Effect of TiF$_3$ catalyst on the tribological properties of carbon black-contaminated engine oils

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ABSTRACT

The effects of a TiF$_3$ catalyst on the tribological behaviour of carbon black-contaminated liquid paraffin and a fully formulated engine lubricating oil (CD SAE15W-40) were investigated using a four-ball tribological test. Scanning electronic microscopy with energy-dispersive spectroscopy, X-ray photoelectron spectroscopy, surface roughness, and thermogravimetric analyses were used to investigate the surface element content, chemical valence state, surface roughness, and initial decomposition temperature of the oil samples, respectively. Results showed that the average wear scar diameter (AWSD) and friction coefficient of the two kinds of carbon black-contaminated lubricants decreased in the presence of 0.5 wt% TiF$_3$. The variation rates of the carbon black-contaminated liquid paraffin and fully formulated engine lubricating oil were 29.45% and 11.54%, respectively, and their initial decomposition temperatures decreased. These phenomena were ascribed to the decomposition of TiF$_3$ catalyst into TiO$_2$ and fluoride that resulted in the formation of improved boundary lubrication films. Moreover, for the fully formulated engine oil, the lubrication additive zinc dialkyldithiophosphate was catalyzed by TiF$_3$, decomposing into polyphosphate, which aided the formation of mixture boundary lubrication films.

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1. Introduction

The drive to save energy and reduce mankind’s dependence on fossil fuels has promoted the development of a wide variety of alternative bio-derived fuels such as bio-ethanol, bio-diesel, and biomass pyrolysis fuel [1–5]. Engines powered by these fuels can benefit from reduced emissions and improved fuel economy. However, the generated soot, a by-product of the combustion process, cannot be eliminated easily [6]. Most of the soot generated during the combustion process is exhausted, but some can also contaminate the lubricant within the sump as a result of blow-by gases, this can be worsened when exhaust gas recirculation is used [7,8]. Soot contamination of the lubricating oil can lead to increased wear in critical components as well as the shortening of oil life and increased frequency of oil changes. Thus, the importance of reducing the tribological impact of soot contamination within the lubricating oil is highlighted.

Soot contamination is a serious issue that has been extensively investigated by both engine and lubrication manufacturers. To date, studies on engine soot mainly focus on soot formation and the associated wear mechanisms. However, the collection of soot particles to evaluate their tribological properties is difficult and very time consuming. Producing reliable data also depends on reproducing soot with consistent properties for use in contamination tests. To address these concerns, several studies have used carbon black, which simulates engine-derived soot. Ratoi et al. [9] used carbon black as engine soot dispersed in an engine oil, assessed the rapid removal of zinc dialkyldithiophosphate (ZDDP) reaction films by abrasion. However, this removal was limited (or even eliminated) by the choice of dispersant additive. Joly-Pottuz et al. [10] found that carbon black particles were highly abrasive between steel surfaces with increased wear and friction. However, they also found that the addition of carbon onions in a lubricant reduced both friction and wear. Olomolehin et al. [11] found that the combination of an alkyl ZDDP and carbon black produced more wear than without the ZDDP additive. Green and Lewis used carbon black simulated engine soot to investigate the oil properties and wear of engine components. They attributed soot wear mechanisms to an engine soot abrasion effect [12–14]. These studies indicate that carbon black can be used as a substitute for engine soot to investigate the friction and wear properties of...
lubricating oil. Many studies have been conducted to investigate the soot induced wear of engine parts with the different tribological tester [15–18]. They indicate that low levels of carbon black can play an important role in strengthening the antiwear properties of an engine’s lubricating oil [13]. The wear effects of carbon black-contaminated lubricating oils on the critical components of engine frictional parts can be decreased by the optimization of a dispersant and solid lubricant. The carbon black used in the present tribological study is a good substitute for engine soot based its morphology, composition, and particle size [19].

Solid fluorine catalysts have been shown to reduce the wear effect of carbon black-contaminated lubricating oils. For example, Nehme [20,21] showed the significant effect of an FeF3 catalyst on the performance of plain ZDDP oil. The tribological and chemical interactions of ZDDP/FeF3 underlying their improved wear performances have also been examined with high performance lubricants and modified PTFE coating on metal surfaces by Elsenbaumer et al. [22]. Mourhatch and Aswath [23,24] used different contact loads and performed several chemistry characterization studies to differentiate the wear mechanisms of ZDDP plain oil and ZDDP oil in the presence of FeF3. Huq and Aswath [25] used a TEM to investigate the anti-wear film/wear particles generated in the present of TiF3 catalyst under boundary lubrication condition. Parekh [26] examined the chemical interactions between ZDDP and FeF3 that yielded a new chemical species responsible for the improved wear performance. There have also been patents registered regarding the use of transition metal fluorides as additives to enhance the activity of ZDDP (see for example Shaub et al. and Aswath et al. [27,28]). Greer [29] suggested that oil ingredients can be catalyzed with appropriate fluorinated materials. As is well known, both TiF3 and FeF3 catalysts can reduce the gas emissions, and also can be used to promote the degradation of ZDDP. This would result in improved antiwear and antifriction properties for engine oils as well as a reduction in sulfur and phosphorous levels.

However, studies on the use of metal fluorides in simulated engine soot-contaminated lubricating oil are limited. As are studies on methods for decreasing the destructive effect of carbon black (soot) contaminated lubricating oil. Therefore, this paper describes a study of the effects of a TiF3 catalyst (0.5 wt%) on the tribological behavior of (1 wt%) carbon black-contaminated liquid paraffin and a fully formulated engine lubricating oil (CD SAE15W-40). A series of comparison experiments were designed to address the efficacy of TiF3 catalyst material to decrease engine soot wear. A systematic approach was used to establish basic wear data and subsequent methods for optimizing the formulation of engine oil with soot.

2. Experimental

2.1. Materials and sample preparation

Commercially available carbon black (CB; Cabot N660R, Shanghai Cabot Chemical Industry Co. Ltd., China) was used as an engine soot alternative. Fig. 1 shows the morphology, chemical composition, and particulate diameter of the CB. These characteristics were compared to true engine soot harvested from the combustion of 0# diesel (Hefei Petrochemical Company, China). They were taken using a HRTEM (high resolution transmission electron microscopy) and show the average particulate diameter sizes and degrees of crystalline for the CB and soot particulates. The average particle diameter of carbon black was 40 nm, and engine soot was 45 nm. The inset diffraction patterns of two carbonaceous materials indicated that a large amount of amorphous carbon existed. The two carbon materials had virtually indistinguishable perturbed graphitic or turbostratic internal structures.

A commercially available TiF3 catalyst was purchased from Alfa-Asia Tianjin Chemical Co., Ltd. Fig. 2 shows the morphology and chemical composition of TiF3.

![Fig. 1. HRTEM images of carbon black and engine soot: (a) carbon black, (b) engine soot.](image)
A base oil liquid paraffin (LP; Hengshui Diji Petrochemical Co., Ltd.) and a fully formulated engine lubricant (CD SAE 15W-40, Sinopec Lubricant Company) were used for this investigation. Their physicochemical properties were measured according to the American Society of Testing Materials (ASTM) standards, as shown in Table 1.

The other reagents such as acetone and ethanol were analytical grade. Tribological tests were conducted using a four-ball tribometer (MQ-800) [30]. The steel balls used in the tests were ASTM grade. Tribological tests were conducted using a four-ball tribometer (MQ-800) [30]. The steel balls used in the tests were ASTM grade. Tribological tests were conducted using a four-ball tribometer (MQ-800) [30]. The steel balls used in the tests were ASTM grade. Tribological tests were conducted using a four-ball tribometer (MQ-800) [30]. The steel balls used in the tests were ASTM grade. Tribological tests were conducted using a four-ball tribometer (MQ-800) [30]. The steel balls used in the tests were ASTM grade. Tribological tests were conducted using a four-ball tribometer (MQ-800) [30]. The steel balls used in the tests were ASTM grade.

Table 1: Physicochemical properties of base oil and engine oil.

| Item                        | Liquid paraffin | CD SAE 15W-40 | Methods |
|-----------------------------|-----------------|---------------|---------|
| Density (kg/m³)             | 0.88            | 0.85          | ASTM D4052 |
| Kinematic viscosity (mm²/s, 40 °C) | 100            | 110.6         | ASTM D445 |
| Viscosity index             | 98              | 142           | ASTM D2270 |
| Sulfur content (wt%)        | No              | 2.5%          | ASTM D4294 |
| Phosphorus content (wt%)    | No              | 0.1%          | ASTM D1091 |
| Water (m/m) %               | Trace           | Trace         | ASTM D6304 |
| Pour point (°C)             | −15             | −24           | ASTM D9  |
| Flash point (°C)            | 210             | 220           | ASTM D93 |
| Acid number (mg KOH g⁻¹)    | 0.014           | 0.035         | ASTM D664 |

To observe the surface morphology and elemental composition of the wear scar area. A surface roughness measurement system (Taylor-Hobson-6) was used to measure the surface roughness of the wear scar on the top surface of the steel ball under 10,000× magnification. The length of the sample was 0.08 mm, and the evaluation length was five times the sample length using a Gaussian filter and a steel ball sensor of 10,000:10 mm.

To distinguish the influential mechanism of the TiF₃ catalyst on the tribological behaviors of engine carbon black-contaminated engine lubricants, an X-ray photoelectron spectroscopy system (ESCALAB250) and a thermogravimetric analyzer (Q5000IR) were used to investigate the elemental chemical valence state in the wear zones of steel balls and the variations in thermal properties of the oil samples, respectively. Oil samples (5 mg to 10 mg) were placed in a platinum pan and heated from 35 °C to 800 °C at a heating rate of 10 °C/min under 8 mL/min oxygen purge.

3. Results and discussion

3.1. Wear resistance

Fig. 3 shows the wear resistances of the oil samples. Fig. 3(a) shows the variations in average wear scar diameter of liquid paraffin with and without TiF₃ catalyst. The AWSD of pure liquid paraffin was 0.444 mm. For the liquid paraffin with 1.0 wt% CB the AWSD was 0.455 mm. This indicates that the CB has little effect on the antiwear properties of liquid paraffin. However, the AWSD decreased to 0.321 mm when the TiF₃ catalyst was added, indicating that TiF₃ particles can improve the antiwear properties of carbon black-contaminated liquid paraffin. The addition of the TiF₃ catalyst in uncontaminated liquid paraffin was also investigated. The results show an AWSD of the pure liquid paraffin increased when compared to the contaminated oil. The lowest observed AWSD was that of the liquid paraffin with 1 wt% CB and 0.5 wt% TiF₃. This phenomenon indicated that CB particles make a contribution to the antiwear property of liquid paraffin. In all, TiF₃ catalyst material had an important function in strengthening the antiwear properties of liquid paraffin and carbon black-contaminated liquid paraffin.

Fig. 3(b) shows the variations in AWSDs of CD SAE 15W-40 with and without the addition of the TiF₃ catalyst. The AWSD of the uncontaminated lubricant was 0.483 mm, but for the CB-contaminated CD SAE 15W-40 this decreased to 0.4678 mm. The addition of 0.5 wt% TiF₃ further reduced the AWSD to 0.4138 mm, which was lower than that of carbon black-contaminated CD SAE 15W-40 lubricant. These results again indicate that the TiF₃...
catalyst plays an important role in reducing wear. The findings for the CD SAE 15W40 lubricant were similar to those for liquid paraffin, i.e., 0.5 wt% TiF3 catalyst addition reduced the wear of engine oil and carbon black-contaminated engine-lubricating oils.

### 3.2. Friction reduction

Fig. 4(a) shows the variations in the friction coefficient of liquid paraffin with and without the TiF3 catalyst. The friction coefficient of pure liquid paraffin was higher than both of liquid paraffin added with 1.0 wt% CB and 0.5 wt% TiF3 catalyst. This is likely to be the result of the poor friction reducing properties of the liquid paraffin component. The addition of 1 wt% CB to the liquid paraffin caused the friction coefficient of oil to decrease and this is likely to an effect of the “roll effect” of dispersed CB particles, similar to that of Green [13]. Adding 0.5 wt% to CB contaminated liquid paraffin caused the friction coefficient to decrease further. This indicates that the TiF3 catalyst caused a significant reduction in friction. A similar reduction in frictional was also above red when the TiF3 catalyst was added to pure liquid paraffin.

Fig. 4(b) shows the variations in friction coefficient of CD SAE 15W-40 lubricant samples. The friction coefficient of carbon black-contaminated CD SAE 15W-40 lubricant was higher than that of pure lubricant. The possible reason for this was that the soot absorbed additives and exerted agglomeration effects within the lubricant [32]. When 0.5 wt% TiF3 catalyst was added to the CB contaminated lubricant, the friction coefficient decreased. This result once again indicates that the TiF3 catalyst significantly reduced friction. To further verify the cause of these observations the TiF3 catalyst was once again added to pure CD SAE 15W40, and the result indicated that this catalyst material did reduce friction.

The above observations indicate that TiF3 catalyst plays an important role in reducing friction for the liquid paraffin and fully formulated lubricating oil, both with and without CB contamination.

### 3.3. Surface analysis

The surface morphologies of the wear zones of steel test samples were observed with an SEM/EDS system to determine whether the simulated soot particulates would promote the wear. Table 2(a) shows the images taken from the surfaces steel balls lubricated using pure liquid paraffin. The black arrows and rectangle represent the striking furrows and grooves on the surface of the wear zone. These are the result of the higher kinematical viscosity of liquid paraffin, causing adhesive wear to occur during the rubbing process. The surface roughness was 0.040 μm, which indicated that the wear of pure liquid paraffin was severe. Table 2(b) shows images of surface morphologies of steel balls using the CB contaminated liquid paraffin. Numerous furrows with broken edges (black arrows) were observed. This phenomenon could be attributed to the fact that carbon black particles were scratching the surfaces. When 0.5% catalyst TiF3 was added to the CB contaminated liquid paraffin, surface
Table 2
Surface roughness and images of steel balls after rubbing for 30 min under different conditions.

| Code | Stationary ball | Rotational ball | Surface roughness (μm) |
|------|-----------------|-----------------|------------------------|
| a    | ![Image](a.png) | ![Image](a.png) | 0.040                  |
| b    | ![Image](b.png) | ![Image](b.png) | 0.050                  |
| c    | ![Image](c.png) | ![Image](c.png) | 0.015                  |
| d    | ![Image](d.png) | ![Image](d.png) | 0.020                  |
| e    | ![Image](e.png) | ![Image](e.png) | 0.055                  |
| f    | ![Image](f.png) | ![Image](f.png) | 0.033                  |
morphologies of the wear zones revealed a reduction in surface roughness to 0.020 μm. The furrows that appeared on the wear zone were less severe than those for the pure liquid paraffin and CB contaminated liquid paraffin in Table 2(d). To further examine the antiwear and antifriction properties of the TiF₃ catalyst, it was added to pure liquid paraffin. Results indicate that the surface roughness decreases continually, and the furrows disappear in the wear zone in Table 2(c). Therefore 0.5 wt% TiF₃ catalyst addition to liquid paraffin can reduce simulated-soot wear.

Table 2(e) reveals the surface morphological images of steel balls of pure CD SAE 15W-40 oil. The appearance of furrows was easily observed on the surface of the rotational ball. The surface roughness was 0.055 μm. Table 2(e–h) shows images of wear scar morphologies of fully formulated engine oil. The surface furrows (Table 2(f)) suggest that wear is more severe than for pure CD SAE 15W-40 oil (Table 2(e)), but surface roughness's were lower. This phenomenon could be due to the fact that local carbon black reunion or undispersed carbon black particles exacerbated wear, this would be consistent with the friction coefficient results. Surface roughness decreased compared to pure SAE CD 15W-40 oil when 0.5 wt% TiF₃ catalyst was present. These results indicated that TiF₃ catalyst strengthens the antiwear and antifriction properties of carbon black-contaminated CD SAE 15W-40 oil.

Fig. 5 shows the variations in element contents in the wear zone for the two kinds of oil tested. The inset in Fig. 5(a) signified that elemental titanium was absorbed onto the wear surfaces during the friction process. Titanium and fluorine elements were not observed when the TiF₃ catalyst (0.5 wt%) was added to the carbon black-contaminated liquid paraffin. This observation was due to the low contents of these elements. Fig. 5(b) reveals that elemental phosphorus was observed on the wear pair without the TiF₃ catalyst in the fully formulated engine lubricant. This result indicated that the additives played an important role in antiwear and friction reduction efficiency. Elemental phosphorus was not

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**Table 2 (continued)**

| Code | Stationary ball | Rotational ball | Surface roughness (μm) |
|------|----------------|----------------|-----------------------|
| g    | ![Image](image) | ![Image](image) | 0.026                 |
| h    | ![Image](image) | ![Image](image) | 0.037                 |

*Notes: (a) LP, (b) LP+1 wt% CB, (c) LP+0.5 wt% TiF₃, (d) LP+1 wt% CB+0.5 wt% TiF₃, (e) CD SAE 15W-40, (f) CD SAE 15W-40+1 wt% CB, (g) CD SAE 15W-40+0.5 wt% TiF₃, and (h) CD SAE 15W-40+1 wt% CB+0.5 wt% TiF₃.*
found when the TiF$_3$ catalyst was added to CD SAE 15W-40 lubricant, which was likely due to its low content. These results suggest that the TiF$_3$ catalyst material significantly contributed to the formation of a boundary lubrication film.

To further examine the effect of the TiF$_3$ catalyst on the tribological behaviors of the CB contaminated engine oils, X-ray photoelectron spectroscopy and thermogravimetric analysis were used to investigate the wear zones and oil samples. Table 3 shows the variations in elemental content in the wear zones with and without the TiF$_3$ catalyst. Titanium and fluorine elements were detected when 0.5 wt% TiF$_3$ was added to the CB contaminated liquid paraffin. Similarly, these two elements along with phosphorus were detected in CD SAE 15W-40 oil. Elemental sulfur was not detected in the CD SAE 15W-40 oil with 1 wt% CB. The reason for this was possible due to the low content of ZDDP, which would have caused the absorptive CB particles or by an “abrasion effect” from the agglomerated carbon black particles [33,34]. The Absorption effect could be expounded via the component analysis of the TiF$_3$ catalyst material. The wear mechanism of CB contaminated engine oils in the presence of the TiF$_3$ catalyst was that the TiF$_3$ catalyst made some contribution to the efficiency of the ZDDP and the TiF$_3$ catalyst material. The wear mechanism of CB contaminated SAE CD 15W-40 oil with 1 wt% carbon black and 0.5 wt% TiF$_3$ were attributed to the synergistic effect of ZDDP and the TiF$_3$ catalyst material.

Moreover, the Ti 2p spectra (Fig. 6(g)) showed that the binding energies at 457.88 eV and 463.5 eV were the characteristic peaks of TiO$_2$. The F1s spectrum (Fig. 6(i)) showed that the only peak at 133.2 eV, which belonged to phosphate. The results of C1s spectral analysis (Fig. 6(h)) showed two peaks at 284.8 eV and 286.3 eV, which were attributed to TiF$_3$ catalyst. The chemical valence state of the titanium was changed into iron oxides (such as Fe$_2$O$_3$ and Fe$_3$O$_4$) in the pure liquid paraffin and with 1 wt% CB. This result indicated that iron atoms were subject to oxidative reactions on the rubbing surfaces. Iron atoms (BE=707 eV) did not completely change into iron oxides in the presence of 0.5 wt% TiF$_3$ catalyst (Fig. 6(e)). This phenomenon indicated that the iron atoms were protected via the lubrication film.

| Samples                | Atom content (at%) |
|------------------------|--------------------|
|                        | C          | O         | Fe       | P       | Ti       | F       | Zn     |
| LP                     | 42.94      | 45.82     | 11.28    | 0       | 0        | 0       | 0      |
| LP+1% CB               | 71.08      | 17.93     | 10.99    | –       | –        | –       | –      |
| LP+0.5% TiF$_3$+1% CB  | 73.39      | 9.48      | 3.57     | –       | –        | 2.94    | 10.62  |
| LP+1% CB               | 75.67      | 11.49     | 6.35     | 1.71    | 4.45     | –       | 0.33   |
| CD SAE 15W-40+1% CB    | 28.68      | 25.05     | 3.20     | 0.44    | 1.42     | 18.57   | 22.64  |

Table 3

| Items                  | Element content (wt%) |
|------------------------|-----------------------|
|                        | C           | O           | Fe       | P       | S        | Ti       | F       | Cr     | Ca     |
| LP+1 wt% CB            | 71.08       | 17.93       | 10.99    | –       | –        | –        | –       | –      | –      |
| LP+1 wt% CB+0.5 wt% TiF$_3$ | 73.39   | 9.48        | 3.57     | –       | –        | 2.94     | 10.62   | –      | –      |
| SAE CD 15W-40+1 wt% CB | 75.67       | 11.49       | 6.35     | 1.71    | 4.45     | –        | –       | 0.33   | –      |
| SAE CD 15W-40+1 wt% CB+0.5 wt% TiF$_3$ | 28.68 | 25.05       | 3.20     | 0.44    | 1.42     | 18.57    | 22.64   | –      | –      |

Table 4

3.4. Wear mechanism analysis

The antiwear and antifriction of carbon black-contaminated liquid paraffin and formulated engine lubricant were ascribed to the formation of boundary lubrication films containing carbon, titanium, and fluorine elements. Fig. 7 shows the schematic diagram of tribofilm formation for liquid paraffin and CD SAE 15W-40 lubricant in the presence of the TiF$_3$. The active components of titanium and fluorine in the oils were physically absorbed in significant amounts on the surfaces of steel balls [38]. During the rubbing process, the chemical reaction for wear played an important role in the formation of a boundary lubrication film. This can be used to explain the antiwear and antifriction mechanisms of CB contaminated engine oils in the presence of the TiF$_3$ catalyst. The chemical valence state of the titanium was changed...
from Ti$^{2+}$ to Ti$^{4+}$. This phenomenon indicated that the TiF$_3$ catalyst decomposed into TiO$_2$ and fluorates, which have better lubrication properties [39,40].

The fully formulated engine oil containing different kinds of lubrication additives such as ZDDP can form a better boundary lubrication film than liquid paraffin oil, thereby resulting in lower AWSD and friction coefficient than CB contaminated liquid paraffin. Moreover, the preferentially absorbed antiwear additives (ZDDP) and the TiF$_3$ catalyst that formed the protective films prevented carbon black from making contact with the steel surface.

Fig. 6. Chemical valence state of chemical in wear zones in the two kinds of carbon black-contaminated engine oils.
During the rubbing process, ZDDP degraded into a glassy-state polyphosphate under the friction force as well as the frictional thermal and the catalytic conditions [20,41-44]. This finding was confirmed by the X-ray photo-electron spectroscopy results showing the phosphorus element in Fig. 7. The catalyzed ZDDP degradation can also be deduced by varying the initial decomposition temperatures of the oil samples (Table 6). The change rates of the initial decomposition temperature of the CB contaminated liquid paraffin and the fully formulated engine oil were 2.5% and 13.47%, respectively. These results sufficiently prove that the TiF3 catalyst played an important role in promoting the decomposition of engine oil additives such as ZDDP [45].
4. Conclusions

(1) The TiF<sub>3</sub> catalyst material makes an important contribution to enhancing the antiwear and antifriction properties of engine oils and in the presence of low levels of contamination.

(2) The average wear scar diameter and friction coefficient of two kinds of carbon black-contaminated engine oils decreased in the presence of 0.5 wt% TiF<sub>3</sub>. The variation in the average wear scar diameter of CB contaminated liquid paraffin and the fully formulated engine lubricant were 29.45% and 11.54%, respectively.

(3) The antiwear and antifriction mechanisms of the TiF<sub>3</sub> catalyst material were attributed to titanium and fluorine elements that themselves assisted in the formation of a boundary lubrication film.

(4) The TiF<sub>3</sub> catalyst played an important role in promoting the decomposition of antiwear additives within the engine lubricating oil. The friction functional transition of the...
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