Lube-Tech
PUBLISHED BY LUBE: THE EUROPEAN LUBRICANTS INDUSTRY MAGAZINE
No.97 page 1

Synergistic Combination of Dimercapto Thiadiazole Derivatives

with Organo-Moly as EP Additives in Greases

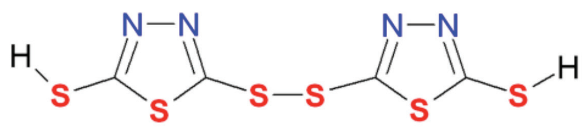
Aili Ma[1], Minli Gu[1], Junbing Yao[1] and Ruiming "Ray" Zhang[2]
[1] *Vanderbilt (Beijing) Trading, Ltd., Beijing, PR China*
[2] *Vanderbilt Chemicals, LLC, Norwalk, CT 06856, USA*

Abstract:
The four-ball test was employed to evaluate the extreme-pressure (EP), antiwear (AW) and friction-reducing (FR) performances of molybdenum dialkyl dithiophosphate, and 2,5-dimercapto-1,3,4-thiadiazole (DMTD) derivatives, i.e., DMTD dimer, and its complex with polyalkylene glycol (PAG), in greases. DMTD dimer and its complex with PAG exhibit excellent EP properties, which can achieve high weld load in lithium complex greases, polyurea greases and calcium sulfonate complex greases. In lithium complex grease, molybdenum dialkyl dithiophosphate possesses outstanding AW and FR performances, which results in low wear scar and low friction coefficient. In calcium sulfonate complex grease, molybdenum dialkyl dithiophosphate provides good EP properties with high last non-seizure and weld loads, and excellent FR performances. But in polyurea grease, molybdenum dialkyl dithiophosphate does not exhibit obvious EP, AW and FR capacities. In lithium complex grease, with the combinations of molybdenum dialkyl dithiophosphate and boron ester or DMTD dimer complex with PAG, excellent EP, AW and FR performances can be achieved simultaneously. In polyurea grease, just the combination of molybdenum dialkyl dithiophosphate and DMTD dimer complex with PAG can get good EP, AW and FR results. In calcium sulfonate grease, the combination of molybdenum dialkyl dithiophosphate and DMTD dimer could achieve high weld load, low wear scar and low friction coefficient.

Keywords:
grease, extreme pressure, glycol, polyglycol, 2,5-dimercapto-1,3,4-thiadiazole, DMTD dimer, molybdenum dithiophosphate, antiwear agents, friction reducing agent, testing.

1. Introduction

Use of anti-friction, antiwear and extreme pressure additives in lubricating oils and greases is a common practice. These antiwear and extreme pressure additives play an important role in forming surface protective films either by adsorption or reaction. Such surface films can prevent direct metal to metal contact, thus provide metal surface protection against wear and weld between metal surfaces in relative motion under high load conditions. 2,5-dimercapto-1,3,4–thiadiazole (DMTD) derivatives are generally used in lubricants as metal passivating agents. Such additives also have antioxidant and antiwear properties, and are used in a wide range of lubricant applications. For example, as an additive for engine oil, gasoline engine oil oxidation stability can be significantly improved. In antiwear hydraulic oils, it can provide good anti-corrosive effect on copper and assist in improving hydrolytic stability [1]. Due to the high sulfur content of DMTD, their derivatives have potential as an extreme pressure additive. Previous studies showed DMTD dimer and DMTD dimer polyether complex, a new type high performance extreme pressure additive for greases, have excellent extreme pressure properties. The structure of DMTD provides its multifunctional properties which allows it to perform as an extreme pressure agent, metal deactivator, metal passivator/antioxidant. As such, this type of additive can overcome the limitations in reduced oxidation resistance and corrosion of copper that are inherent problems with other traditional EP additives [2-8]. DMTD dimer has following chemical structure:



This additive in its physical form is a solid/powder and has been shown to exhibit excellent extreme pressure performance in four-ball EP test [2, 9]. In four-ball EP test, most base greases will have four-ball weld point between 126 kgf and 160 kgf. When 2.0% DMTD dimer is added to these base greases, four-ball weld point can be increased to between 250 and 400 kgf. When DMTD dimer treat rate is increased to 3.0%, four-ball weld point can reach between 620 kgf.. and up to 800 kgf or above [9]. Extreme pressure performance of DMTD dimer comes from its bidentate adsorption on the metal surface [9]. Figure 1 is a diagram of this bidentate adsorption, i.e. the two ring structure of DMTD oriented parallel to the metal surface to form a bidentate complex structure, and if only one ring is desorbed from the surface, the molecule is still attached to the surface by the other ring.

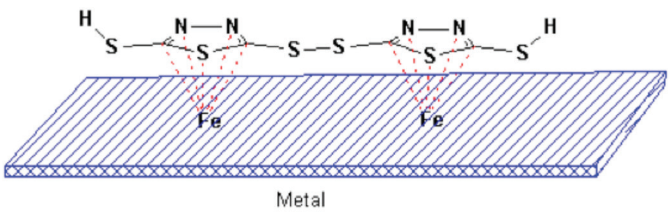


Figure 1. *DMTD dimer adsorption on metal surface.*

Four-ball weld point results of DMTD dimer in different base greases are listed in Table 1 [2]. As can be seen from Table 1, DMTD dimer exhibits good extreme pressure properties.

Grease Type	Four-Ball Weld Point, kgf	
	Base grease	+3% DMTD Dimer
Ca Complex	400	800
Bentonite Clay	126	315
Al Complex	160	500
Li Complex	200	800
Polyurea	100	315

Table 1. *Extreme pressure performance of different greases with 3.0% DMTD dimer.*

DMTD dimer can be dissolved in a polyalkylene glycol (PAG) solution to obtaining a biodegradable liquid product of DMTD/PAG complex. The product has excellent Timken extreme pressure properties and good Four-ball extreme pressure performance [8, 9]. Instead of bidentate adsorption of DMTD dimer, DMTD/PAG complex forms multidentate adsorption on the surface, the strongest adsorption possible [9]. DMTD/PAG complex adsorption on metal surface is shown in Figure 2.

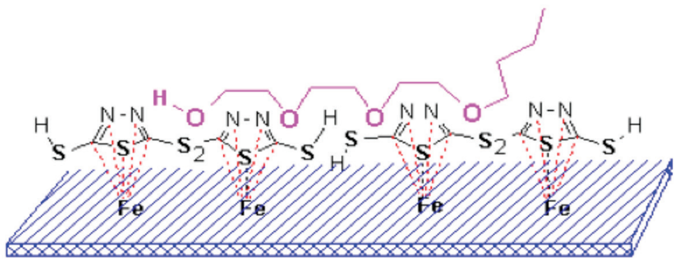


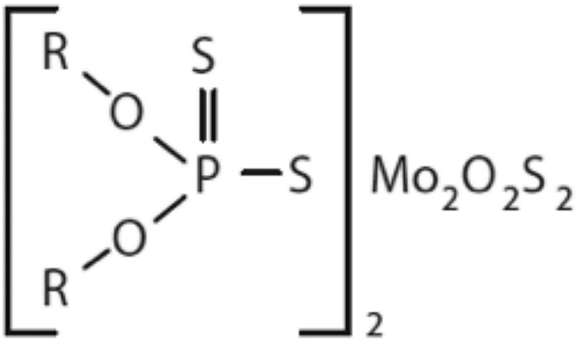
Figure 2. *adsorption of DMTD dimer / butoxy triethylene glycol complex on metal surface.*

Excellent EP performance supports the theory of such strong surface adsorption. Table 2 lists DMTD/PAG complex EP performance in various base greases [8, 9]. As can be seen from Table 2, this additive at low treat rates of 2% can provide a Timken OK load of up to 80 pounds and four-ball weld point up to 400 kgf in some base greases. To achieve this level of extreme pressure performance, normally heavy metals-containing EP additive is needed at 5% treat rate.

Base Grease	Treat Rate，m%	ASTM D2509: Timken OK load, lb	ASTM D2596: Four-ball weld，kgf	ASTM D2266: Four-ball wear, mm
Simple Li	2.0	80	400	0.67
	1.5	70	315	0.59
	1.0	50	250	0.63
Li Complex	2.0	80	400	0.60
	1.5	60	315	0.64
Al Complex	2.0	80	315	0.95
	1.5	50	250	---
Polyurea	3.0	40	250	0.84
	2.0	40	200	1.02

Table 2. *Extreme pressure properties of DMTD/PAG complex in different base greases.*

Molybdenum dialkyl dithiophosphate (MoDDP) is generally considered as a friction-reducing and antiwear additive, but it also can act as extreme pressure additive. Its chemical structure is as follows:



Extreme pressure performance of molybdenum dithiophosphate is mainly reflected in its ability to significantly improve last non-seizure load by reducing the four-ball wear scar diameter and steady state friction coefficient of the oil treated with this additive. A four-ball friction and wear tester was used in the evaluation of friction, wear and extreme pressure properties of a 650 SN base oil treated with this additive. Standard ASTM D4172 four-ball wear test method conditions were used, except test load was reduced from 40 kgf to 30 kgf for the base oil, only. All the other tests were run at 40 kgf load, 1200rpm, 60 minutes and 75°C. The base oil without additives could sieze at 40 kgf. The ASTM D2783 four-ball EP test method was used to measure the extreme pressure properties . Standard test conditions of 1760 rpm, 10 seconds and room temperature were observed. The molybdenum dialkyl dithiophosphate additive evaluated is a typical product of MoDDP (molybdenum content of 8.1%,phosphorus content of 6.1%, sulfur content of 12.3%) [10]. Test results are shown in Table 3.

	Four-Ball Wear, mm	C of F	LNSL, Kgf	Weld Point, Kgf
650 SN Base oil	0.802 (30Kgf)	0.100 (30Kgf)	36	100
+ 1.0% MoDDP	0.478	0.083	95	160
+ 2.0% MoDDP	0.376	0.077	100	160

Table 3. *Four-ball friction and wear tests on 650 SN base oil with MoDDP.*

As can be seen from Table 3, LNSL value of oil treated with MoDDP will increase from 36 kgf to 95-100 kgf, showing good extreme pressure performance but the weld point is only improved marginally. For four-ball wear test, the wear scar diameter under load of 30 kgf for base oil is 0.802 mm, by adding 1.0% and 2.0% MoDDP , the wear scar diameter under 40 kgf load is reduced to only 0.478 mm and 0.376 mm, respectively. It can also be seen from Table 3, the coefficient of friction (C of F) for oil with MoDDP will be reduced by 20%, from 0.083 to 0.077.

In general, though extreme pressure additives in grease can greatly improve the weld point, this often leads to lower antiwear performance of the grease, resulting in an increase in four-ball wear scar. As we know, MoDDP additive not only can provide excellent anti-friction and antiwear properties, but also can significantly improve the last nonseizure load. While on the other hand, DMTD derivatives can improve the EP performance in either 4-ball weld point or Timken OK load or both. Although for any lubricant oil or grease, four-ball weld point, the last nonseizure load (LNSL), four-ball wear scar diameter and friction coefficient are often mutually restrained since all these additives are competing for the same metal surface area for adsorption. In this paper, a combination of DMTD derivatives as EP additive and MoDDP as antiwear additive and friction reducer in various base greases were studied with several common grease performance evaluation test methods. It is expected that the combination of DMTD extreme pressure additive and molybdenum dialkyl dithiophosphate antiwear agent can provide the best balance of extreme pressure, antiwear and anti-friction properties in treated greases.

2. Experimental / Materials and Methods

2.1 Base Greases and Additives

Base greases used in this study include a lithium complex grease, a polyurea grease and a calcium sulfonate complex grease. All three base greases were obtained from real production batches courtesy of several grease manufacturers. DMTD dimer [10] used in this study has a sulfur content of 62.0-67.0% and a nitrogen content of 17.4-19.4%. DMTD dimer/polyalkylene glycol complex [10] has a sulfur content of 20-28%, and a nitrogen content of 6.0 to 10.0%. Molybdenum dialkyl dithiophosphate (MoDDP) has molybdenum, phosphorus and sulfur contents of approximately 8.1%, 6.1% and 12.3% respectively. All three additives are available commercially [10].

2.2 4-Ball Friction and Wear Test

Standard ASTM D2266 four-ball friction and wear test method was used to evaluate additive performance in lubricating grease. Experimental conditions were: 40 kgf load, 1200 rpm speed, 60 minutes, 75°C. Real-time recording of coefficient of friction during the test is also available with the specific four-ball test machine used, in addition to measurement of wear scar diameters.

2.3 Four-Ball EP test

Standard ASTM D2596 four-ball EP test method was used to evaluate additive EP performance in greases. Experimental conditions were: 1770 rpm speed, time duration 10 seconds. Both last nonseizure load (LNSL) and weld point were measured.

3. Results and Discussion

3.1 DMTD derivatives and molybdenum dialkyl dithiophosphate synergistic combination in lithium complex grease

MoDDP, DMTD dimer and DMTD/PAG complex were added to the lithium complex base grease at the indicated treat levels. Four-ball wear and extreme pressure tests were performed on the treated grease, see results in Table 4.

Grease	Wear Scar, mm	C of F	LNSL, Kgf	Weld point, kgf
Li Complex base grease	0.552	0.119	48	126
+ 1.0% MoDDP	0.378	0.077	94	160
+ 2.0% MoDDP	0.365	0.076	114	160
+ 3.0% MoDDP	0.359	0.077	121	200
+ 2.0% DMTD dimer	0.650	0.113	66	400
+ 1.0% DMTD/PAG complex	0.685	0.105	82	250
+ 2.0% DMTD/PAG complex	0.766	0.086	94	315
+ 2.0% MoDDP + 1.0% DMTD dimer	0.385	0.066	121	250
+ 1.0% MoDDP + 2.0% DMTD dimer	0.461	0.077	88	400
+ 2.0% MoDDP + 2.0% DMTD dimer	0.441	0.064	88	315
+ 1.0% MoDDP + 1.0% DMTD/PAG complex	0.412	0.067	82	250
+ 1.0% MoDDP + 2.0% DMTD/PAG complex	0.418	0.060	94	315

Table 4. *Additive performance on friction, wear and extreme pressure properties in treated lithium complex base grease.*

As can be seen from Table 4, MoDDP has excellent friction and wear performance in lithium complex grease. After adding MoDDP, both the friction coefficient and four-ball wear scar diameter, have been substantially decreased, while the last nonseizure load has been increased greatly. After adding extreme pressure agents DMTD dimer and DMTD/PAG complex, extreme pressure performance of the lithium complex grease was greatly improved. Both LNSD and weld point have been increased significantly, especially the weld point. But the four-ball wear scar diameter has been increased, indicating that these DMTD derivatives are good at improving EP performance but are poor in antiwear or wear resistance.

On the other hand, it is obvious from Table 4, that combinations of MoDDP and DMTD dimer or DMTD/PAG complex, can significantly improve both extreme pressure, antiwear/friction performance simultaneously in lithium complex grease. Figure 3 and Figure 5 showed the different effects on friction reducing performance between individual additive and additive combinations. And Figure 4 and Figure 6 showed the different effects on antiwear performance between individual additive and additive combinations.

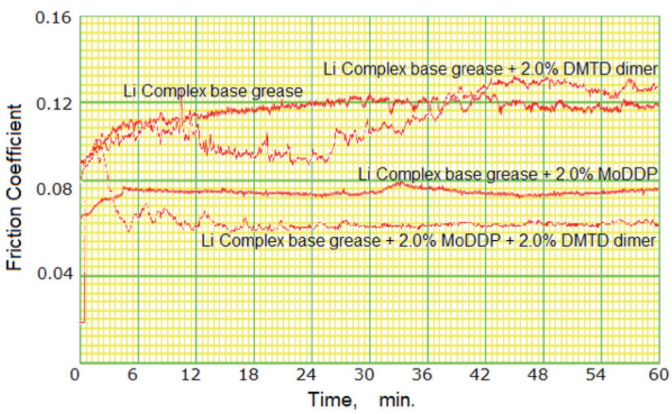


Figure 3. *Friction reducing performance of MoDDP and DMTD dimer in lithium complex grease.*

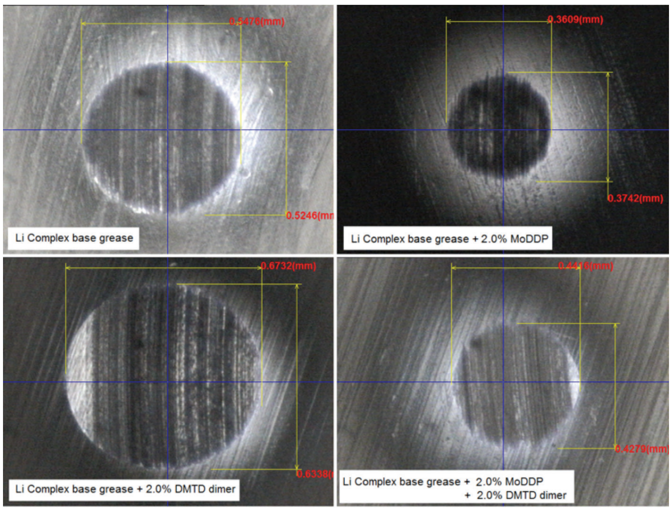


Figure 4. *Antiwear performance of MoDDP and DMTD dimer in lithium complex grease.*

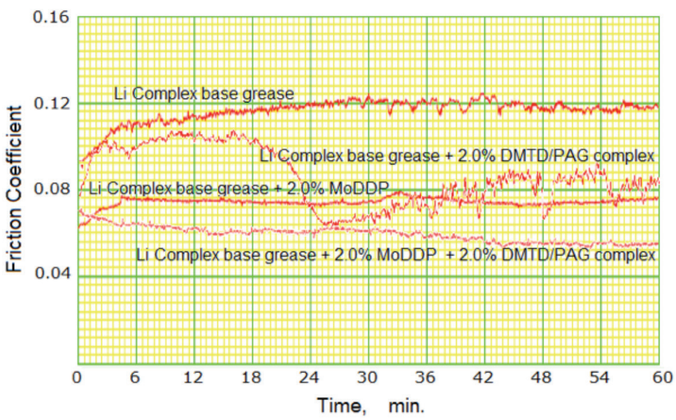


Figure 5. *Friction reducing performance of MoDDP and DMTD/PAG complex in lithium complex grease.*

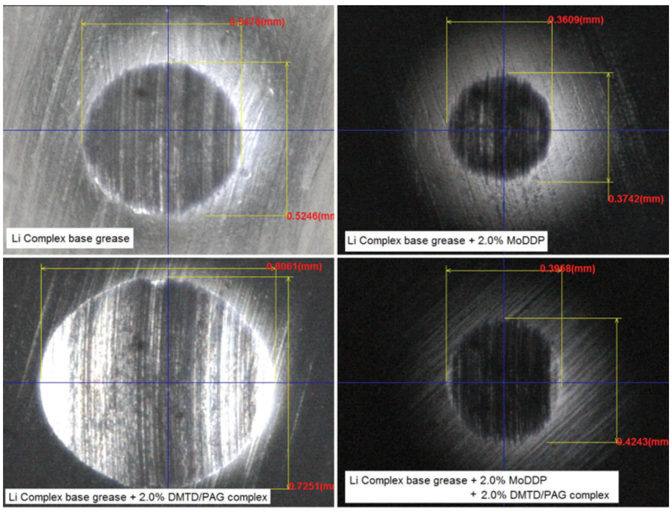


Figure 6. *Antiwear performance of MoDDP and DMTD/PAG complex in lithium complex grease.*

3.2 DMTD derivatives and molybdenum alkyl dithiophosphate synergistic combination in polyurea grease

MoDDP, DMTD dimer and DMTD/PAG complex were added to the polyurea base grease at the indicated treat levels. Four-ball wear and extreme pressure tests were performed on the treated grease, results shown in Table 5.

Grease	Wear Scar, mm	C of F	LNSL, Kgf	Weld Point, Kgf
Ca Sulfonate Complex base grease	0.375	0.098	100	315
+ 1.0% MoDDP	0.396	0.087	88	400
+ 2.0% MoDDP	0.373	0.072	152	400
+ 2.0% DMTD dimer	0.531	0.086	94	620
+ 2.0% DMTD/PAG complex	0.472	0.102	71	400
+ 1.0% MoDDP + 2.0% DMTD dimer	0.521	0.096	48	620
+ 2.0% MoDDP + 2.0% DMTD dimer	0.426	0.078	40	620
+ 1.0% MoDDP + 2.0% DMTD/PAG complex	0.472	0.104	76	500
+ 2.0% MoDDP + 2.0% DMTD/PAG complex	0.475	0.096	44	500

Table 5. *Additive performance on friction, wear and extreme pressure properties in treated polyurea base grease.*

Table 5 Additive performance on friction, wear and extreme pressure properties in treated polyurea base grease

As can be seen from Table 5, polyurea grease treated with MoDDP does not show any improvement in extreme pressure performance. Its friction reducing and antiwear properties are also not obvious. But this does not mean that all organic molybdenum additives are not effective in polyurea greases. As a matter of fact, molybdenum dibutyl dithiocarbamate, i.e. a MoDTC [10] with molybdenum content of approximately 28% and sulfur content of about 24.5% is very effective in friction reducing and antiwear performance in the same polyurea used in this study. Adding 1.0% and 2.0% of MoDTC in the polyurea grease can effectively reduce friction coefficient from 0.089 to 0.071 and 0.058, respectively. It can also reduce 4-ball wear scar diameter from 0.423 mm to 0.359 mm and 0.349 mm, respectively. At the same time, the weld point can be improved from 250 kgf to 315 kgf. Therefore, MoDTC might be more effective than MoDDP in polyurea greases (data for MoDTC treated grease is not shown in Table 5).

It can also be seen from Table 5, polyurea grease treated with DMTD extreme pressure agents DMTD dimer and DMTD/PAG complex, the weld point of the grease can be effectively increased, but there is no improvement in four-ball wear scar diameter, indicating that these additives are poor in antiwear performance. But unexpectedly, 2.0% DMTD/PAG complex can reduce friction coefficient from 0.089 to 0.077 in the treated grease, showing a strong friction reducing performance. When combination of MoDDP and DMTD dimer or DMTD/PAG complex was used in this grease, the weld point of the treated grease can remain at high values (though LNSL is lower), and four-ball wear scar diameter is smaller than when only DMTD extreme pressure agent was used, although still higher than the value for the base grease. This indicates that MoDDP can be used to improve the antiwear performance when DMTD containing extreme pressure agents are used. When combination of 2.0% MoDDP and 2.0% DMTD/PAG complex was used, the overall performance of the polyurea grease is well balanced with a high weld point, a low wear scar diameter and a small coefficient of friction.

3.3 DMTD derivatives and molybdenum alkyl dithiophosphate synergistic combination in calcium sulfonate complex grease

MoDDP, DMTD dimer and DMTD/PAG complex were added to the calcium sulfonate complex base grease at the indicated treat levels. Four-ball wear and extreme pressure tests were performed on the treated grease, results shown in Table 6.

Grease	Wear Scar, mm	C of F	LNSL, Kgf	Weld Point, Kgf
Ca Sulfonate Complex base grease	0.375	0.098	100	315
+ 1.0% MoDDP	0.396	0.087	88	400
+ 2.0% MoDDP	0.373	0.072	152	400
+ 2.0% DMTD dimer	0.531	0.086	94	620
+ 2.0% DMTD/PAG complex	0.472	0.102	71	400
+ 1.0% MoDDP + 2.0% DMTD dimer	0.521	0.096	48	620
+ 2.0% MoDDP + 2.0% DMTD dimer	0.426	0.078	40	620
+ 1.0% MoDDP + 2.0% DMTD/PAG complex	0.472	0.104	76	500
+ 2.0% MoDDP + 2.0% DMTD/PAG complex	0.475	0.096	44	500

Table 6. *Additive performance on friction, wear and extreme pressure properties in treated calcium sulfonate complex base grease.*

As it can be seen from Table 6, molybdenum dithiophosphate MoDDP can provide some extreme pressure performance in calcium sulfonate complex grease, and friction reducing effect is also relatively obvious, but there is almost no antiwear improvement. This is mainly due to the calcium sulfonate complex base grease having very good antiwear performance, making MoDDP less effective. Overall, calcium sulfonate complex grease treated with 2.0% MoDDP performed pretty well. The weld point was increased from 315 kgf to 400 kgf, and last nonseizure load was increased from 100 kgf to 152 kgf , friction coefficient was lowered from 0.098 to 0.072, and wear scar diameter at 0.373 mm is still considered very good.

It can also can be seen from Table 6, adding an extreme pressure agent such as DMTD dimer or DMTD/PAG complex to calcium sulfonate complex grease, can effectively improve the weld point of the grease, especially when DMTD dimer was added. When 2.0% DMTD dimer was added to the grease, the weld point can reach 620 kgf. In fact, when 3.0% DMTD dimer was added to the grease, the weld point will reach 800 kgf (data not shown in Table 6). But, in both cases when DMTD dimer or DMTD/PAG complex was added to the grease, the grease will have an increased four-ball wear scar diameter, indicating that antiwear performance of the grease actually deteriorated. When combination of MoDDP and DMTD/PAG complex was used, the overall performance of the grease did not show any major improvement, except a slight increase of the weld point to 500 kgf. On the other hand, when a combination of 2.0% MoDDP and 2.0% DMTD dimer was used, the treated grease gave a very high weld point (620 kgf) , small wear scar diameter (0.426 mm) and low coefficient of friction (0.078).

4. Conclusions

(1) DMTD extreme pressure agents, DMTD dimer and DMTD/PAG complex, exhibit excellent extreme pressure performance. Adding these EP agents to lithium complex grease, polyurea grease and calcium sulfonate complex grease can effectively improve the four-ball weld point of these greases.

(2) Molybdenum dialkyl dithiophosphate (MoDDP) has excellent friction reducing and antiwear performance in lithium complex grease. This additive can greatly reduce wear scar diameter and friction coefficient in lithium complex grease. In calcium sulfonate complex grease, it has good extreme pressure properties (increasing the last nonseizure load and weld point in four-ball EP test), and excellent friction reducing properties. In polyurea grease, it does not show obvious extreme pressure, antiwear and anti-friction properties.

(3) When combination of molybdenum dialkyl dithiophosphate (MoDDP) and DMTD dimer or DMTD/PAG complex was used in the lithium complex grease, the treated grease exhibited excellent friction reducing, antiwear and extreme pressure properties.

(4) When combination of molybdenum dialkyl dithiophosphate (MoDDP) and DMTD/PAG complex was used in the polyurea grease, the treated grease exhibited excellent friction reducing, antiwear and extreme pressure properties.

(5) When molybdenum dialkyl dithiophosphate (MoDDP) was used in the calcium sulfonate complex grease, the treated grease achieved very high weld point, reduced wear scar diameter and lowered the coefficient of friction.

References

[1] Chen, Lihua; Zhang, Chunhui; Discussion on Function and Mechanism of Metal Deactivators. Lubrication and Seal, 2003, (1): 73-76 (in Chinese).
[2] Hoffman, D. M., Feher, J. J., Lubricating Compositions Containing 5,5'-Dithiobis (1,3,4-Thiadiazole-2-Thiol), US Patent No. 4,517,103 (1985).
[3] Karol, T., Maleic Derivatives Of 2,5-Dimercapto-1,3,4-Thiadiazoles and Lubricating Compositions Containing Same, US Patent No. 5,055,584 (1991).
[4] King, J.P., Hill, B. L., Thiadiazole Compounds and Lubricant Additives thereof US Patent No. 5,102,568 (1992).
[5] Karol, T., Polyether Glycol Derivatives Of 2,5-Dimercapto-1,3,4-Thiadiazole, US Patent No. 5,138,065 (1992).
[6] Karol, T., Luo, R. J., Ether Derivatives Of 2,5-Dimercapto-1,3,4-Thiadiazoles, US Patent No. 5,194,621 (1993).
[7] Karol, T., Tepper, R. J., Bis-1,3,4-Thiadiazole Compounds and Lubricating Compositions Containing Same, US Patent No. 5,849,925 (1998).
[8] Karol, T., Tepper, R. J., Thiadiazole Additives and Lubricating Compositions Containing the Same, US Patent No. 6,365,557 (2002).
[9] Karol, T., Thiadiazole Technology: Motor Oil Antiwear and Grease Extreme Pressure Additives, Technical Paper of R. T. Vanderbilt Company.
[10] Product Brochure of Vanderbilt Chemicals, LLC, 2013.

LINK
www.vanderbiltchemicals.com