Investigate on the tribological properties of additives in tetra polyurea grease

Tao Bai¹,³ and Fei Geng¹,²,³,a

¹School of material science and engineering, Shanghai Institute of Technology, 201400 Shanghai, China
²Department of Chemistry and Materials Engineering, Changshu Institute of Technology, 215500 Changshu, Jiangsu, China
³Suzhou Huifeng Lubricant Co., Ltd, Heshi Industrial Park, Zhitang Town, 215538 Changshu, Jiangsu, China

Abstract. In this paper, the effects of five different additives on the tribological properties of tetra polyurea greases prepared under the same conditions were studied. The friction coefficient, friction force, wear scar diameter, PB and PD of the tetra polyurea greases prepared under the conditions of the five additives were examined by a four-ball friction tester. The steel mesh oil separation of the tetra polyurea grease prepared with different additives under the same conditions was tested and compared with the tetra polyurea grease prepared without additives. The results showed that the type and amount of additives basically had no effect on the steel mesh oil separation of the tetra polyurea grease. The steel mesh oil separation content was maintained at 0.6% around. The tetra polyurea grease prepared with the additive of fluorinated graphite has excellent lubricating properties and abrasion resistance compared to several other additives. In addition, the tribological properties of tetra polyurea grease prepared with the constant change of fluorinated graphite content are also constantly changing. The wear scar diameter at the content of 2% is 0.3146mm. At this time, the friction coefficient and friction force value are the minimum.

1. Introduction

In the environment of high-speed industrial development, the use of various types of high-temperature, high-load, high-speed mechanical equipment imposes higher requirements on industrial grease¹. In recent years, the high-dropping greases such as composite lithium grease, polyurea grease, and composite calcium sulfonate grease have been widely studied by scholars²-⁴. As a grease with broad development prospects of polyurea grease, since it came out, due to its excellent lubrication performance and long service life, it has been gradually applied in food, bearings, automobiles, machinery and equipment. As the traditional metal soap-based greases contain metal ions that can catalyze oxidation of the grease during use⁵, metal soap greases tend to have a shorter lifespan in industrial use and have a higher frequency of grease replacement. Because the polyurea compounds grease have not contained metal ions and have strong oxidation stability, stability and hydrophobicity, the polyurea greases exhibit a number of excellent properties such as higher dropping point, good water resistance, excellent lubrication performance and long service life, it has been gradually applied in food, bearings, automobiles, machinery and equipment. As the traditional metal soap-based greases contain metal ions that can catalyze oxidation of the grease during use⁵, metal soap greases tend to
have a shorter lifespan in industrial use and have a higher frequency of grease replacement. Because the polyurea compounds grease have not contained metal ions and have strong oxidation stability, stability and hydrophobicity, the polyurea greases exhibit a number of excellent properties such as higher dropping point, good water resistance, excellent pumpability, oxidation stability, and acid and alkali resistance[6-7]. The tetra polyurea grease is prepared from the organic compounds containing four urea groups thickened base oil[8]. Since the urea-containing compound itself has excellent anti-oxidation, anti-water showering properties, the tetra polyurea grease prepared by thickening the base oil with a tetra polyurea compound containing four urea groups has excellent colloidal stability, oxidation resistance, thermal stability, water resistance and higher resistance to temperature[9], which often used in the contact lubrication areas with high load, high pressure, high speed, wide temperature range and high frictional resistance. Due to the polyurea grease products without a good lubrication performance[10] under the circumstances of high temperature, extreme pressure, wear and others, in this paper, the tetra polyurea grease by the way of adding additives[11] into it and prepared the tetra polyurea grease with good extreme pressure, wear resistance properties and making a comparative research on the wear resistance of several used additives.

2. Experimental part

2.1 Material

Octadecyl amine (99.8%, Shandong Paini Chemistry Co. Ltd.), Ethylenediamine (purity 99.5%, Jiangsu Qiangsheng Chemical Co., Ltd.), Diphenylmethane diisocyanate (99.5%, Shanghai Zhaoqing Trade Co., Ltd.), mineral oil 150BS (392 mm2/s, 40℃), Graphite fluoride (fluorine content 65%, Shanghai Fubang Chemical Co., Ltd.), Molybdenum disulfide (99.9%, Qingdao Jinchengshan Chemical Co., Ltd.), Graphene (carbon content 95.24%, Changzhou Sixth Element Materials Technology Co., Ltd.), Graphite (98%, Qingdao Haiyan Carbon Materials Co., Ltd.), Boron Nitride (98%, Liaoning Pengda Technology Co., Ltd.)

2.2 Laboratory apparatus

Reactor (500ml, self-made), three-roll grinding machine (S150 type, Changzhou Longxin Chemical Machinery Co., Ltd.), Four-ball friction testing machine (MS-10J type, Xiamen Tianji Automation Co., Ltd.), electric drying oven (202-00AB type, Tianjin Taisite Instrument Co., Ltd.)

2.3 Preparation of tetra polyurea grease

Preparation:

Firstly, the base oil and ethylenediamine were added to the reactor and the mixture was heated and stirred at 80℃, next, the dissolved and heated diphenylmethane diisocyanate is added to the reaction vessel and the reaction is heated to 90℃ to carry out the reaction. Then, the heated and dissolved octadecylamine oil solution is added to the reactor and the temperature is raised to 100℃ and stirred at this temperature for 60min. After the end of the above reaction, the reactor was heated to 190℃ and subjected to a constant temperature reaction for 40min. After the reaction was completed, a cold oil and an additive were added for cooling and stirring. Finally, it can be ground in a three-roll mill to obtain a tetra polyurea grease product.

2.4 Performance test

2.4.1 Dropping point test

The drooping points of the lubricating greases were tested according to GB/T3498 standard using a drooping point tester (Shanghai Puhang Petroleum instrument technology research institute SPH4929).
The test method was as follows: with the handle of spoon pressed the grease into a grease cup and removed the excess grease around the mouth of the grease cup with a scraper, rotating the metal bar along the inner wall of the grease cup to remove the grease outside the inner wall and a layer of smooth film was left. After placing the bracket and adjusting the height of the thermometer, the test sample was placed into the dropping point tester, and then heated and recorded the value of thermometer when the first drop of oil dropped from the grease cup.

2.4.2 Cone penetration test of the lubricating greases
The cone penetration test of the lubricating greases were tested based on GB/T269 standard with a lubricating grease cone penetration tester (Shanghai Puhang Petroleum instrument technology research institute SPH269). First, take a sufficient amount of the sample into the clean and standard grease cup, and squeezed the grease cup tightly with a scraper to avoid the air bubbles into it. Then the sample was put on the platform of the cone penetration tester with the projecting portion on the surface removed, turned on the switch and the values of the cone before and after the cone falling for 5s were tested respectively. Finally, the value of cone penetration was obtained by calculating the difference between the vertebral body before and after the drop.

2.4.3 Steel mesh oil separation test
This method was based on SH/T0324 standard. A 10g±0.01g grease samples was placed into a conical steel mesh and the top of the sample was in an oval shape. The weight of the assembled steel mesh oil separator was weighed before the test, and hanged the steel mesh in the steel mesh oil separator and put it in an incubator for 30h at the temperature of 100°C±1°C. After the end of the experiment, taken out the steel mesh oil separator and cooled it to room temperature then taken out the steel mesh and weighed the weight of the steel mesh oil separator. The steel mesh oil separation content of the grease can be obtained by calculating the difference in mass before and after the oil separator.

2.4.4 Four-ball friction test
The four-ball friction test of the lubricating greases were carried out on a four-ball friction tester (Xiamen Tianji Automation Co. Ltd. MS-10J) based on ASTM D2596-82 standard. The grease sample of 27°C±8°C was put in a clean ball box with three clean steel balls embedded, and the other clean steel ball was installed on the main shaft of the tester. The rotate speed, load and running time were separately set according to the comprehensive abrasion, sintering load (PD) and maximum non-seizure load (PB).

3. Results and discussion

3.1 Basic physicochemical information analysis of tetra polyurea grease under different additives conditions
In this paper, the tetra polyurea grease was prepared and the tetra polyurea grease under the conditions of five different additives was prepared. From Figure 1 and Table 1, it can be seen that different additives only have a certain impact on the appearance of the tetra polyurea grease, the drop point and cone penetration of tetra polyurea grease prepared under different additive conditions substantially has not change.

**3.2 The steel mesh oil separation analysis of tetra polyurea grease under different additive conditions**
From Figure 2, it can be seen that after baking for 24h at 100°C, the steel mesh oil separation rate of tetra polyurea grease is 0.59%, the oil separation rate of the tetra polyurea grease prepared under the additive conditions of fluorinated graphite, molybdenum disulfide, boron nitride, graphene and graphite was 0.58%, 0.61%, 0.60%, 0.59% and 0.61% respectively. It can be seen that whether additives are added or not which have not affect the steel mesh oils separation of the grease at 100°C.

3.3 Tribological performance comparison analysis

Extreme pressure anti-wear performance is an important indicator to investigate grease lubrication performance, in this paper, a four-ball friction tester was used to conduct extreme pressure anti-wear test on the tetra polyurea grease and the tetra polyurea grease prepared under the conditions of five different additives. A comparative study was conducted on the extreme pressure anti-wear performance.

![Graph showing PB value test of tetra polyurea grease under different additive conditions.](image1)

![Graph showing PD value test of tetra polyurea grease under different additive conditions.](image2)

The load performance and sintering performance of tetra polyurea grease under the several different additive conditions was tested and compared in this paper, as shown in Figure 3 and Figure 4, at the condition of tetra polyurea grease without additives, the PB value is 598N and the PD value is 980N. The loading capacity and the sintering performance of the tetra polyurea grease after adding five different additives have been improved. The loading performance and the sintering performance of the tetra polyurea grease with the fluorinated graphite are the best, the PB value reached 863N and PD value reached 1960N, which is because fluorinated graphite is a three-dimensional layered structure and has good lubrication properties. After the fluorinated graphite is added
to the tetra polyurea grease, the fluorinated graphite particles adhere to the surface of the tetra polyurea fiber due to hydrogen bonding interaction with the tetra polyurea molecule, when the grease is in used, the frictional auxiliary groove formed in the mechanical contact friction part will make the fluorinated graphite particles of the three-dimensional layered structure be filled and have a certain support and anti-friction effect so that the formed oil film is not easily destroyed. Therefore, compared with other additives, fluorinated graphite can better improve the loading performance and sintering ability of tetra polyurea grease.

Figure 5. Friction change chart of tetra polyurea grease under different additive conditions. (a) tetra polyurea grease (b)tetra polyurea grease with graphene additives (c)tetra polyurea grease with molybdenum disulfide additives (d)tetra polyurea grease with graphite additives.

Figure 6. Wear scar diameter test of tetra polyurea grease under different additive conditions. (a)tetra polyurea grease (b)tetra polyurea grease with fluorinated graphite additives (c)tetra polyurea grease with molybdenum disulfide additives (d)tetra polyurea grease with boron nitride additives (e)tetra polyurea grease with graphene additives (f)tetra polyurea grease with graphite additives.

In this paper the friction property of tetra polyurea grease under different additive condition was tested and analyzed, as shown in Figure 5, the friction force of the tetra polyurea grease prepared by the three additives with the best friction properties is compared with that of the tetra polyurea grease prepared without additives, it can be seen that the use of fluorinated graphite as the additive for the tetra polyurea grease has the least friction and is far less than the tetra polyurea grease without additives. This shows that fluorinated graphite has excellent anti-friction properties as an additive for tetra polyurea grease compared to other types of additives. as shown in Figure 6, The average wear scar diameter of using fluorinated graphite as the tetra polyurea additive was 0.35mm, the average wear scar diameter of the tetra polyurea grease without additive was 0.68mm, and the average wear scar diameter of using other additives was respectively 0.51mm, 0.50mm, 0.61mm, 0.64mm, which can be seen that the use of fluorinated graphite as the additive of the tetra polyurea grease can improve its tribological properties more efficiently, expand the scope of use of the tetra polyurea grease, and greatly reduce
the friction loss during the use of the machine, extend the service life of the machine, reduce the use cost and have a good application prospect.

3.4 Analysis of tribological properties under different pressure conditions

![Figure 7](image.png)

Figure 7. The friction force value with the load pressure changes in the four-ball friction test of tetra polyurea grease prepared with fluorinated graphite as the additive. \( U \) is the friction force and \( N \) is the load pressure.

With the constant change of load pressure, as shown in Figure 7, the friction force in the four-ball friction test of tetra polyurea grease prepared with fluorinated graphite as an additive is also constantly changing. Friction under constant load pressure of 400N is constantly changing due to unstable force at the beginning, when suddenly the load pressure is increased to 500N, the friction force of the steel ball is subject to a greater friction, with the passage of time, the friction force gradually stabilizes at about 0.3. When the load pressure is increased to 600N, the friction force is slightly increased and the force is in a stable state, when the load pressure is increased to 1000N, the friction curve is increased from 0.35 to less than 0.6, the friction curve has a large change. However, the friction curve is still in a steady state under 1000N pressure conditions. From the change of the friction force curve under different load pressure conditions, it can be found that the tetra polyurea grease prepared with fluorinated graphite as an additive has good resistance to friction and wear reduction with a load of about 600N, and has a very large load pressure of 1000N, good mechanical friction stability, and still maintain good anti-friction and anti-wear properties.

3.5 Analysis of tribological properties of tetra polyurea grease with fluorinated graphite additive

![Figure 8](image.png)

Figure 8. Friction coefficient changes with fluorinated graphite content in tetra polyurea grease. As shown in Figure 8, as the content of fluorinated graphite in the tetra polyurea grease continues to
increase, the average coefficient of friction begins to decrease after turning for 10s at 1,450rpm/min at 392N load, which shows that the tribological properties of tetra polyurea grease are continuously improving. The tribological coefficient is 0.007 when the amount of fluorinated graphite added is 2%, which is a 38% reduction compared to the friction coefficient of 0.0113 of which no fluorinated graphite added, the average friction coefficient at this point has reached a minimum value. When the addition amount of fluorinated graphite is further increased, the tribological coefficient starts to increase and exceeds the average coefficient of friction when fluorinated graphite is not included. It can be seen that a small amount adding of fluorinated graphite can improve the tribological properties of tetra polyurea grease and reduce its tribological loss value. When the adding amount is more than 2.0%, as the content of fluorinated graphite increases which start to reunion and adsorbs on the surface of the tetra polyurea fiber so that the surface of the friction pair cannot form a lubricant film. Small particles of fluorinated graphite cannot enter the dimples on the surface of the friction pair, and the fluorinated graphite agglomerates destroy the lubricated structure of the tetra polyurea grease. Thus, when the amount of fluorinated graphite added was increased to 3%, the friction coefficient of the tetra polyurea grease was 0.016, which was 41.6% higher than that of the tetra polyurea.

4. Conclusion
a. Different kinds of additives can improve the tribological properties and lubricity of tetra polyurea grease, improve its PB and PD value, reduce the wear loss, and it has no effect on the basic physical and chemical properties such as dropping point, cone penetration, and oil separation effect of tetra polyurea grease.
   b. The anti-friction wear resistance, lubricity, PB, and PD values of the tetra polyurea greases prepared with fluorinated graphite have greatly improved and increased. When the addition amount of fluorinated graphite reached 2%, the wear spot and friction coefficient of the tetra polyurea grease prepared were the smallest, which were 0.3146mm and 0.007 respectively. The maximum values of PB and PD were 863N and 1960N. The tetra polyurea grease has the best lubricating properties and the best friction reduction and wear resistance.
   c. The use of fluorinated graphite as an additive for the tetra polyurea grease can improve the extreme pressure, anti-wear performance and mechanical load stability of the tetra polyurea, reduce the friction loss in the use of mechanical equipment, and extend the use range of the tetra polyurea grease, extend the service life of machinery and equipment and reduce production costs.

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Reference
[1] Z.B. Li, L.H. Dong, Y.Q. Gao, The research status and development trend of polyurea grease, Pet. Pro. App. Res. 31(05), 18-22(2013)
[2] J.G. Yi, Structure and application of calcium sulfonate complex grease, Auto. Tech. Mats. 03, 40-43(2005)
[3] M.J. Jiang, X.C. Guo, J.X. Dong, G.X. Chen, Study on the lithium complex grease, Lubr. Eng. 05, 25-28+31(2000)
[4] F.L. Li, T.J. Bao, Y. Wang, Y. Zhang, Y.Y. Li, Research on polyurea grease used on submarine, Lubr. Eng. 39(04), 121-126(2014)
[5] S.X. Zhang, X.B. Wang, G.Q. Zhao, Z.Q. Lei, The investigation on tribological behaviors of borates in polyurea grease, Lubr. Eng. 35(11), 77-81(2010)
[6] Y. Hu, X.B. Min, The technical status and development trend of polyurea grease, Gansu Sci. Tech. 16, 52-53+187(2008)
[7] G.Q. Zhao, S.X. Zhang, X.B. Wang, W.M. Liu, The relationships of thickener structures and
properties of polyurea grease, Lubr. Eng. 37(07), 5-9(2012)

[8] M.J. Jiang, X.C. Guo, H.R. Fu, Study on the factors influencing the performance of lithium complex grease, Pet. Pro. Petroche. 41(04), 63-67(2010)

[9] L. Li, B.J. Wu, Q.L. Liu, Influences of diurea-based grease composition on the performance of high-temperature hardening, Pet. Pro. App. Res. 31, 34-41(2013)

[10] H.W. Sun, D.J. Liu, J. Long, P. Wang, Test analysis and application of poly-urea grease in bearing, Bear. (03), 25-28(2005)

[11] Z.F. Cao, Y.Q. Xia, Tribological properties of non-sulfur phosphorus additive in polyurea grease, Pet Pro. Petroche. 47(01), 71-75(2016)