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Study on the Proportion Law of Sulfur Extreme Pressure Additives Based on Response Surface Methodology

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Keywords ： EP additives; proportion law; Box-Behnken design; response surface methodology

ABSTRACT

Extreme pressure (EP) additives are an important component of gear oils, which are used to prevent gears from sticking, ploughing and other wear under extreme working conditions, and to protect tooth surfaces and extend the service life of gear oils. The anti-friction and anti-wear properties of three extreme pressure single agents under the contact pressure of 1.2 GPa were studied in this paper, and the optimal concentration range of the three additives was determined. The action mechanism of additives was analyzed by XPS and SEM. To combine the advantages of the three additives and study the proportion law of the three additives, taking the additive concentration as the input, the COF and the wear rate as the response, Box-Behnken design (BBD) sampling method was used to select the experimental data. The relationship between the concentration and COF and wear rate was obtained through the response surface methodology (RSM) with Design Expert software, and the influence of the concentration of three additives on the response value was discussed through the RSM curve. The optimized concentration ratio was obtained through the desirability analysis. Then the friction and wear value of the predicted value were verified through the experiment, and the error was within 4%.

INTRODUCTION

Automobile is one of the most common and important tools in modern society, which plays an irreplaceable role in social production and life. Gear oil is the blood of vehicle, which is related to the normal operation of vehicle parts. Under the condition of high load, high speed and high temperature, the gear oil is often cracked due to the insufficient strength of the lubricating film, which leads to serious wear of the gear and affects the normal operation of the vehicle (Parenago et al., 2017; Qu et al., 2015). Anti-wear additive is to protect the surface of gear and bearing, prevent the wear and sintering of moving parts, and improve the reliability of engine under this extreme pressure lubrication condition (Mohammadtabar et al., 2019; Spikes, et al., 2008).

Although there are many reports that various new no sulfur or phosphorous additives have been developed (Huai et al., 2020; Johnson et al., 2017; Rastogi et al., 2012), sulfur-based additives are still the mainstream additives for gear oils. The organic sulfide forms a physical adsorption film, an anti-wear film of iron mercaptan and an extreme pressure film of iron sulfide on the surface of the relatively moving iron-based friction pair (Ma et al., 2009; Mamedova et al., 2017; Mistry et al., 2013). At present, most of the research is focused on single agent, because of the large amount of data, it is difficult to explore the proportion law of a variety of additives. Therefore, it is very important to find a suitable data analysis method to reduce the amount of data. Response surface methodology (RSM) (Baş et al., 2007) is a method to optimize the experimental conditions. Through the regression fitting of the process and the drawing of response surface and contour, the response values corresponding to each factor level can be easily obtained. At present, RSM is mainly used in industrial design (Redhwan et al., 2018; Urbiola-Soto et al., 2016), food processing (Jiang et al., 2010; Nwabueze et al., 2010), drug preparation (Badgujar et al., 2015), composite material preparation (Srivabut et al., 2019; Homkhiew et al., 2013) and so on. With the development of tribology, response surface analysis has also been gradually applied to analyze and process friction data and optimize the selection of lubricants.

In tribology field, many predecessors have carried out research on the effects of lubricants,

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surface morphology and friction parameters on friction and wear based on RSM and achieved fruitful results. Maatallah et al. (2016) conducted experimental designs by RSM to analyze the relationship between the failure of EHL rolling contact in highly polluted media and surface parameters. Srivastava et al. (2008) used RSM and central composite design (CCD) to model the effect of working variables on surface roughness performance in the Solid Lubricant Assisted Machining process. Garc´ıa et al. (2018) proposed an experimental design method based on Ra measurement for optimization of machined surface roughness. Gupta et al. (2015) described the RSM and particle swarm optimization (PSO) technology in the minimum quantity lubricant environment. Kim et al. (2013) and Kumar et al. (2013) studied wear behavior of materials, and found the most important factors by RSM. Ossia et al. (2009) did research on wear resistance and lubricity of acid in biodegradable castor oil base material by RSM with Box-Benhken design. Rajmohan et al. (2016) and Haron et al. (2010) established models of tool wear based on RSM, and came to the conclusion that the influence of feed rate is more significant when processing metal materials.

This article is mainly to study the influence of the concentration of phosphate ammonium salt, thiophosphate ammonium salt, and dithiophosphate ammonium salt in gear oil on friction and wear. XPS and SEM were used to analyze the wear mechanism of different additives. The response surface method was used to analyze the proportion laws of these three additives, and the optimal concentration was found through the response surface. In order to verify the prediction results，the COF and wear rate of friction area lubricated with predicted additives ratio were tested through ring-block tests.

EXPERIMENTAL PROCEDURES

Tribological tests

The tribological tests were conducted by a ring-block tester (Fig. 1). The contact pressure was 1.2 GPa; the rotate speed was 500 r/min and every test lasted for 30 min. The value of COF was collected by torque sensor (HCNJ-103, Beijing Haibohua Technology Co., Ltd., Beijing, China). The grade of base oil was 80W-90 (GL-5). Additive #1 and #2 were sulfur phosphorus type, and additive #3 was nitrogen phosphorus type, provided by PetroChina Lanzhou Lubricant Research and Development Center. The rings and blocks were made of bearing steel with a surface roughness Ra of 0.056 μm and quenched to ensure that the hardness researched 750 ± 50 HV.

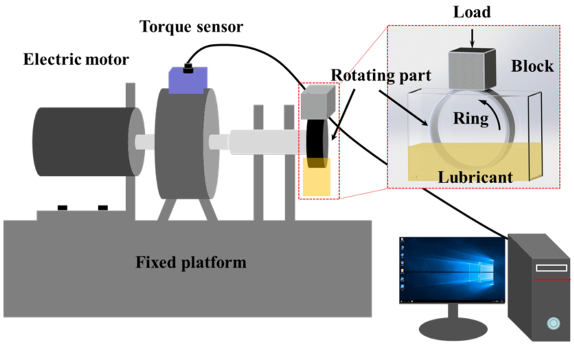

Fig. 1. Schematic diagram of ring-block testing machine.

Characterization methods

To analyze the functional groups and structure of additives, the infrared spectrum was detected by a Fourier infrared spectrometer (Nicolet iS50, Thermo Fisher Technology (China) Co., Ltd., China). XPS analysis was used to detect the composition of the friction film on the worn surface to analyze the mechanism of anti-friction and anti-wear. And the spectrum was obtained by X-ray photoelectron spectroscopy (Thermo Fisher ESCALAB Xi+, Thermo Fisher Technology (China) Co., Ltd., China). The surface morphology of wear scars was observed by a tungsten filament scanning electron microscope (SEM, EVO 10, Carl Zeiss optics Co., Ltd., Germany).

RESULTS AND DISCUSSION

Infrared spectrum

To detect the molecular structure and optical energy group composition of the three additives, the infrared spectra of the additives were obtained by Fourier infrared spectroscopy (Fig. 2). The wavenumber of additive #1 at 1380, 2860, 2870 and 2970 cm^{-1} indicated that it contained saturated and unsaturated hydrocarbon bonds, such as $-CH_2-$, benzene ring, etc. 841cm^{-1} and 810 cm^{-1} showed that additive #1 contained σCH para-disubstitution. 1015cm^{-1} and 1220 represented C-O-P(=S)-O-C and C-O groups. Therefore, the additive #1 was ammonium thiophosphate. Additive #2 had peaks at wavenumber of 2870, 2930, 2960, 746, 898, 1360, 1620, 1296 and 1015 cm^{-1}, indicating that it contained saturated and unsaturated C-H, σCH ortho-disubstitution of benzene ring, N-H, P-S and C-O-P(=S)-O-C groups, and it could be inferred that additive #2 was ammonium dithiophosphate. In the infrared spectrum of additive #3, 1380, 2870 and 1930 cm^{-1} were C-H stretching vibrations, representing the presence of $-CH_3$, and 887 cm^{-1} was $-CH_2-$. The peaks of 1210, 1040 and 1620 cm^{-1} in the spectrum represented P=O, C-N and N-H, respectively. It could be explained that #3 was a phosphate ammonium salt additive.

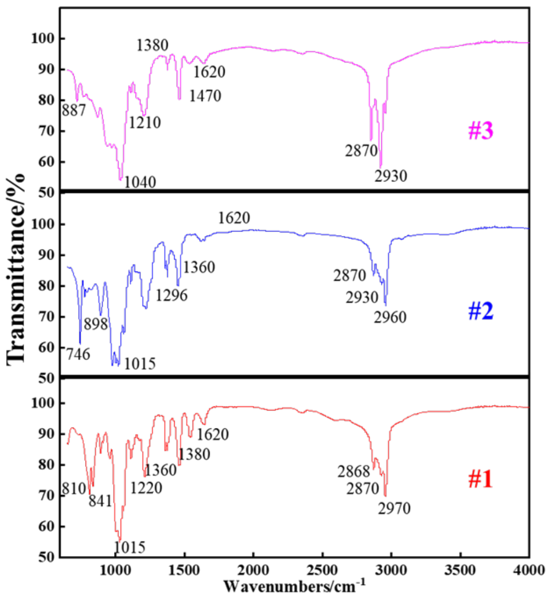

Fig. 2. Infrared absorption spectra of additives

Friction and wear

The tribological performance test results of the 3 additives were shown in Fig. 3. The COF of additive #1 was first decreased and then slightly increased with the increasing of concentration, and the COF of additives #2 and #3 decreased with the increasing of concentration (Fig .3a). The figure showed that the additive #1 had the lowest COF at the concentration of 1.0 wt% which indicated it had best anti-friction effect, and #3 was the worst. Besides, it could be seen that the optimum concentration of single agent #1 was about 1.2 wt%. Fig. 3b was the wear rate of additives under different concentration, and it illustrated that as the concentration increased, the wear rate of additives #2 and #3 had been decreasing, and #1 first decreased and then had a slightly increase. The best anti-wear ability was additive #2, probably because it was a disulfide compound, which could form more denser sulfur-containing transfer film on the friction interface, thus having excellent anti-friction and anti-wear effects.

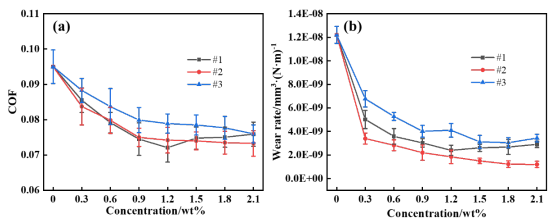

Fig. 3. The curve chart of COF (a) and wear rate (b) of bearing steel friction matching pair with additive concentration (#1: phosphorothioate amine salt additive; #2: dithiophosphate amine salt additive; #3: phosphate amine salt additive)

XPS analysis

The composition of friction film with different additives was analysis by XPS, and the results were shown in Fig. 4. The wear scar with additive #1 tested Fe, O and N elements. The characteristic peaks of Fe_{2p} were 708.3 eV, 709.6 eV, 710.7 eV, 713.1 eV and 719.8 eV, respectively, representing Fe_2O_3, FeO, $Fe_2(SO_4)_3$ and Fe^{3+} (Fig. 4a). The element characteristic peaks of O_{1s} also indicated that these substances were contained (Fig. 4b). The characteristic peak positions of N_{1s} were 396.6 eV and 400.5 eV, which indicated that the friction films contained organic amine compounds and $(NH_4)_3PO_4$ (Fig. 4c). The Fe, N, P elements on wear scar with #2 additive was tested by XPS. It could be seen from the characteristic peak position of the photoelectron spectrogram of Fe_{2p} that the friction film contained FeS, Fe_2O_3, $Fe_2(SO_4)_3$ and Fe_3O_4 (Fig. 4d). N1s had a characteristic peak at 399.39 eV, and P2p had characteristic peaks at 133.6 eV and 133.7 eV, indicating that it contained $(NH_4)_3PO_4$ and $P_2O_7^{4-}$ ion complex (Fig. 4e and f). The wear scar with #3 additive detected Fe, N, P elements, and the results showed that the friction films were mainly composed of Fe_2O_3, $FePO_4$, $P_2O_7^{4-}$, $(NH_4)_3PO_4$ and amine-containing organics (Fig. 4g, h and i).

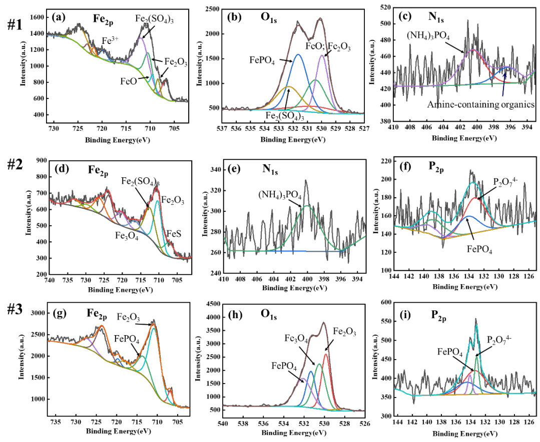

Fig. 4. XPS analysis of wear scars with different additives

SEM analysis

The SEM images of bearing steel block wear surface after ring-block tests were shown in Fig. 4. In Fig. 5a, the wear scar width was 1156 μm under the lubrication of gear oil with no additives, and there was serious ploughing wear and surface metal peeling in the friction area. The wear scar width of additive #1 was 827 μm, and the ploughing wear could be observed at high magnifications (Fig. 5b). The friction area with the smallest wear scar width was the friction surface lubricated with additive #2, which was 723 μm. And there was severe ploughing wear in local area (Fig .5c). Fig. 4d indicated that the wear scar width of additive #3 was 885 μm, a little bigger than #1 and #2, but the overall wear surface was relative smooth, and there was only a slight mark of ploughing wear. Sulfur-based and phosphorus-based additives have synergistic antifriction, anti-wear and extreme pressure effects. Nitrogen-containing organic amines can be better adsorbed on the metal surface, have obvious synergistic effect with sulfur-based additives, and can effectively improve the bearing capacity of oil products. Under extreme pressure friction conditions, #1 additive formed high oxidized phosphoric acid and sulfate, and organic amines were adsorbed on the friction interface to form a friction film to reduce friction and wear. The #2 additive was ammonium dithiophosphate, so in addition to high oxidized sulfate and phosphate, lamellar FeS was also formed, which had better tribological properties. Different from #1 and #2 additives, #3 did not contain sulfur, and nitrogen-containing organic matter would adhere closely to the friction interface, so iron phosphate and organic amines formed a transfer film at the friction interface, which would protect the friction interface from being scratched. For the organic matter had poor abrasion resistance, smooth and wide wear scars appeared on the friction pair surface.

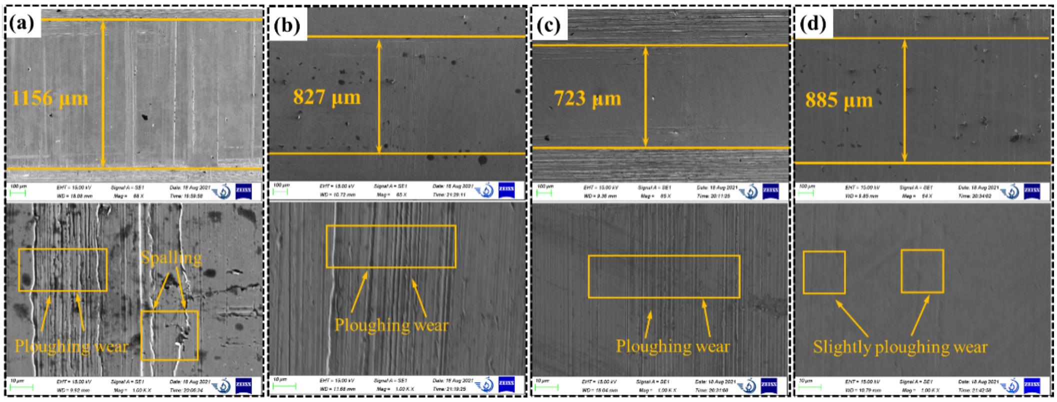

Fig. 5. SEM images of wear surfaces lubricated by gear oil with different additives ((a) no additive; (b) additive #1; (c) additive #2; (d) additive #3)

Analysis and optimization with RSM

Through the tribological experiment, #1 has the best anti-friction ability, #2 has good anti-wear ability, and #3 has good anti-sintering ability, but has poor anti-wear ability. Therefore, these three additives can be compounded to complement each other's advantages and improve the overall anti-friction and anti-wear ability. The RSM was used to find the optimal ratio of three additives.

RSM is a commonly used optimization method to solve multivariable problems. Choose reasonable experimental design methods, use multiple regression equations to fit the relationship between the response and multiple factor variables, and use multiple regression equations to replace the actual response value and the relationship between the variables to achieve parameter optimization. The Design Expert software was used to analyze the data and plot relevant graphs. The design method used in this experiment is Box-Behnken design (BBD), the different concentrations of three additives are set as three factors, and the COF and wear rate are the response values. According to the friction and wear test results, the optimal concentration range of #1 additives is 0.5~1.5 wt%, while the concentration range of #2 and #3 additives is 1.0~2.0 wt%. Therefore, when designing the experiment with BBD method, #1 additive high factor is set to 1.5, low factor is set to 0.5, #2 and #3 additives high factor is set to 2.0, and low factor is set to 1.0. And the numeric factor setting of BBD was shown in Table 1.

Table 1 Numeric factors setting of Box-Behnken design

	Name	Units	Low	High
A	#1	wt%	0.5	1.5
B	#2	wt%	1.0	2.0
C	#3	wt%	1.0	2.0

Table 2 Different impact factors and corresponding response data

A: #1 wt%	B: #2 wt%	C: #3 wt%	Response 1: COF	Response 2: Wear rete $mm^3 \cdot (Nm)^{-1}$
1.00	2.00	1.00	0.07532	1.7312E-009
1.00	1.00	1.00	0.07542	2.2370E-009
1.00	1.50	1.50	0.07456	2.2863E-009
1.00	2.00	2.00	0.07265	2.3456E-009
1.00	1.50	1.50	0.07455	2.3652E-009
0.50	1.50	1.00	0.07452	2.5132E-009
0.50	1.00	1.50	0.07346	3.7733E-009
1.00	1.50	1.50	0.07521	2.4635E-009
1.00	1.00	2.00	0.07449	2.3549E-009
1.50	1.00	1.50	0.07629	2.6131E-009
1.50	1.50	1.00	0.07685	2.3556E-009
1.50	1.50	2.00	0.07509	3.0408E-009
1.00	1.50	1.50	0.07511	2.0092E-009
1.50	2.00	1.50	0.07523	3.0978E-009
0.50	1.50	2.00	0.07198	2.7937E-009
0.50	2.00	1.50	0.07312	2.3604E-009
1.00	1.50	1.50	0.07455	2.0132E-009

According to the parameter range in Table 1, 17 parameter combinations shown in Table 2 were obtained. Based on each parameter combination, different concentrations of additives were added to gear oil as lubricant for tribological tests. And then recorded the COF and calculated wear rate as the response values. The relationship between all impact factors and responses were shown in Table 2.

During the RSM analysis of the data, after the square root of the wear rate value, the selected model had more insignificant lack-of-fit and less error. According to the analysis of impact factors and response data, the fit summary of common models was counted, and the results were shown in Table 3 and 4. In the table, a small sequential p-value means the highest order polynomial with significant additional terms and no aliasing model is selected. In the "lack of fit" item, if the p-value is greater than the F-value, the model can fit the data accurately. And in "adjusted" and "predicted" items, the larger the R^2 value, the higher the reliability of the model. Therefore, according to the data in Table 3 and 4, the 2FI model was selected in response 1 and quadratic model was selected in response 2. The equations of the 2 models were Eq. (1) and (2).

Table 3 Fit summary of models (Response 1: COF)

Source	Sequential p-value	Lack of fit F-value	Lack of fit p-value	Adjusted R^2	Predicted R^2	
Linear	<0.0001	1.44	0.3855	0.9051	0.8627	
2FI	0.0402	0.61	0.7197	0.9442	0.9216	Suggested
Quadratic	0.3983	0.38	0.7706	0.9464	0.8876	
Cubic	0.7706			0.9272		Aliased

Table 4 Fit summary of models (Response 2: wear rate)

Source	Sequential p-value	Lack of fit F-value	Lack of fit p-value	R^2	Adjusted R^2	
Linear	0.4318	5.96	0.0505	0.1846	-0.0172	
2FI	0.2724	5.95	0.0530	0.4383	0.01163	
Quadratic	0.0012	0.2005	0.8911	0.9349	0.8546	Suggested
Cubic	0.8911			0.9434	0.8122	Aliased

Response 1:

$$y_1 = a + a_1x_1 + a_2x_2 + a_3x_3 + a_4x_1x_2 + a_5x_1x_3 + a_6x_2x_3 \quad \text{Eq. (1)}$$

Response 2:

$$y_2 = \{\ b + b_1x_1 + b_2x_2 + b_3x_3 + b_4x_1x_2 + b_5x_1x_3 + b_6x_2x_3 + b_7x_1^2 + b_8x_2^2 + b_9x_3^2\ \}^2 \quad \text{Eq. (2)}$$

Where,

x_1, x_2 and x_3 are the concentrations of #1, #2 and #3 additives respectively; y_1 and y_2 are the values of COF and wear rate.

The RSM models of friction coefficient and wear rate were obtained by analyzing the experimental data (Table 2) and calculating the coefficients of Eq. (1) and Eq. (2). respectively. And the models' equations were shown in following Eq. (3) and Eq. (4).

$$\begin{aligned} COF = {} & 0.07241 + (2.505e-3)x_1 + (2.495e-3)x_2 \\ & -(1.45e-4)x_3 - (7.2e-4)x_1x_2 \\ & +(7.8e-4)x_1x_3 - (1.74e-3)x_2x_3 \end{aligned} \quad \text{Eq. (3)}$$

$$\begin{aligned} Wear\ rate = \{ & (1.09e-4) - (8.2e-5)x_1 - (4e-5)x_2 \\ & +(1.1e-5)x_3 + (1.7e-5)x_1x_2 \\ & +(3.8853e-6)x_1x_3 + (5.5932e-6)x_2x_3 \\ & +(2.4e-5)x_1^2 + (3.68e-6)x_2^2 \\ & -(6.44e-6)x_3^2\ \}^2 \end{aligned} \quad \text{Eq. (4)}$$

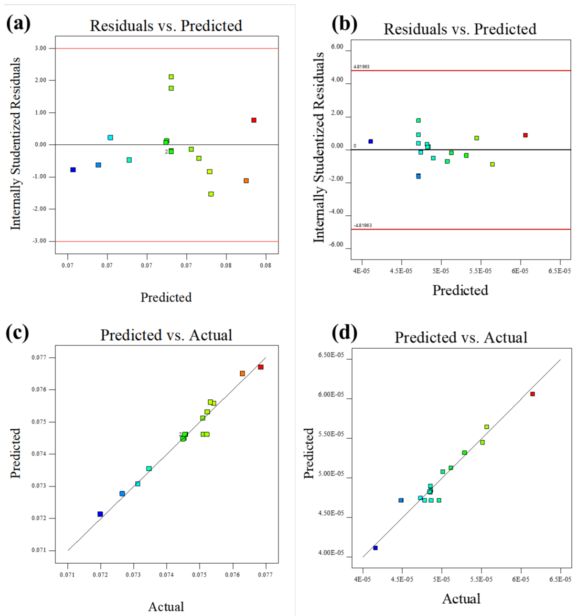

Fig. 6. (a) and (b) distribution diagram of residual

and predicted value of COF and wear rate; (c) and (d) distribution diagram of actual and predicted values of COF and wear rate

Bring the actual values into the above models for further accuracy analysis of the corresponding models. Fig. 6 was used to describe the accuracy of the response surface model. (a) and (b) were the distribution diagrams of the relationship between the residual error and predicted value of COF and wear rate respectively, and (c) and (d) were the relationship carves between predicted and actual value of COF and wear rate respectively. Fig. 6(a) and (b) showed that the residuals were distributed up and down the horizontal axis and did not gather at one end, which indicated that the models were reliable and highly accurate. The predicted and actual values of COF and wear rate were almost on a 45° curve, indicating that the experimental value and the predicted value had a high degree of fit, and the predicted value could be a good substitute for the experimental value (Fig. 6c and d). From the above data, we could see that the data in Fig. 5 verified the accuracy of the two models mentioned above.

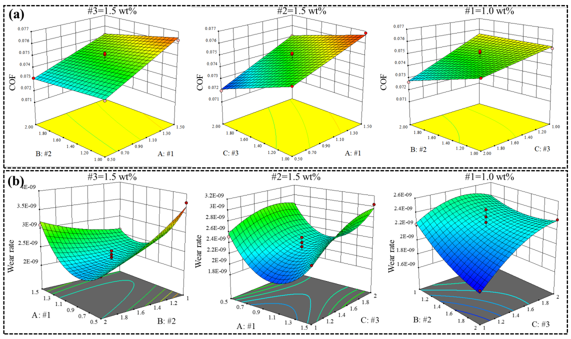

Fig. 7. The influence of interaction items on response values of (a) COF and (b) wear rate

Fig. 7 depicted the effect of interaction relative response values on COF and wear rate. In Fig. 7a, when the concentrations of additive #3 was 1.5 wt%, the value of #1 had a great impact on COF, and their numbers showed positive correlation. When the #1 value was the smallest, the COF was the lowest and #2 lead to subtle changes in COF. When #2 was fixed at 1.5 wt%, the COF was in a lower state if the value of #1 was smaller or the value of #2 was larger. When the value of #1 was1.0 wt%, the smaller the concentration of additive #2 and #3, the lower the COF. The effect of interaction items on response of wear rate was shown in Fig. 7b. From the figure, when the concentration of additive #3 was 1.5 wt%, the wear rate was minimum under the condition of that #1 was 0.8 wt% and #2 was 1.8 wt%. If the value of #2 was 1.5 wt%, minimal wear of the friction pair was got when #1 was 1.1 wt% and #3was 1.0 wt%. And if the concentration of #1 was fixed at 1.0 wt%, the minimum wear was obtained when the value of #2 was 2.0 wt% and #3 was 1.0 wt %. Fig. 6 mainly described the effect of dual variables on friction and wear, and provided a certain reference for the subsequence optimization of the ratio.

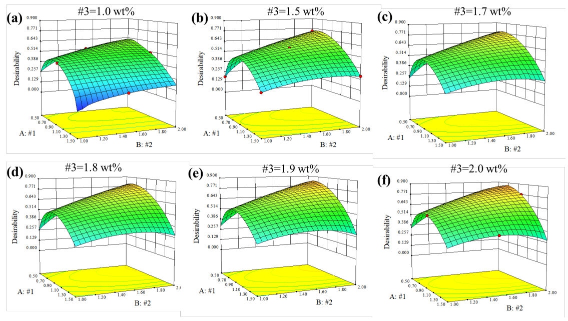

Fig. 8. Three-dimensional diagram of desirability of different additive concentrations

To select the optimal ratio, gave the same weight to the response values of COF and wear rate, and calculated the desirability under each concentration. Fig. 8 was charts showing the relationship between interaction factors and desirability when maximum desirability could be obtained. Fig. 8 (a-f) illustrated the desirability varied with the concentration of additive #1 and #2 when #3 changed from 1.0 wt% to 2.0 wt%. The entire desirability response surface increased with the increase of concentration of additive #3, and the highest value was achieved when #1 was 0.7 wt% and #2 was 1.9 wt%. Under this condition, the highest desirability was 0.87.

Experimental verification

According to the predicted results, 3 different ratios were selected for tribological tests, and compared with the predicted values. The concentration ratio was shown in Table 5. A, B and C represented the different concentration ratios of the three additives, and their desirability was 0.871, 0.786 and 0.728 which was got through the RSM solution. Fig. 9 was the histogram of COF and wear rate values of the actual teat and predicted results. The actual value was COF and the amount of wear tested by the ring-block tests, and the predicted value was calculated by Eq. 3 and Eq .4. In Fig. 9a, the actual value of average COF of group A and B was slightly lower than the predicted value, and the actual value of group C was higher than the predicted. In addition, the difference between the two values did not exceed 3%. Fig. 9b indicated that the actual value of wear rate of group A was slightly lower than the predicted one, while the actual wear rate was higher than the predicted value in group B and C. And the prediction error of the wear rate was less than 4%. Fig. 9 showed that the COF and wear rate formulas obtained by RSM for three additives had a relatively high accuracy, and the error rate was within 4%. And the desirability of group A was the highest with a value of 0.87, so its COF and wear were the smallest, which was in line with the results of the model.

Table 5 The ratio of additives concentration selected for tribological tests

	Additive #1 /wt%	Additive #2 /wt%	Additive #3 /wt%	Desirability
A	0.7	1.9	2.0	0.870
B	0.8	1.6	2.0	0.786
C	0.6	2.0	1.4	0.728

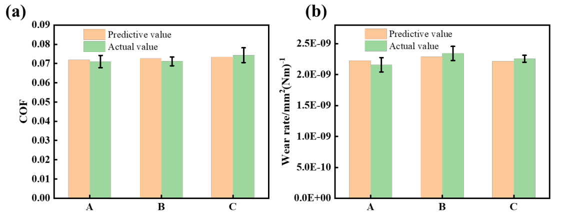

Fig. 9 COF (a) and wear rate (b) values of the actual teat and predicted results

CONCLUSIONS

In this paper, the tribological tests were performed with the three single additives to obtain the COF and the wear rate. Then, XPS and SEM were used to analyze worn surface, combining the different components of the three additives to infer the friction mechanism. Moreover, according to the different characteristics of the three additives, different concentration ratios were carried out, the COF and wear rate were sampled by the BBD method, and the relationship between the COF and wear and the concentration of the three additives was obtained by RSM, and the two responses are comprehensively performed desirability analysis. And finally selected three different concentration ratios with different desirability to conduct tribological tests to verify with the predicted value. The following conclusions could be drawn.

1) The anti-wear effect of ammonium dithiophosphate additives was the best, while the wear surface of ammonium phosphate additives was flatter without serious furrow or adhesive wear.

2) Through RSM analysis, the correlation between the ratio of different additive concentration and the response value of COF and wear rate was significant, and the formula of COF and wear rate with additive concentration was obtained through BBD sampling method.

3)When the concentrations of additives #1, #2, and #3 were 0.7 wt%, 1.9 wwt%, 2.0 wt%, respectively, the desirability was the highest, and the tribological test results showed that the COF and wear rate formula and the desirability prediction error of RSM were less than 4%.

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基于響應面法的硫系極壓添加劑配比規律研究

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摘 要

極壓（EP）添加劑是齒輪油的重要組成部分，用于在極端工況下防止齒輪黏著、犁溝和其他磨損，並保護齒面，延長齒輪油的使用壽命。本文研

究了三種極壓單劑在 1.2 GPa 接觸壓力下的摩擦磨損性能，確定了三種添加劑的最佳濃度範圍。通過 XPS 和 SEM 分析了添加劑的作用機理。爲了綜合三種添加劑的優點，研究三種添加劑的配比規律，以添加劑濃度爲輸入，COF 和磨損率爲響應，采用 Box-Behnken 設計（BBD）抽樣方法選擇實驗數據。通過響應面法（RSM）和 Design Expert 軟件得到了添加劑濃度與 COF 和磨損率之間的關係，並通過 RSM 曲線討論了三種添加劑濃度對響應值的影響。通過可取性分析，得到了最佳濃度比。通過實驗驗證了預測值的摩擦磨損值，誤差在 4%以內。