): 108-109,112
[8] Wang J, Liu X Y, Chen X J Dispersion stability of Nano MOS2 in Grease J. Petroleum Refining and chemical industry, 48(10)
[9] Liu Huabin. Surface modification and application of nano-oxide particles. D. Changsha: Hunan University, 2012:52-54
[10] Cao Zhi, Li X H, Zhang Z J. Effect of surface modified SiO2 nanoparticles on antiwear properties of Lithium Grease. Journal of Tribology, 2005, 25(5).
[11] Zhang Tao. Novel Fabrication Techniques and applications of rubber composites. D. Beijing: North University of China, 2012:17-18
[12] Zhang Yumeng. Lubrication characteristics of Lithium Grease. D. Qingdao: Qingdao Technological University, 2015:28-31
[13] Lubricating greases -- determination of drop point -- S, 1985
[14] "Method for the determination of drop points in lubricating greases over a wide temperature range", revision S, 2007
[15] Jiang Liang. Determination of oil separation from Lubricating Grease Steel Mesh by cone-mesh method. J. Petroleum Technology, 2011, 29(2): 71-73
[16] Lubricating greases -- determination of load carrying capacity -- S, 1982
[17] Xue Jin, Zhang Jiuyuan, Wang Chuntao. Application of infrared spectroscopy in analysis of bearing grease. J. Bearing, 2003, 11(7): 2-4
[18] Lin Xianfu. Modern pop analysis methods. D. Shanghai: East China University of Science and Technology, 2009
[19] Pan Jb, Qian M, Zhou Bin. Progress in soap fiber structural system of Lubricating Grease J. Lubrication and sealing, 2018, 43(6): 2-3