

Retraction

Retracted: Influence of Sulfur and Additives on Wear of Exhaust Valve Seat of Cylinder Head

Complexity

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This article has been retracted by Hindawi following an investigation undertaken by the publisher [1]. This investigation has uncovered evidence of one or more of the following indicators of systematic manipulation of the publication process:

- (1) Discrepancies in scope
- (2) Discrepancies in the description of the research reported
- (3) Discrepancies between the availability of data and the research described
- (4) Inappropriate citations
- (5) Incoherent, meaningless and/or irrelevant content included in the article
- (6) Manipulated or compromised peer review

The presence of these indicators undermines our confidence in the integrity of the article's content and we cannot, therefore, vouch for its reliability. Please note that this notice is intended solely to alert readers that the content of this article is unreliable. We have not investigated whether authors were aware of or involved in the systematic manipulation of the publication process.

Wiley and Hindawi regrets that the usual quality checks did not identify these issues before publication and have since put additional measures in place to safeguard research integrity.

We wish to credit our own Research Integrity and Research Publishing teams and anonymous and named external researchers and research integrity experts for contributing to this investigation.

The corresponding author, as the representative of all authors, has been given the opportunity to register their agreement or disagreement to this retraction. We have kept a record of any response received.

References

- [1] J. Zhao, S. Zhang, Z. Dou, Y. Sun, J. Wan, and L. Du, "Influence of Sulfur and Additives on Wear of Exhaust Valve Seat of Cylinder Head," *Complexity*, vol. 2021, Article ID 4762184, 14 pages, 2021.

Research Article

Influence of Sulfur and Additives on Wear of Exhaust Valve Seat of Cylinder Head

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In this paper, taking a certain type of high-power diesel engine exhaust valve abnormal wear phenomenon as an example, we conduct research on the exhaust valve surface micromorphology characteristics, contact surface accumulation products, additive transition layer, and combustion test. These passed diesel sulfur content comparative test, diesel additive composition analysis, and high-sulfur-content and low-sulfur-content diesel and diesel oil additive action test. At present, there is no authoritative research on the influence of sulfur content in diesel on valve seat wear of high-power diesel engines, and the protection mechanism of diesel additives on the valve seat is not clear. The sulfur in diesel, like the lead in gasoline, has long been known to resist wear in the valve seats of high-power diesel engines; just as gasoline additives compensate for the loss of lead, diesel oil additives seem to compensate for the loss of sulfur. Tests show that a uniform carbon deposition layer is formed on the contact surface after the diesel is burned, and the carbon deposition layer is more densely and uniformly adsorbed on the contact surface under the action of diesel additives to form an antiwear layer. Tests also show that the sulfur in diesel has no effect on the wear resistance of the valve seat.

1. Introduction

In the field of ship propulsion power, a certain type of high-power diesel engine has experienced frequent large-scale exhaust valve abnormal wear phenomenon since 2019. Serious wear phenomenon, only in the diesel engine factory test (running about 35 hours), appeared about 2 mm exhaust valve seat wear. Because this type of diesel engine has no built-in hard seat, seat wear is the cylinder head body wear, more than 1.5 mm wear, and cylinder head has been unable to repair huge loss. At the beginning, the authors studied the structure design, parts quality, and high temperature hardness matching of valve seat and valve and found no cause related to valve seat wear. With the improvement of people's awareness of environmental protection, in order to prevent further pollution of ocean and atmosphere caused by Marine diesel emissions, the 70th session of the Marine Environment Protection Committee of the International Maritime Organization (IMO) issued the relevant amendments, guidelines, and circulars of the International

Maritime Agreement Regarding Oil Pollution (MAROPL) [1–3]. Significant reduction of sulfur content in Marine diesel is required. China has taken a more proactive approach towards controlling emissions from ships, a mobile source of pollution. Starting from January 1, 2019, China has required the use of diesel fuel for vehicles, agricultural machinery, and inland and offshore ships. Currently, the sulfur content of diesel fuel for vehicles has been limited to less than 10 ppm and is classified as low-sulfur diesel. The frequency of seat wear of high-power diesel engines in China also started from 2019, and there is an obvious corresponding relationship.

Fuel will induce the wear of the exhaust seat hole of the cylinder head, which originally occurred in the gasoline lead-free improvement of the vehicle engine. From 1976 to 1986, European and American countries started the lead-free movement of gasoline in order to reduce the atmospheric pollution caused by lead in gasoline. As a result, it was found that severe wear would occur to the exhaust valve seat holes of cylinder head [4]. Scholars found that the lead

element used for antiknock in gasoline, after combustion, will form lead oxide, lead sulfate, with the exhaust stroke attached to the exhaust valve cylinder head seat hole sealing interface. These lead oxides and salts have a low hardness and play a role of solid lubrication in the sealing interface and also avoid oxidation of the cylinder head seat hole in contact with high temperature gas. As the lead is removed from the gasoline, the above solid lubricant disappears, and the oxidation products of the cylinder head seat hole are embedded into the exhaust valve seal cone, greatly worsening the roughness of the friction surface, causing grinding of the cylinder head seat hole, and then causing abnormal wear [5]. Subsequently, scholars have studied the influence of various elements in gasoline on the wear resistance of exhaust valve-cylinder head seat hole. Kent and Finnigan [6] found that phosphorus in gasoline also had a certain inhibition effect on exhaust valve seat hole wear, but the extent of inhibition was much smaller than lead. Schoonveld et al. [7] found that even a small lead content can effectively protect the exhaust valve-cylinder head seat hole, while more lead content is required to maintain the wear inhibition effect under high engine working conditions.

The general countermeasures for exhaust valve seat wear of high-power diesel engines include the following:

- (1) The exhaust valve seat with embedded special seat [8].
- (2) Diesel oil is added with antiwear additives [9, 10]. The solution of the built-in hard valve seat avoids the wear of the cylinder head body, but as the operating time increases, the hard valve seat or valve will still be worn. Regarding the antiwear mechanism of the additives, Pyle and Smrca [11] found that the products after combustion of lubricating oil additives in gasoline engines also have wear inhibition effect on exhaust valve seat holes, but the inhibition efficiency is much lower than that of gasoline; that is, there is a certain time lag. However, the antiwear mechanism of the additives used in high-power diesel engines is still unclear.

In this paper, we studied the micromorphological characteristics of the exhaust valve seat surface, the accumulation product of the contact surface, the additive transition layer, and the combustion test. Through the test, we have clarified that the sulfur content in diesel has no effect on valve seat wear. We also learned that the antiwear mechanism of diesel additives on valve seats is mainly to adsorb carbon deposits, making the carbon deposits more uniform and dense, and forming an antiwear protective layer.

2. Materials and Methods

2.1. About the Wear Mechanism Analysis

Materials: cylinder head with worn valve seat: the main chemical composition of the cylinder head is gray iron. Worn air valve: the main material of the exhaust valve is NiCr20TiAl.

Methods: after dissecting the worn valve seat and valve, conduct a microscopic analysis of the worn contact surface to observe the condition of the worn surface and the chemical composition of the contact surface. The test devices are shown in Table 1.

2.2. Sulfur Content Comparison Test

Materials: a certain type of high-power diesel engine, -10# diesel with high sulfur content (1200 ppm sulfur content), the low-sulfur 0# vehicle diesel (2.5 ppm sulfur content).

Methods:

Test 1: this type of high-power diesel engine first uses high-sulfur diesel to run for 500 hours and then replaces low-sulfur diesel to run for 500 hours. Observe the degree of wear of the valve seat before and after replacement.

Test 2: on these two high-power diesel engines, -10# diesel and 0# vehicle diesel were, respectively, used for comparison test using the same test bench. Observe the wear of the valve seat.

It should be noted that the service life of the valve seat and valve of this type of high-power diesel engine is 12000 hours.

2.3. Analysis of Additive Components

Materials: a certain type of antiwear additive.

Methods: an additive is a light yellow transparent homogeneous liquid sample, so it is first tested and analyzed by FT-IR infrared spectroscopy and ultraviolet spectrometer, verification with the UV spectrum detection.

The solid substance was detected using an FT-IR infrared spectrometer and compared with the infrared spectrum of the additive. The test devices are shown in Table 2.

2.4. Contact Surface Analysis

Materials: 4 unworn exhaust valves were selected as samples for analysis. They are as follows: low-sulfur diesel (0#), low-sulfur diesel with an additive (0#+), high-sulfur diesel (-10#), and high-sulfur diesel with an additive (-10#+).

Methods: the sediments on the contact surface were sampled, and elemental analysis was carried out using electronic energy scattering spectrum (EDS).

In order to further clarify the antiwear mechanism. Typical elements such as S, O, Ca, and C in the sediments were analyzed by X-ray electron spectroscopy to determine the chemical valence state of the elements, and then to determine the chemical composition of the sediments on the contact surface between the air valve and the seat. The test devices are shown in Table 3.

TABLE 1: Wear mechanism analysis test devices.

Device	Model
Scanning electron microscopy	SEM, EVO18
The X-ray photoelectron spectroscopy	XPS ESCALAB MK II

TABLE 2: Sulfur content comparison test devices.

Device	Model
Infrared spectrometer	NIR-M-T1
Ultraviolet spectrometer	UV1800PC

TABLE 3: Contact surface analysis test devices.

Device	Model
Scanning electron microscopy	SEM, EVO18
The X-ray photoelectron spectroscopy	XPS ESCALAB MK II

2.5. Combustion Experimentation

Materials: low-sulfur diesel (0#), high-sulfur diesel (-10#), and diesel with a concentration of 9.5% after adding thiophene.

Methods: take 0.30 g of low-sulfur diesel (0#) and high-sulfur diesel (-10#) for combustion, collect the carbon deposit generated after combustion, and analyze the weight and element of the carbon deposit.

Take 0.30 g of diesel fuel with 9.5% sulfur content after adding thiophene for combustion, collect the carbon deposit generated after combustion, and analyze the weight and element of the carbon deposit. The test devices are shown in Table 4.

3. Results

3.1. *Wear Mechanism Analysis.* Basic influencing factors of mechanical wear of valve seat are as follows [9].

- (1) Friction value μ
- (2) Temperature
- (3) Contact Pressure p_{max}
- (4) Material characteristic, e.g., yield strength $R_p(T)$ or hardness $HB(T)$

3.1.1. *Analysis on Micromorphology of Wear Surface of Valve Seat.* The cylinder head material of a high-power diesel engine is grey iron. There have been many, since the early scholars of the internal combustion engine valve seat wear made a lot of theoretical research. So the following research attempts to explore the wear mechanism through the wearing micromorphological characteristics of valve seat.

According to the microstructure characteristics, as shown in Figures 1–3, the surface of the valve seat is tongue-shaped, and the tongue layers are interlaced, which increases the friction coefficient between the valve and the valve seat. Ductile inclusion deformation occurs after wear as a result of increased valve clearance and increased temperature.

TABLE 4: Combustion experimentation devices.

Device	Model
Scanning electron microscopy	SEM, EVO18
Combustion device	SXD-956

3.1.2. *Micromorphological Characteristics of Corresponding Wear Valve.* The microscopic appearance of the wear valve in Figures 4 and 5 shows that the high coefficient of friction causes local material from the cylinder head seat (gray cast iron) to be transferred to the surface of the valve (nickel based alloy) during disc and seat contact, as shown in Figure 6.

3.1.3. *Conclusion.* From the above micromorphology analysis, based on the research of Guo et al. [12] and Wang and Liu et al. [13], it can be concluded that the friction coefficient is the main factor at the beginning of wear. The high coefficient of friction permits a partial transfer of seat material to the disc resulting in viscous wear. High coefficient of friction also increases the temperature of the contact surface and contributes to seat wear and tongue deformation. After further development of wear, in the advanced state of wear, deformation (resistance) of cast iron plays a major role.

3.2. Test Verification

3.2.1. Effective Antiwear Methods

(1) Sulfur Content Comparison Test

Test 1: during the initial operation of this type of high-power diesel engine, -10# diesel with high sulfur content (1200 ppm sulfur content) was used for 500 hours. During the period, the valve clearance was normal, and no valve seat wear was found during disassembly and inspection. After 500 hours, the low-sulfur 0# vehicle diesel (2.5 ppm sulfur content) was replaced. The valve seat began to wear after only 20 hours of operation, and the amount of wear was large (12 of 20 cylinders were worn).

Test 2: on these two high-power diesel engines, -10# diesel and 0# vehicle diesel were, respectively, used for comparison test using the same test bench. The use of low-sulfur 0# vehicle diesel began to wear out after only 10 hours of operation (9 of 20 cylinders were worn).

For the ship service of this type of diesel engine, the research shows that the frequency of valve seat wear is low when the sulfur content is higher than 500 ppm diesel for a long time. Seat wear of long-term diesel fuel with sulfur content less than 50 ppm is extremely serious, which affects the normal attendance of ships.

(2) *Additive Comparison Test.* Another method of antiwear is to add a fuel antiwear additive for a comparative test based on the antiwear experience of the vehicle. In this type of diesel engine, 0# vehicle diesel with low-sulfur content and a

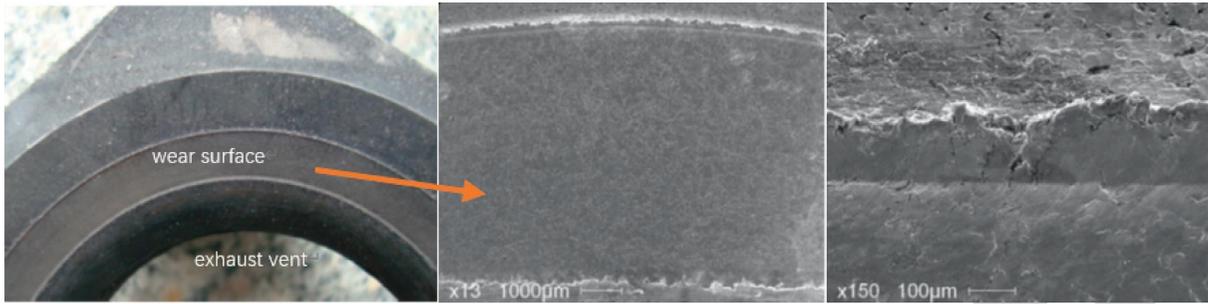


FIGURE 1: Material dislocation and deformation tongues on seat surface of cylinder head.

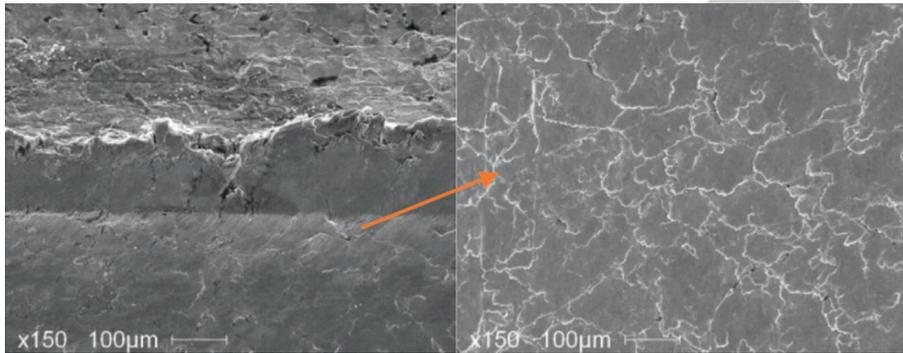


FIGURE 2: Outlook of wear.

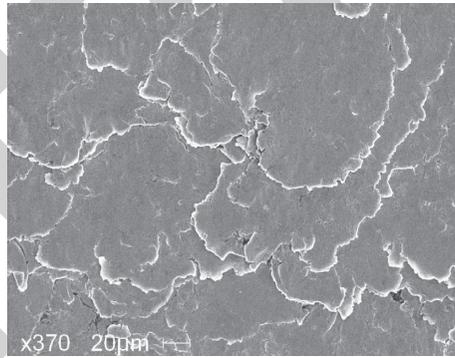


FIGURE 3: Tongue-shaped deformation.



FIGURE 4: Surface condition of wear valve.

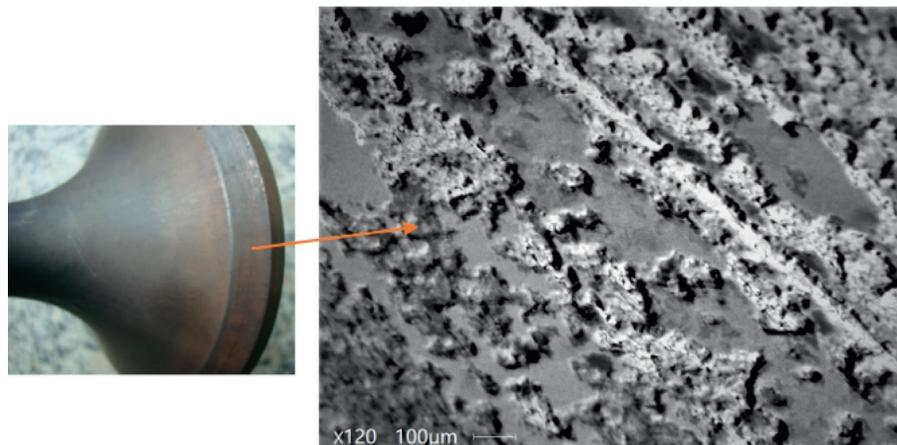


FIGURE 5: Amplification of wear.

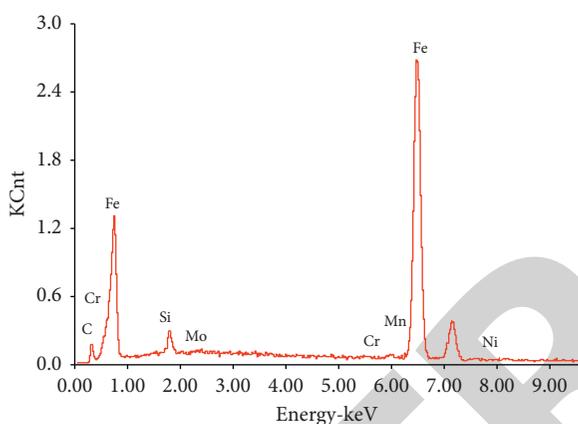


FIGURE 6: Elemental analysis of valve contact surface.

fuel additive are used for 1000 hours (>80% operating condition for about 900 hours) without wear on the valve seat.

From the above two tests, it can be seen that diesel with high S content and additives have obvious effect on seat wear resistance, but the wear resistance mechanism is still unclear.

3.2.2. Analysis of Additive Components. For a certain type of antiwear additive used in the experiment, it is widely used in the field of automobile engines. In order to clarify the antiwear mechanism of additives on high-power diesel engines, the additives were tested and analyzed.

(1) Additive Testing. An additive is a light yellow transparent homogeneous liquid sample, so it is first tested and analyzed by FT-IR infrared spectroscopy and ultraviolet spectrometer. The results are shown in Figure 7.

It can be seen from the detection results of its infrared spectrum (Figure 7(a)) that there is a strong absorption peak at 1740 cm^{-1} , which is mainly attributed to the characteristic absorption peaks of ester carbonyl. The characteristic absorption peaks of 1230 cm^{-1} and 1043 cm^{-1} belong to the C-O-C structure. 1170 cm^{-1} is caused by the symmetric stretching vibration of the S=O bond. The other symmetric

stretching vibration of the S=O bond should be the absorption peak of 1043 cm^{-1} , which is coincident with the characteristic absorption peak of C-O-C structure. 1376 cm^{-1} , 1461 cm^{-1} , 2853 cm^{-1} , 2910 cm^{-1} , and 2955 cm^{-1} are all C-H stretching vibration absorption peaks in the alkyl structure. The above analysis results indicate that the additive is an alkyl compound containing characteristic functional groups such as C=O, C-O-C, and S=O.

Analysis of the UV spectrum detection results of additives (Figure 7(b)) shows that there are two characteristic absorption peaks. The characteristic absorption peak of high absorption intensity at 216.35 nm belongs to S=O structure, and the wide band of low absorption intensity at 270.33 nm belongs to the characteristic band of carbonyl compounds. This result is consistent with the infrared spectrum detection results, again confirming that the additive contains C=O, S=O and other characteristic functional groups.

The additive contains metal potassium, so it can be inferred that the additive is a potassium salt of sulfonic group. For a sulfonate, in most cases, it should be in the state of a solid salt, and the additive is a viscous liquid. So, the additive is a mixture of solvent and sulfonate.

Based on the above conjecture, the additive is separated into two substances by the extraction method.

(2) Solid Substance Detection in Additives. The solid substance was detected using an FT-IR infrared spectrometer and compared with the infrared spectrum of the additive. The results are shown in Figure 8. Through infrared spectrum database retrieval, the solid is docusate group salt. Combined with the product introduction, the solid is docusate potassium, with the structure shown in Figure 9.

3.2.3. Solvent Detection in Additives. The FT-IR infrared spectrometer was used to analyze the solvent sample, which was also compared with the additives. The results are shown in Figure 10. The characteristic absorption peak of the solvent sample coincides with that of additives at 1376 cm^{-1} , 1461 cm^{-1} , 2853 cm^{-1} , 2910 cm^{-1} , and 2955 cm^{-1} ; that is, the solvent only has the stretching vibration absorption peak of

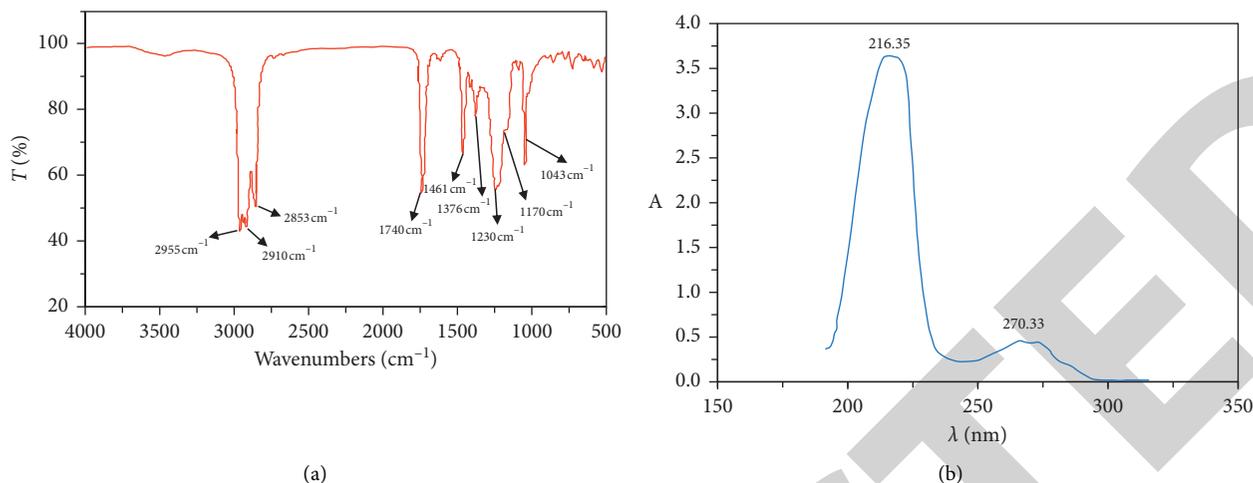


FIGURE 7: Infrared spectrum (a) and ultraviolet spectrum (b) of additives.

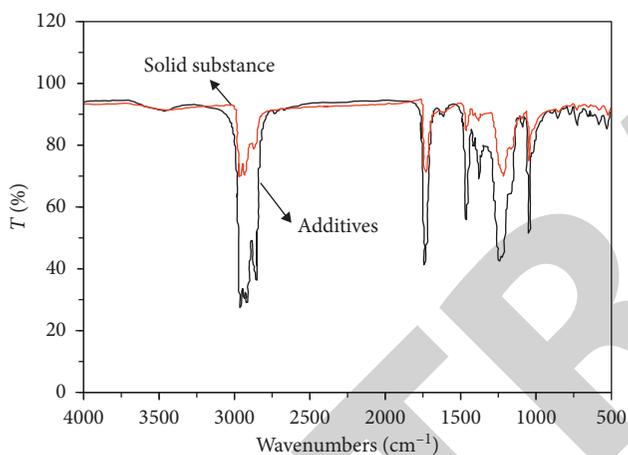


FIGURE 8: Infrared spectra of solvents and solids.

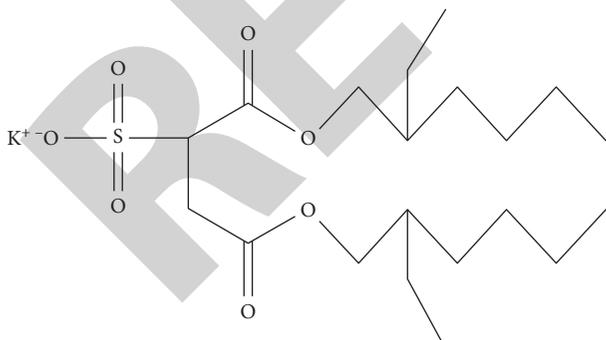


FIGURE 9: Molecular structure diagram of docusate sodium of solid material.

saturated C-H, indicating that the solvent is a saturated alkane compound.

Table 5 shows the partial physical and chemical properties of the solvent. Through the analysis of its viscosity, pour point, and freezing point data, combined with the detection results of infrared spectroscopy, it is known that

the solvent should be a kind of solvent oil. Compare the density of different solvent oils. It can be known that the solvent is 200# aliphatic hydrocarbon solvent oil.

3.2.4. Preliminary Analysis of the Mechanism of Additives.

The existence of ester group and sulfonic acid group in the additive makes it show strong polarity, while the polar compound has strong adsorption capacity on the metal surface. In addition, the larger molecular size of docusate makes it form a strong and thick protective film on the metal surface to prevent direct contact between metals, so as to achieve better antiwear effect. At the same time, when sulfonic acid compounds act on the friction dual surface, they react with the friction surface by friction, heat, exoelectron, self-catalysis, and so on, forming sulfur-containing inorganic film or $\text{Fe}_2\text{O}_3\text{-FeS}$ extreme pressure reaction film in the presence of iron oxide. The reaction film has an extremely high bearing capacity. When the additive is used in lubricating oil, its load-carrying capacity can reach more than 150 kg, so it can play the role of antiscratch and antisintering, showing a good antiwear load-carrying capacity.

3.2.5. Mechanism Analysis of High-Sulfur- and Low-Sulfur-Content Diesel and Additives.

In order to analyze the influence mechanism of different sulfur content diesel oil and additives on antiwear, 4 unworn exhaust valves were selected as samples for analysis. They are low-sulfur diesel (0#), low sulfur diesel with an additive (0#+), high-sulfur diesel (-10#), and high-sulfur diesel with an additive (-10#+). See Table 6 for details.

As can be seen from 6, carbon deposition plays a key role in reducing engine exhaust valve wear. When carbon accumulation is large, it will be attached to the sealing surface of inlet valve and exhaust valve to form a protective film, which will not appear obvious wear, but when carbon accumulation is small, there will be a lot of wear due to the absence of protective film. At the same time, additives have a great influence on the formation of the deposit. After

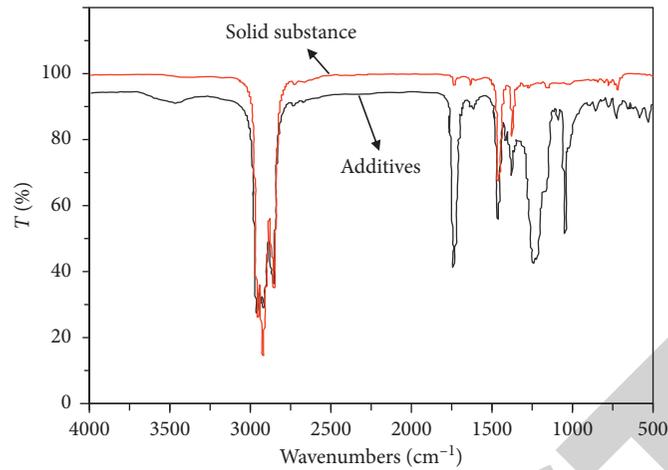


FIGURE 10: Comparison of IR spectra of additives and liquid substances.

TABLE 5: Test results of physical and chemical properties of liquid substances.

Order number	Test items	Result
1	Viscosity (mm^2/s , 25°C)	2.00
2	pour point ($^\circ\text{C}$)	-48
3	Freezing point ($^\circ\text{C}$)	-50
4	Density (g/cm^3)	0.7989

TABLE 6: Inspection results of exhaust valve.

Items	Contact surface	Noncontact surface	Run time
0#	Black discontinuous deposit, valve disc is not worn, corresponding valve seat wear	Blue	20 hours
0#+	Dark black continuous deposits, valve disc is not worn, valve seat is not worn	Dark brown	20 hours
-10#	Dark black continuous deposits, valve disc is not worn, valve seat is not worn	Black carbon deposit	20 hours
-10#+	Dark black continuous deposits, valve disc is not worn, valve seat is not worn	Dark brown	20 hours

combustion of low-sulfur diesel without additives, the contact surface formed a discontinuous deposit layer, and the deposit layer became continuous and uniform after adding additives. In addition, the deposits of high-sulfur diesel fuel are evenly distributed after long-term operation and combustion.

3.2.6. Sampling Analysis of Sediments at the Contact Surface. The sediments on the contact surface were sampled, and elemental analysis was carried out using electronic energy scattering spectrum (EDS). The results were shown in Table 7.

From the above data, it can be seen that Ca, S, C, O, and other elements are present in the surface of the exhaust valve after combustion with different diesel. In addition to the above elements, there is also a large amount of potassium K in the sediment after using additives element, as shown in Table 7.

3.2.7. Contact Surface Analysis. Cut the exhaust valve and analyze the structure and elements of the deposits on the contact surface. The results are as follows.

As shown in Table 8, in the same run-in period of the valve, after the use of low-sulfur diesel alone, the contact

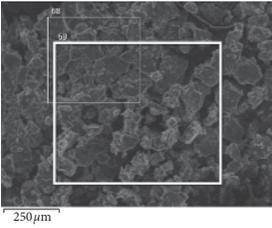
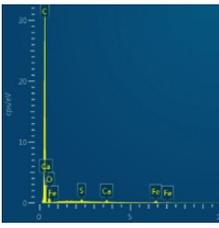
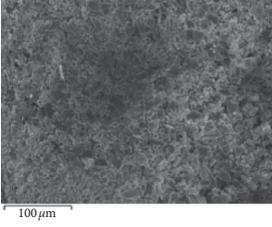
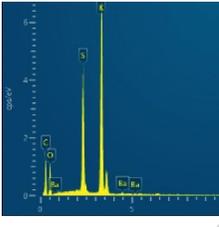
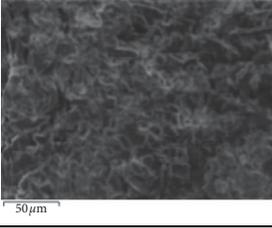
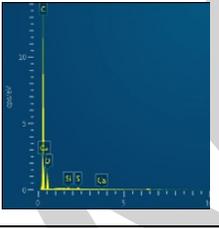
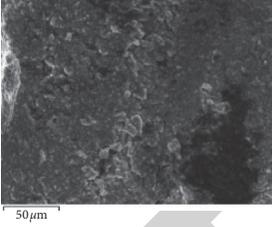
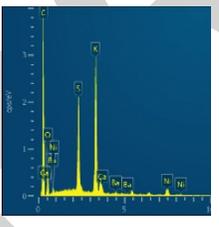
surface of the exhaust valve presents discontinuous black sediments, which are loose and granular. When low-sulfur diesel was added with additives, the sediments presented continuous belts in the same time, and the deposition morphology also changed from the original granular shape to a uniform and dense belt. For the valve using high-sulfur diesel, the surface sediments are evenly distributed without additives, but the structure is relatively loose. When the additives are used, the contact surface presents a dense structure with uniform distribution.

3.2.8. XPS Analysis. In order to further clarify the antiwear mechanism. Typical elements such as S, O, Ca, and C in the sediments were analyzed by X-ray electron spectroscopy to determine the chemical valence state of the elements, and then to determine the chemical composition of the sediments on the contact surface between the air valve and the seat.

The following conclusions can be drawn from the XPS analysis results, as shown in Figure 11.

After using different diesels, the main component of the sediment on the contact surface is carbon, and its binding energy value is 284.6 eV, which is zero-valent carbon, that is, amorphous carbon. The binding energy of oxygen element

TABLE 7: Contact surface element analysis.

0#			Element	Atomic ratio
			C	87.81
			O	11.85
			S	0.08
			Ca	0.08
			Fe	0.17
Summation	100.00			
0#+			Element	Atomic ratio
			C	46.95
			O	31.44
			S	7.26
			K	14.21
			Ba	0.14
Summation	100.00			
-10#			Element	Atomic ratio
			C	83.19
			O	16.72
			Si	0.03
			S	0.05
			Ca	0.02
Summation	100.00			
-10#+			Element	Atomic ratio
			C	78.48
			O	13.76
			S	2.47
			K	4.36
			Ca	0.19
Ni	0.67			
Ba	0.07			
Summation	100.00			

in the sediments at the contact surface is 531.8 eV, corresponding to the oxygen element with a -2 valence. The contact sediments contain sulfur with a binding energy value of 168.2 eV, corresponding to sulfur in sulfonic acid.

In the absence of additives in diesel, the contact surface sediments contain calcium, and the binding energy value is 347.4 eV, which belongs to $+2$ valence calcium. Combined with the above binding energy value of sulfur, it can be determined that calcium exists in the form of calcium sulfonate according to the standard data manual.

After adding additives to diesel, the contact surface potassium content is extremely low, because the XPS analysis signal is too weak, and only after adding additives to low-sulfur diesel, weak signal was detected.

3.2.9. Combustion Experimentation. Diesel engine emissions of harmful components in the exhaust gas, in addition to the conventional carbon monoxide (CO), nitrogen oxides (NO_x) and hydrocarbons (HC), and diesel sulfur, are closely related to sulfur oxide (SO_x) and particulate matter (PM). The combustion of sulfur compounds in diesel fuel produces sulfur dioxide (SO₂) and sulfur trioxide (SO₃), collectively known as SO_x, which are harmful gaseous emissions. At the same time, SO_x is partially

transformed into sulfate, sulfonate, and other particulate components [14–19].

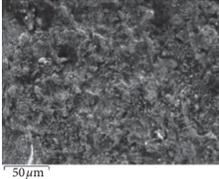
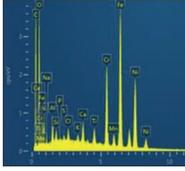
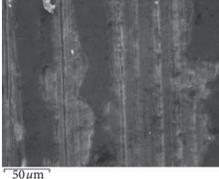
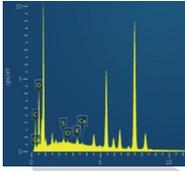
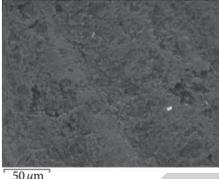
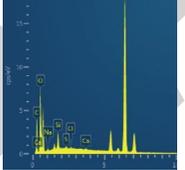
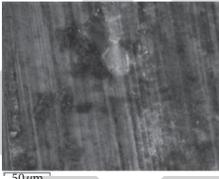
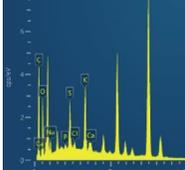
The sulfur compounds in diesel oil mainly exist in the form of thiophene; so far scholars have reached the consensus. The mechanism by which thiophenes burn remains unclear. The early studies on the combustion of thiophene were mainly carried out by experiments [20–24], and the combustion products detected were mainly alkynes, H₂S and CS₂.

(1) *Carbon Deposition Analysis.* Take a certain amount of low-sulfur diesel (0#) and high-sulfur diesel (–10#) for combustion, collect the carbon deposit generated after combustion, and analyze the weight and element of the carbon deposit. The results are as follows.

Through the above test results, there is no difference in the products obtained after combustion of 0# and –10# diesel, all of which are carbon deposition (Sulfur element is not detected in EDS, as shown in Table 9). The biggest difference is the amount of carbon produced by the two, in which the carbon produced by combustion of –10# diesel is about twice that of 0#.

(2) *Combustion Test of Low-Sulfur Diesel with Sulfur Added.* Adding thiophene to low-sulfur diesel fuels increases the sulfur content. The results showed that although the sulfur

TABLE 8: EDS analysis results of exhaust valve contact surface.

		Element	Atomic ratio	
0#			C	60.38
			O	22.55
			Na	0.77
			Al	0.80
			Si	0.24
			P	0.07
			S	0.11
			Cl	0.24
			K	0.14
			Ca	0.46
			Ti	0.41
			Cr	2.64
			Mn	0.11
			Fe	6.43
Ni	4.65			
	Summation	100.00		
0#+			Element	Atomic ratio
			C	41.91
			O	55.79
			S	0.61
			Cl	0.39
			K	0.97
			Ca	0.34
	Summation	100.00		
-10#			Element	Atomic ratio
			C	44.85
			O	52.20
			Na	0.53
			Si	1.89
			S	0.23
			Cl	0.13
Ca	0.16			
	Summation	100.00		
-10#+			Element	Atomic ratio
			C	61.27
			O	30.95
			Na	1.62
			P	0.20
			S	2.00
			Cl	0.32
			K	3.14
Ca	0.49			
	Summation	100.00		

content in diesel oil reached 9.5%, no sulfur element was detected on the surface of the steel block attached with combustion products after burning at 500°C, as shown in Table 10.

4. Test Summary

4.1. Influence of Sulfur Content in Diesel. Combustion tests show that 0#, -10# high-sulfur diesel generates serious carbon deposits after combustion, except that -10# high-sulfur diesel generates significantly more carbon deposits than 0# diesel. In addition, sulfur element is not detected in the carbon deposits produced by both methods, but sulfonic acid components (EDS, XPS results) are also present in the contact surface. At 500°C, sulfur dioxide on the steel surface cannot form sulfide

such as ferrous sulfate, much less sulfonate than the organic matter. Based on this, it can be judged that the sulfur element mainly comes from sulfonates in additives or lubricants. The sulfur element in diesel oil is completely discharged as sulfur dioxide during combustion. Therefore, the sulfur content in diesel has no key influence on the antiwear performance. This can be proved by the surface morphology of exhaust valve without additives for high-sulfur diesel fuel, and -10# diesel fuel has high-sulfur content, but the deposit layer formed is still loose, and its main component is carbon element. In actual operation, the antiwear performance of -10# diesel on the valve seat is better than that of 0# diesel, which is due to the high carbon accumulation generated during combustion of -10# diesel. -10# diesel is a straight-run diesel without hydrotreating. It contains a large amount of aromatic

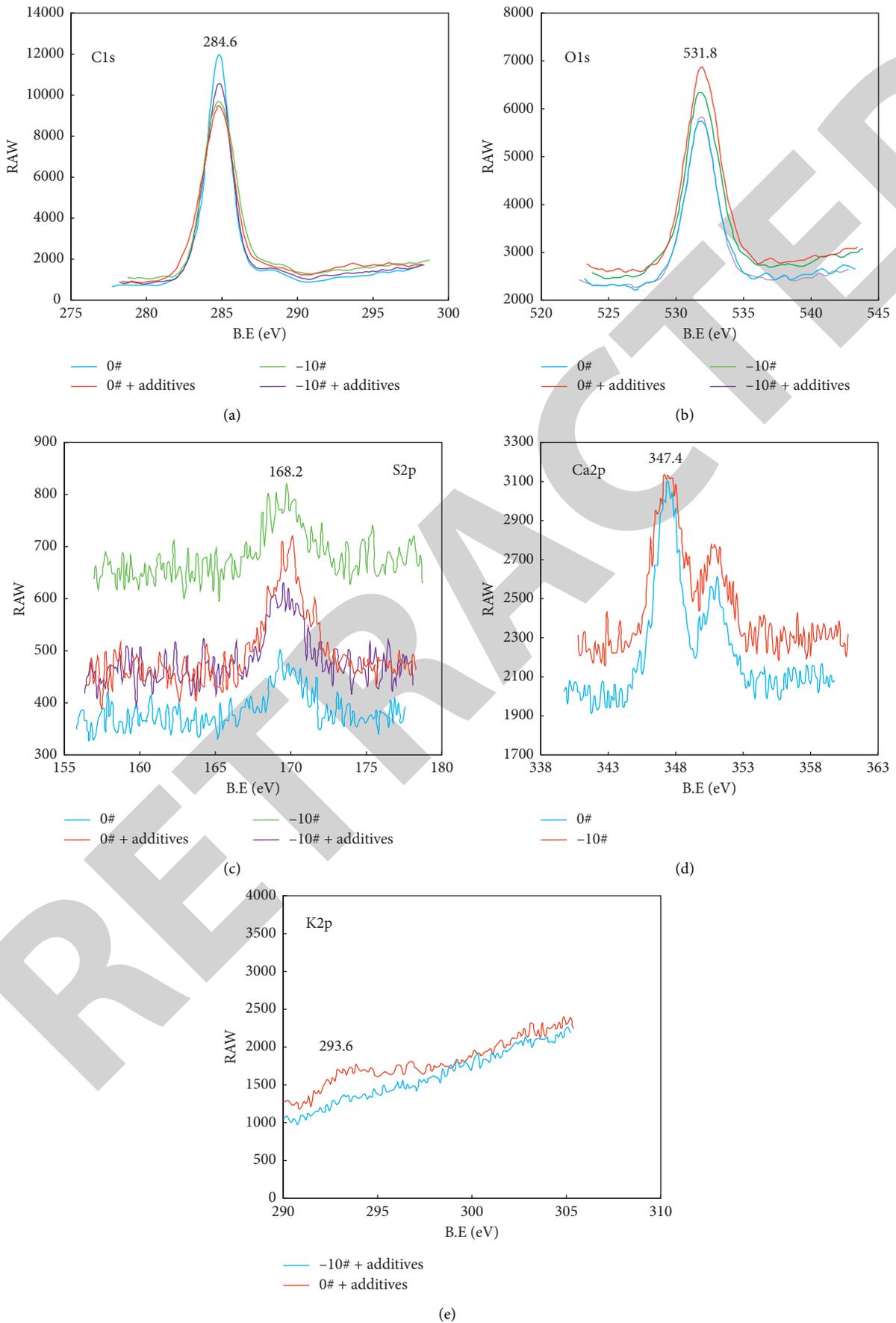


FIGURE 11: XPS analysis results of typical elements.

TABLE 9: Combustion test results of different diesel fuels.

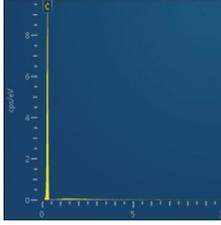
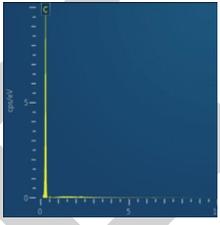
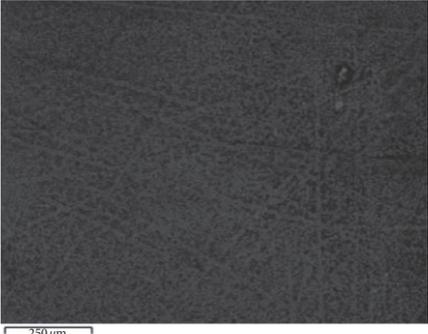
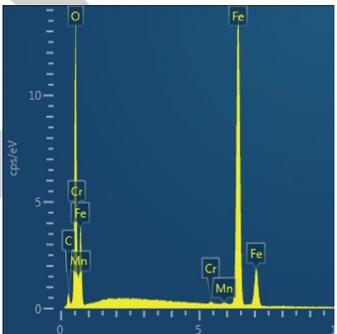
	0#	-10#
Diesel fuel quality (g)	0.30	0.30
Produce carbon deposition mass (g)	0.009	0.0199
Carbon deposition rate (%)	0.029	0.066
Analysis of carbon deposition elements		

TABLE 10: Combustion test results of diesel fuels with high-sulfur content.

	
Element	Atomic ratio
C	11.79
O	52.25
Cr	0.15
Mn	0.16
Fe	35.65
Summation	100.00

hydrocarbons in its components. As the internal carbon content of aromatic compounds (1:1 hydrocarbon ratio) is higher than that of alkane compounds (e.g., gasoline, 1:2 hydrocarbon ratio), a large amount of carbon accumulation will be generated during combustion. However, 0# diesel oil is formed by cracking hydrogenation, and the content of aromatics in the components is relatively small, and the amount of carbon accumulation during combustion is also small. When -10# diesel fuel burns, a large amount of carbon deposition is distributed on the contact surface of the valve and seat. After rotating and rolling of the valve, a layer of loose carbon deposition (EDS analysis results) is formed, which plays a certain role in protecting the valve and seat.

Accordingly, when the diesel with additives is used, the contact surface of exhaust valve can show a uniform and dense deposit layer after a short time of operation (EDS analysis results). It can be concluded that the main factor of reducing exhaust valve wear is not the sulfur content in diesel, but how to form a uniform deposit on the contact surface of exhaust valve the CAS number of some chemicals in the test is shown in (Table 11).

Attached List 1

TABLE 11: CAS number of used chemicals.

Chemical items	CAS number
Sulfur	7704-34-9
Lead	7439-92-1
Lead sulfate	7446-14-2
Potassium	7440-09-7
Thiophene	110-02-1

4.2. *The Role of Additives.* The additive contains polar compounds with strong adsorption capacity on the metal surface, which makes it adsorb on the metal surface to form a firm and thick protective film, preventing direct contact between metals. In addition, sulfonic acid compounds are difficult to burn due to the presence of sulfonic acid groups in additives and lubricants and still exist in the form of sulfonic acid. When discharged through the exhaust valve, the sulfonate is a high-viscosity substance, forming adhesion on the surface of the seat. At the same time, the sulfonate also adhered to the amorphous carbon, which was rolled in the rotation of the valve, and then formed a uniform and dense carbon layer on the contact surface of the valve and seat.

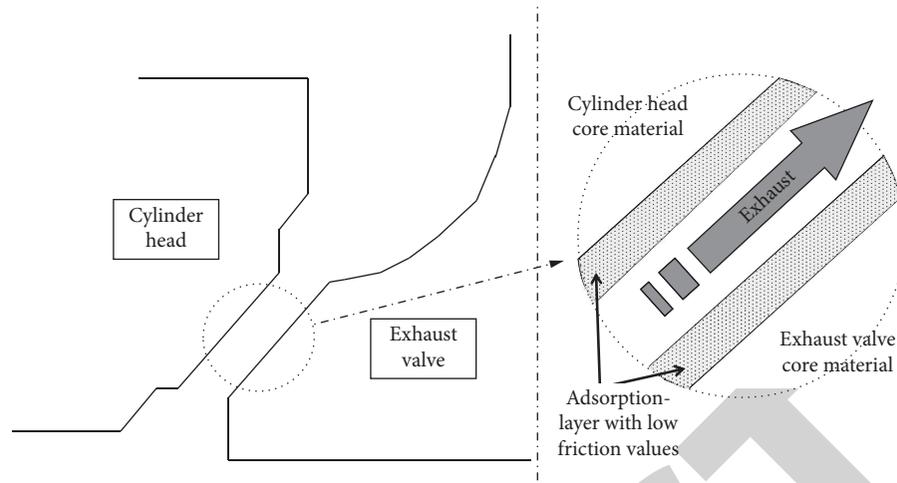


FIGURE 12: Schematic diagram of antiwear mechanism.

The elemental analysis results from EDS and XPS can also be indirectly proved. Due to the electronic energy scattering spectrum of EDS, the analysis depth of the surface can reach the micron level, and elements with a micron depth can be detected, while the XPS analysis depth is only a few nanometers. The following elements cannot be detected. As a result, the abovementioned EDS and XPS analysis results are different. After adding the additive (potassium docusate), the EDS analysis showed that there was a large amount of potassium in the valve seat contact surface. Especially after adding the additive-high-sulfur diesel fuel, the contact surface showed a uniform carbon deposit. The potassium content of EDS analysis reached 3.14%, but XPS was not detected. The main reason is that the additive adsorbed carbon deposits and covered the surface, which caused no potassium detection by XPS. It can be seen that the role of additives on the surface of the exhaust valve is that polar compounds adsorb on the metal surface to form a protective film. On this protective film, the sulfonate adheres to amorphous carbon and forms a uniform and dense carbon deposit layer, and the schematic diagram of the antiwear layer is shown in Figure 12. Under the protection of these two layers of film, it plays the role of antiscratch and antisintering, showing good antiwear bearing capacity.

4.3. Antiwear Mechanism. Based on the above analysis, the antiwear mechanism of high-power diesel engine exhaust valve system is as follows:

Diesel fuel mixed with ester and sulfonate compounds (potassium polyester in additives, calcium petroleum sulfonate naturally introduced in lubricants) is burned in the combustion chamber through the injection nozzle. Diesel fuel generates mixtures of carbon dioxide, sulfur dioxide, water, and amorphous carbon after combustion. Additives in diesel fuel have strong polarity, which results in a strong protective film adsorbed on the metal surface of the exhaust valve system and prevents direct contact between the metals. Sulfonates, which are difficult to ignite, adhere to the above protective film surface when discharged through the exhaust valve. At the same time, the sulfonate adheres to amorphous

carbon and forms a uniform and dense carbon deposit on the contact surface of exhaust valve system by rotating and compacting the valve, thus protecting the exhaust valve and playing a role in antiwear.

The main reason for wear of 0# diesel without additives is that, on the one hand, the diesel fuel burns more fully with very little carbon deposit, which makes it difficult to form deposits on the friction surface. On the other hand, due to lack of adhesive additive, carbon deposition on the friction surface becomes harder to adsorb, despite the lubricating oil into calcium petroleum sulfonate, but the content is very few, so in the short term, it is difficult to adsorb enough amount of sediment deposit formation. This is also the main reason for the discontinuous deposits on the contact surface of 0# diesel exhaust valves.

The reason why -10# diesel does not cause wear when it is not added additives is that a large amount of carbon deposition is produced when the fuel is burned. At the same time, due to the presence of trace calcium sulfonate naturally brought into the friction surface, although the content of sulfonate is small, it can absorb a large amount of carbon deposition and thus form sediments to protect the seat from wear.

5. Conclusion

- (1) The antiwear mechanism of exhaust valve system is the same when different diesel is used, because diesel forms a uniform carbon deposit on the contact surface after combustion, which reduces wear.
- (2) The function of diesel additive is to form a protective film on the metal contact surface of the exhaust valve system, adsorb carbon, and make it evenly distributed on the contact surface, so as to protect the exhaust valve system from wear.
- (3) The combustion of -10# diesel produces a large amount of carbon deposition, which is the main reason for its antiwear performance.
- (4) Sulfur in diesel does not participate in the formation of antiwear layer.

In summary, this paper found that sulfur in diesel fuel is discharged from the cylinder in a gaseous manner after high temperature combustion, and sulfur is not detected on the exhaust valve disc and valve seat. The reason why diesel with high-sulfur content is more conducive to the wear resistance of the valve seat during use is that diesel with high sulfur content produces more carbon deposits than diesel with low sulfur content, and the antiwear protective layer of the valve seat is positive. Its carbon deposits. In the process of continuous flapping and friction between the valve and the valve seat, a small amount of carbon deposits will quickly wear out, and the valve seat will lose its protective layer. The role of diesel additives is to make the carbon deposit more uniformly and tightly adhere to the valve seat surface even when only a small amount of carbon deposits is produced, and to improve the quality of the protective layer. Therefore, the sulfur content in diesel does not have any effect on the valve seat wear of high-power diesel engines.

At present, effective valve seat antiwear methods are mainly the use of fuel additives and inlaid hard valve seats. However, some diesel engines cannot inlay a hard valve seat due to the compact structure of the combustion chamber, and the gas valve is extremely easy to wear after the hard valve seat is inlaid. Other diesel engines cannot use premixed fuel tanks because of their compact cabin structure, so they cannot effectively use fuel additives. The intake valve seat of most diesel engines can be lubricated with lubricating oil, but the exhaust valve seat cannot effectively lubricate the contact surface between the valve disc and the valve seat due to the exhaust back pressure. In the future, it can be considered that the lubricating oil in the diesel engine flows from the cylinder head to the inner cavity of the valve seat and then flows to the contact surface, reducing the working temperature and reducing the friction between the valve seat and the valve disc.

Data Availability

All the data, models, and code generated or used during the study appear in the submitted article.

Conflicts of Interest

The authors declare that they have no conflicts of interest to this work.

References

- [1] Maritime Safety Administration of the People's Republic of China, *Notification on the Implementation of the 2011 Amendment to Annex VI of the 1973 International Convention for the Prevention of Pollution from Ships*, International Maritime Organization, London, UK, 1978.
- [2] Maritime Safety Administration of the People's Republic of China, *Announcement on the Announcement of the Implementation Plan of the Global Marine Fuel Sulfur Limit Regulations 2020*, <https://www.msa.gov.cn/page/article.do?articleId=7917B172-1CB6-421E-881C-25E5D00001B3>, 2019.
- [3] Ministry of Transport of the People's Republic of China, *Notice on Printing and Distributing the Implementation Plan for Ship Air Pollutant Emission Control Areas*, https://xxgk.mot.gov.cn/jigou/haishi/201812/t20181220_3146515.html, 2018.
- [4] W. Giles, "Valve problems with lead free gasoline," *Gasoline*, vol. 80, pp. 1475–1483, 1971.
- [5] "Investment of the mechanism of exhaust valve seat wear in engines run on unleaded gasoline,"
- [6] W. L. Kent and F. T. Finnigan, *The Effect of Some Fuel and Operating Parameters on Exhaust Valve Seat Wear*, SAE International, Warrendale, PA, USA, 1971.
- [7] G. A. Schoonveld, R. K. Riley, S. P. Thomas, and S. Schiff, "Exhaust valve recession with low-lead gasolines," *Fuel and Lubricants*, vol. 95, pp. 700–712, 1986.
- [8] F. Lai, S. Qu, Y. Duan et al., "The wear and fatigue behaviours of hollow head & sodium filled engine valve," *Tribology International*, vol. 128, pp. 75–88, 2018.
- [9] R. C. Hutcheson, "Valve seat recession-an independent review of existing data," SAE International, Warrendale, PA, USA, 2000-01-2015, 2000.
- [10] P. Forsberg, P. Hollman, and S. Jacobson, "Wear mechanism study of exhaust valve system in modern heavy duty combustion engines," *Wear*, vol. 271, no. 9-10, pp. 2477–2484, 2011.
- [11] W. R. Pyle and N. R. Smrcka, "The effect of lubricating oil additives on valve recession in stationary gaseous-fueled four-cycle engines," SAE International, Warrendale, PA, USA, 932780, 1993.
- [12] H. Guo, B. Zhuo, and J. Peng, "Design and research on friction of valve seat," *Journal of Internal Combustion Engine*, vol. 19, no. 3, pp. 258–262, 2001.
- [13] L. Wang and Z. Liu, "General situation of research on engine exhaust valve failure mechanism at home and abroad," *Journal of Wuhan University of Technology*, vol. 5, pp. 83–86, 2000.
- [14] H. Liu, C. Wang, X. Kong, W. Liu, C. Jin, and Z. Zheng, "Effect of hydrocarbon group components on diesel engine emission," *Journal of Environmental Science*, vol. 40, no. 2, pp. 479–491, 2020.
- [15] S. Hou, F. Dong, X. Liu, Y. Yang, Y. Guo, and H. Liu, "Diesel fuel characteristics for heavy-duty diesel combustion," *Journal of Internal Combustion Engine*, vol. 4, pp. 289–295, 2016.
- [16] W. Chen, J. Wang, and S. Shijin, "Influence of diesel quality on engine emission performance," *Automotive Engineering*, vol. 8, pp. 657–663, 2008.
- [17] H. Dong, Q. Liu, and X. Xu, "Effect of sulfide in diesel on engine performance," *Petroleum Refining and Chemical Work*, vol. 40, no. 6, pp. 42–44, 2009.
- [18] S. Li, *Research on SOX Emission of Marine Diesel Engine*, Zhejiang Ocean University, Zhoushan, China, 2017.
- [19] S. Zhou, L. Jing, and T. Xu, "Research on ship SOX emission control technology," *Diesel Engine*, vol. 5, pp. 14–19, 2015.
- [20] J. Heiss, K.-P. Zeller, and B. Zeeh, "Massenspektrometrische fragmentierung einiger schwefelhaltiger aromatischer heterocyclen sowie ihrer sulfoxide und sulfone," *Tetrahedron*, vol. 24, no. 8, pp. 3255–3266, 1968.
- [21] C. D. Hurd, R. V. Levetan, and A. R. Macon, "Pyrolytic formation of arenes. II. Benzene and other arenes from Thiophene, 2-Methylthiophene and 2-(Methyl-14 C)-thiophene," *Journal of the American Chemical Society*, vol. 84, no. 23, pp. 4515–4519, 1962.

- [22] H. Ur Rahman Memon, A. Williams, and P. T. Williams, "Shock tube pyrolysis of thiophene," *International Journal of Energy Research*, vol. 27, no. 3, pp. 225–239, 2003.
- [23] J. K. Winkler, W. Karow, and P. Rademacher, "Gas-phase pyrolysis of heterocyclic compounds, part 1 and 2: flow pyrolysis and annulation reactions of some sulfur heterocycles: thiophene, benzo[b]thiophene, and dibenzothiophene. A product-oriented study," *Journal of Analytical and Applied Pyrolysis*, vol. 62, pp. 123–141, 2000.
- [24] N. R. Hore and D. K. Russell, "The thermal decomposition of 5-membered rings: a laser pyrolysis study," *New Journal of Chemistry*, vol. 28, no. 5, pp. 606–613, 2004.

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