# THE EFFECT OF DIDECYLAMINE AND DI-n-DODECYL GROUP CONTAINING BORATE ESTER ADDITIVES ON FRICTION AND WEAR

by

***Nihat PARLAK[a], Latif OZLER[b*], and Ahmet Orhan GORGULU[c]***

[a] Technical Sciences Vocational School, Mus Alparslan University, Mus, Turkey
[b] Department of Mechanical Engineering, Faculty of Engineering, Firat University, Elazig, Turkey
[c] Department of Chemistry, Faculty of Science, Marmara University, Istanbul, Turkey

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*Various studies aim to reduce wear and material loss in machines where parts are in relative motion and contact. Damage caused by the wear of the material leads to work loss and financial issues. Various additives are added to oils to reduce financial losses that occur due to material wear. The widespread use and superior properties of boron minerals have drawn researchers' attention, leading to the incorporation of borate additives into oil lubricants. In this study, two different borate ester additives containing Didecylamine and Di-n-Dodecyl groups were synthesized, and their effects on wear, friction, and temperature were experimentally investigated. The additives were mixed into 10W-40 motor oil at concentrations of 0.2%, 0.6%, 1%, and 3% by weight. Experiments were conducted using a four-ball wear test device under varying speeds and contact forces. In the experiments carried out with BE1 and BE2 doped engine oil under 200 N, 400 N, and 600 N loads, it was found that the increase in the additive increased the amount of wear. In the experiments carried out with BE1 and BE2 added oils under different loads, it was observed that the increase in the additive ratio caused the contact surface and increased the amount of wear, friction coefficient, and temperature. The lowest wear amount was observed in oils with 0.2% BE2 under a 200 N load. The study concluded that adding borate ester additives to commercially available motor oils is unsuitable.*

Key words: *wear, friction, borate ester, synthesizing, engine oil, oil additive*

## Introduction

Friction is one of the most important negative causing material damage and economic losses in the industry [1]. To reduce friction, prevent excessive heating, and minimize damage to machine components, solid and liquid lubricants are employed. However, additive-free lubricants often prove ineffective in achieving sufficient friction reduction. To address this limitation, various additives are incorporated into lubricants [2, 3]. These additives include friction modifiers, extreme pressure agents, anti-wear additives, antioxidants, detergent-dispersants, and corrosion inhibitors [4].

The continuous improvement of lubricant formulations and increasingly stringent environmental regulations have restricted the use of traditional sulfur- and phosphorus-containing additives. This has made the development of environmentally friendly additives an

* Corresponding author, e-mail: lozler@firat.edu.tr

important research area. In this context, boron-containing additives have been extensively studied, with various boron-based compounds being synthesized and utilized as lubricant additives [5]. Literature reviews demonstrate that many boron-containing additives exhibit superior tribological properties [4-11]

In this study, two different borate esters containing Didecylamine (BE1) and Di-n-Dodecyl groups (BE2) were synthesized due to the promising potential of boron compounds as oiling additives for moving parts in relative motion. Special boron additives are added to commercially available additive motor oils by service centers during maintenance and repair. This study aimed to investigate the effects of synthesized borate ester additives on wear and friction when used in motor oils.

## Material and method

To investigate the effects of two different synthesized borate ester additives on oil lubricants, analyze wear behavior under extreme pressure, and determine friction characteristics, experiments were conducted using a four-ball wear test device, fig. 1.

The oil used in the experiments is 10W-40 synthetic engine oil. The properties of the engine oil used in the experimental study are given in tab. 1.

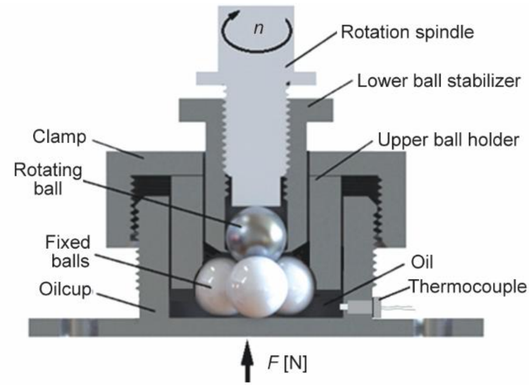


**Figure 1. Elements of the four ball wear device**

**Table 1. Properties of engine oil used in the experimental study**

| Property | Value |
|---|---|
| SAE viscosity grade | 10W-40 |
| Density at, 15 °C, [kgL$^{-1}$] | 0.870 |
| Flash point, COC [°C] | 234 |
| Pour point [°C] | –33 |
| Viscosity, 40 °C, [mm$^2$s$^{-1}$] | 97 |
| Viscosity, 1000 °C, [mm$^2$s$^{-1}$] | 14,3 |
| Viscosity index | 151 |

For this experimental study, borate ester additives were mixed into commercially available SAE10W-40 motor oil at various concentrations. Parameters analyzed included wear scar diameter (WSD), coefficient of friction (COF), temperature variation, and wear type. Two different borate ester compounds were used as oil additives in the experiments. Boron ester compound containing additives Didecylamine and Di-n-Dodecyl groups was obtained in three steps and according to the methods stated in [12, 13]. The borate ester compound containing didecylamine groups was designated as BE1 borate ester, fig. 2, while the compound containing di-n-dodecyl groups was labeled as BE2 borate ester, fig. 3.

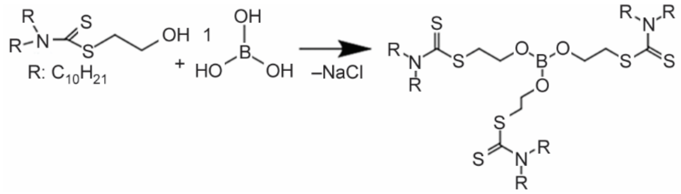


**Figure 2. Borate ester containing didecylamine groups**

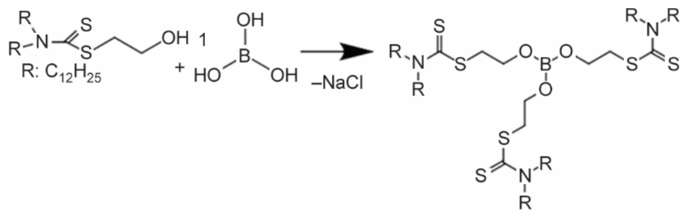


**Figure 3. Borate ester containing Di-n-Dodecyl groups**

The test oils were prepared by mixing borate esters into 10W-40 motor oil at concentrations of 0.2%, 0.6%, 1%, and 3% by weight [8, 9, 14-17]. A Thermomac-TM-II-6C mechanical mixer was used to homogenize the mixture at 1500 rpm for 30 minutes.

Experimental parameters were determined based on literature studies [7-9, 14-16] and preliminary tests. The values used in this experimental study are presented in tab. 2.

**Table 2. Experimental parameters**

| Experiment parameter | The value of |
|---|---|
| Contribution rate [%] | 0.2, 0.6, 1, 3 |
| Applied force [N] | 200, 400, 600 |
| Number of revolutions [rpm] | 1200, 1400 |
| Temperature [°C] | Room temperature |
| Time [minutes] | 60 |

The experiments were conducted at room temperature without preheating, under constant contact pressure and rotational speeds, for durations of 60 minutes following the ASTM D5183-95 standard. Tribological tests utilized AISI 52100 (100 C6) standard steel balls with a diameter of 12.7 mm and hardness of 63 HRC.

Force and torque measurements were performed using a two-axis load cell, with data transferred to a computer via a VTA-1704 data acquisition device. Linear progression force was applied using a dual-stage pressure-controlled pneumatic cylinder powered by a 9 bar compressed air compressor, fig. 4.

### *Fourier-transform infrared spectra*

Fourier-transform infrared (FT-IR) spectroscopy is a widely used method in basic sciences, health sciences, and engineering for identifying molecular bonds. Infrared spectra obtained through FT-IR can help identify the chemical composition or bonds within an unknown molecule or compound. The primary use of infrared spectroscopy is to provide structural information about the presence of specific functional groups in a sample [5, 6, 18]. The FT-IR measurements were performed using an Agilent Cary 630 (FT-IR) device.

### *Determination of the friction coefficient*

Average torque values were used to calculate the friction coefficient using the following equation [7, 14]:

$$\mu = \frac{T\sqrt{6}}{3Wr} \tag{1}$$

where $\mu$ is the friction coefficient, $T$ [Nm] – the friction torque, $W$ [N] – the load, and $r$ [mm] – the distance between the center of the contact surface of the lower balls and the rotational axis.

This distance is 3.67 mm for balls with a diameter of 12.7 mm.


**Figure 4. Image of the wear test set-up**

### *Measurement of wear scar diameter*

Following the ASTM D4172 standard, the WSD on the three stationary balls was measured using a PME Olympus Tokyo brand optical microscope located in the Department of Mechanical Engineering at Fırat University, fig. 5. Before and after each experiment, the oil reservoir, clamping components, and test balls of the four-ball wear device were thoroughly cleaned with acetone and dried using compressed air to eliminate any residual particles. The trace diameters (WSD) of the dried balls after the test were measured with an optical microscope according to the ASTM D4172 standard in parallel (horizontal) and vertical positions to the lines on the wear surface. If the WSD measurements showed an error of more than 10%, the experiments were repeated, and the arithmetic mean of the three measurements was taken [19]. Based on the data obtained, the average values of WSD and friction coefficients were calculated as reported values.

**Figure 5. Optical microscope used to measure the ball wear trace diameter**

## Findings

### *The FT-IR spectra*

Figure 6 presents the FTIR spectra of the BE1 and BE2 additives. The highest absorption peak was observed at approximately 2919 $cm^{-1}$, which was attributed to the C–H stretching vibration (butane). The second-highest absorption peak, detected at 2852 $cm^{-1}$, corresponds to the medium-intensity C–H stretching bond (butane) [18]. It is known that the B–O bonds in borate ester molecules exhibit infrared absorption peaks in the wavenumber range of 1430–1355 $cm^{-1}$ [5, 6, 9, 20]. For both BE1 and BE2 additives, absorption peaks were observed at 1409 $cm^{-1}$. Finally, the peak at approximately 721 $cm^{-1}$ was assigned to the bending vibrations of various borate bonds [5, 6].

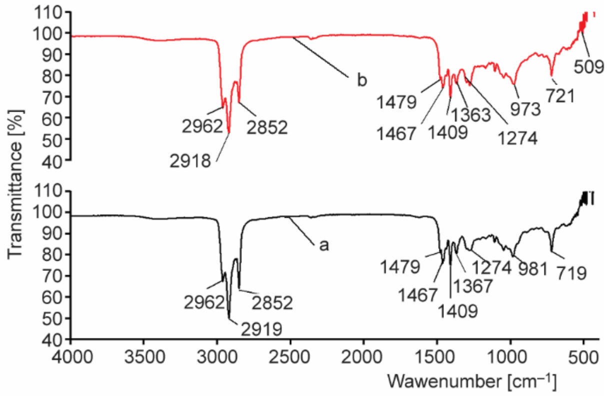


**Figure 6. The FT-IR spectra; (a) BE1 and (b) BE2**

### *Determination of wear amounts*

Wear tests were conducted under loads of 200 N, 400 N, and 600 N, with speeds of 1200 rpm and 1400 rpm, for 60 minutes at room temperature, and borate ester additives were tested at concentrations of 0.2%, 0.6%, 1%, and 3%. The WSD on the stationary balls were measured under 5× magnification using a metallurgical microscope with a 1/100 scale, and the averages were calculated fig. 7.

When examining the effect of the additive on wear, the lowest wear amount was obtained with 0.2% BE2 under a 200 N load and a speed of 1200 rpm. For oils without additives, the WSD was 0.48 mm, whereas it was 0.53 mm for oils with 0.2% BE1, 0.59 mm with 0.6% BE1, and 0.63 mm with 3% BE1. In experiments with BE2, the WSD decreased to 0.52 mm with 0.2% BE2, 0.54 mm with 0.6% BE2, and significantly increased to 0.74 mm with 3% BE2, fig. 8. At a 400 N load, WSD for oils with 0.2% BE1 and BE2 were 0.53 mm, while they increased to 0.62 mm for 0.6% BE1 and 0.65 mm for 0.6% BE2. At a 3% additive concentration, the WSD was 0.63 mm for BE1 and 0.73 mm for BE2. The experiments indicated that additive concentrations above 0.2% did not positively impact the WSD. Yang *et al.* [20] reported that increasing the concentration of borate ester additives in synthetic oils raised both friction and wear. This was attributed to differences in polarity between the additive and the oil, which influenced adsorption capability and reaction activity [18, 20]. Higher concentrations of additives were thought to affect the compactness and continuity of the oil film, there-by increasing wear amounts [8, 18]. Another study using a synthetic oil lubricant with borate ester additives under high contact pressure reported that borate ester additives did not provide adequate friction-reducing effects [21].

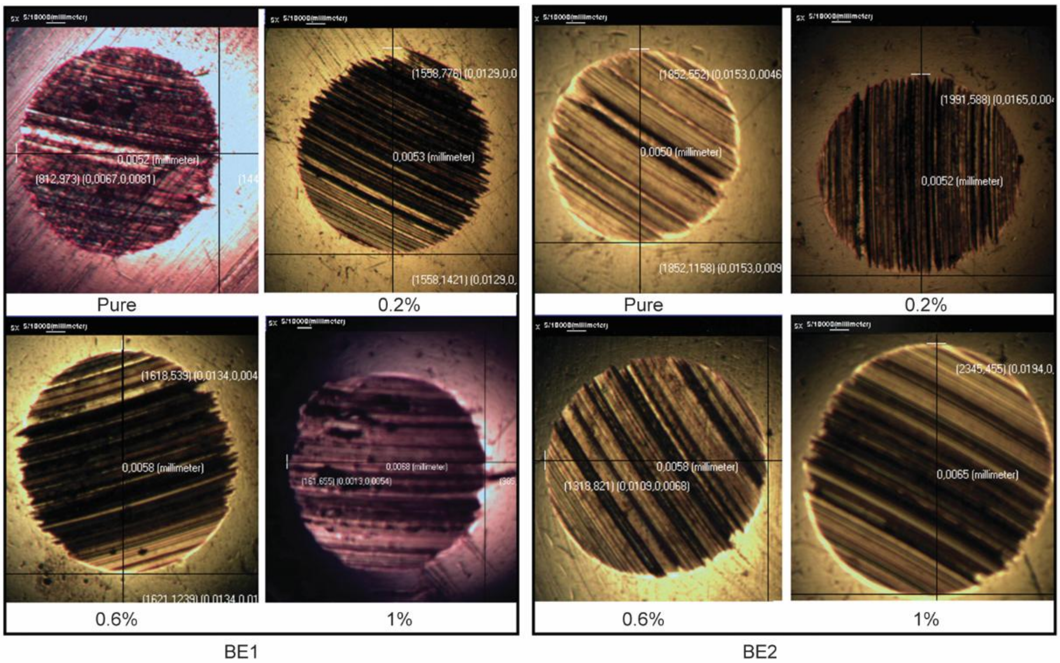


**Figure 7. Optical microscope images at 1:100 scale of ball wear in additive oil environment (1200 rpm, 400 N)**

In experiments conducted at 1200 rpm with 0.2% additive oils, WSD were close to those of oils without additives. This finding is consistent with the results of Xiong *et al.* [22]. They used additive concentrations ranging from 0.1% to 0.5% and found that the lowest WSD occurred at a 0.3% concentration, which they deemed optimal. However, the slightly higher WSD observed in this study may be attributed to the additives already present in the test oil. In both studies, increasing the additive concentration resulted in larger WSD, as shown in SEM images of fig. 9.

The SEM images of the balls used in the experiments are shown in fig. 10. Under a load of 400 N with oils without additives, abrasive wear and the formation of micro-pits were identified. With oils containing 0.6% BE1, adhesive wear was observed, along with the formation of capillary cracks and larger micro-pits. For experiments conducted with 0.6% BE2 oils, adhesive wear resulted in continuous micro-cracks and more pronounced micro-pits along a defined line. At a 600 N load and 1% additive concentration, abrasive wear was dominant, with mechanical fractures and expanded micro-pits evident in specific areas.

### *Determination of COF*

The effect of borate ester additives added to mineral oil at various ratios on the COF is given in fig. 11. When the effect of the additive ratio on the COF in the experiments with BE1 additive oils is examined, the COF was 0.033 in the experiments with unadded oil under

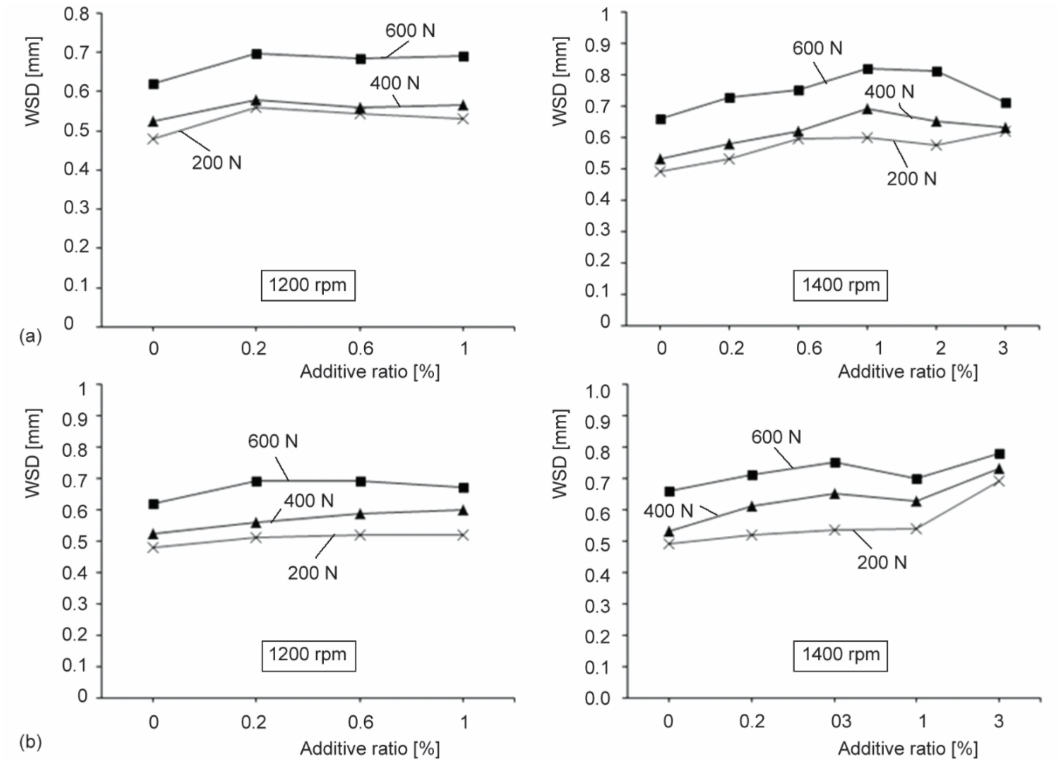


**Figure 8. The wear graph in additive oil environment; (a) BE1 and (b) BE2**

1400 rpm and 200 N load, 0.037 under 400 N load, and 0.048 under 600 N load, fig. 11. The 0.2% BE1 additive on the COF, 0.037 was obtained at 200 N and 0.2% oil additive, while 0.041 was obtained under 400 N load and 0.051 was obtained at 600 N with a slight increase. In 0.2% BE2 additive oils, the COF increased compared to BE1 additive oils, and 0.063 was obtained under 200 N load, 0.067 under 400 N load, and 0.088 under 600 N load. In BE1 and BE2 additive oils, a 3% increase in the additive ratio increases the COF by approximately 200%. These values obtained are consistent with the wear trace diameters of the balls shown in fig. 9. In SEA10W-40 oil with borate ester additives, it was observed that the increase in the additive ratio did not have a positive effect on the COF, and at high additive ratios, the COF increased excessively, fig. 11.

High contact pressure also increases the COF. Increasing the contact pressure causes plastic deformation on the contact surface, increasing the contact area, the shear stress in the contact area, and the COF. In addition, as a result of high contact pressure, oil film thickness and contact stress decrease, resulting in boundary oiling [14]. The increase in friction at high contact force is due to the high shear strength or surface roughness of tribofilms formed by additives. The friction behavior exhibits a response corresponding to the formation of a film between the contacts under boundary lubrication conditions [23]. In addition, the increasing temperature during operation increases the viscosity of the oil lubricant. Increasing the concentration of the additive acts more on the contact zone, adsorbing more on the surface, and slightly decreasing the COF [22, 24].

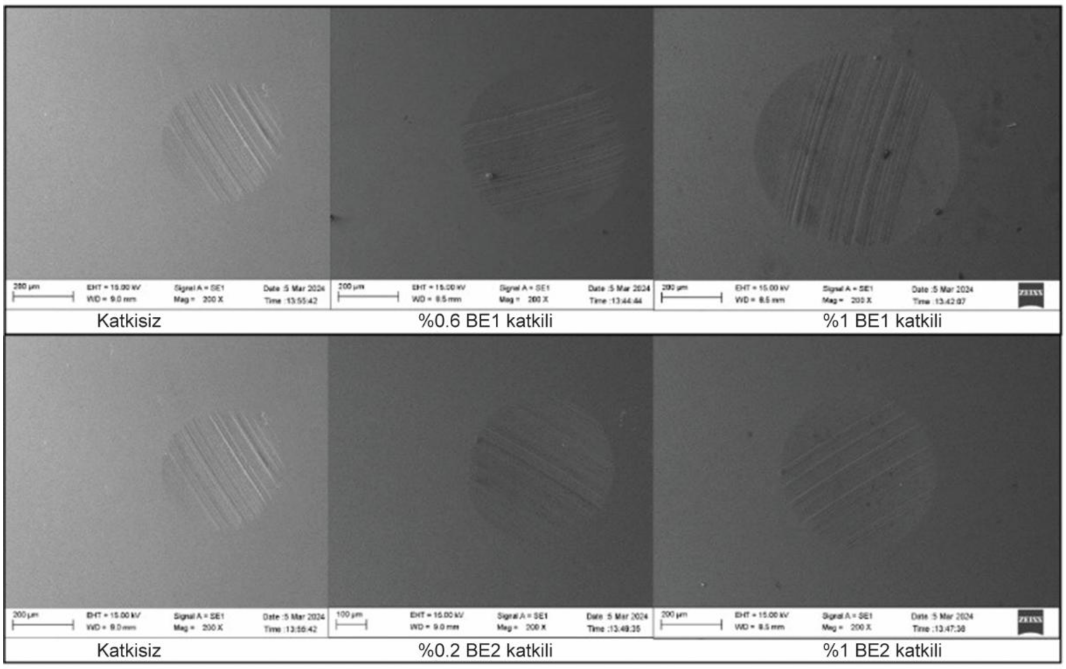


**Figure 9. The SEM images of wear of balls in non-doped and doped oil environment (1200 rpm, 400 N)**

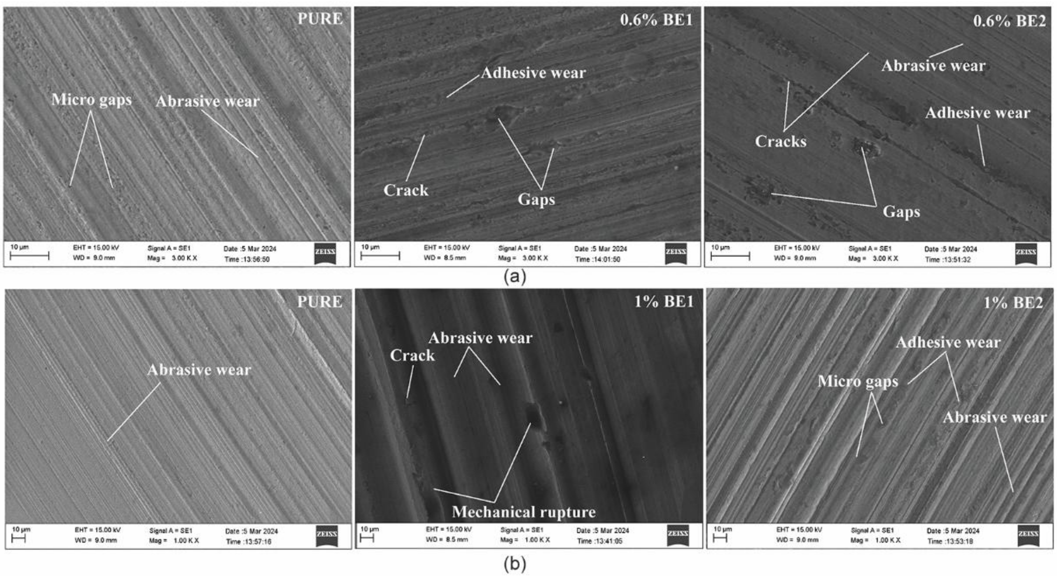


**Figure 10. The SEM images of ball wear under doped oil, 1200 rpm, (a) 400 N and (b) 600 N**

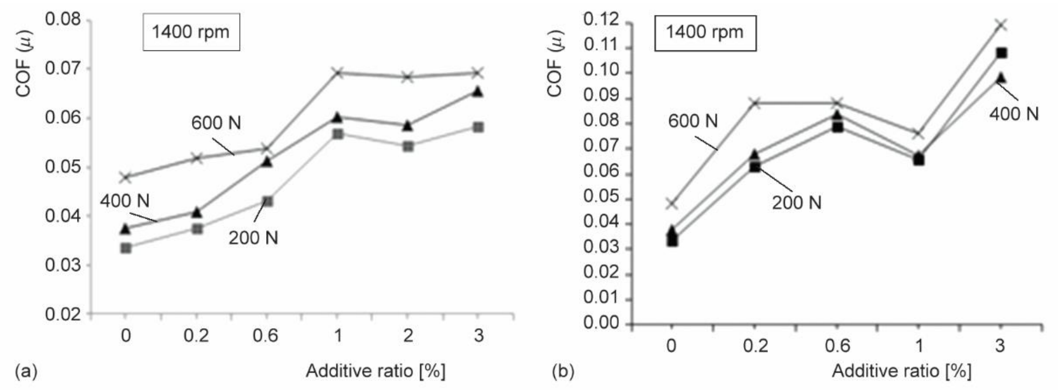


**Figure 11. The effect of additive ratio on COF; (a) BE1 and (b) BE2**

*Temperature measurements*

The effect of oil additive concentrations on the oil temperature in the contact region is shown in fig. 12. Experiments conducted at 1400 rpm and 400 N contact pressure at room temperature revealed that the oil temperature in the contact region was 44 °C for oils containing 0.2% BE1, while it increased by 7% to 47 °C for oils containing BE2. When using 1% BE1, the temperature was 45 °C, whereas it increased by approximately 11% to 49 °C for oils with BE2. In experiments with 0.2% BE1 oils, there were no significant changes in the contact region oil temperature. However, at higher additive concentrations, the temperature in the contact region increased. In addition, in the experiments performed under 400 N contact pressure, it was observed that the contact zone temperature of BE1 additive oils was lower than that of BE2 additive oils. These results aligned with the findings on the COF and wear amounts. As contact pressure increased, the temperature in the contact region rose. Higher contact pressure caused plastic deformation in the contact area, thinning the oil film layer and creating boundary lubrication conditions [14]. The increase in friction forces due to higher contact pressure further raised the contact region temperature [25].

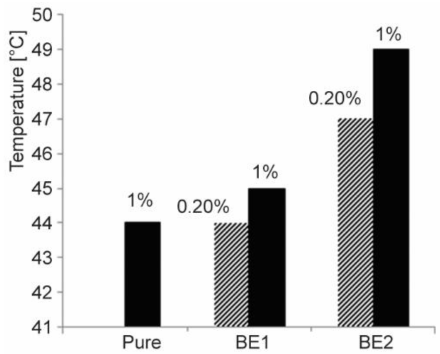


**Figure 12. The effect of addetiverate on temperature (1400 rpm, 400 N)**

## Results

In this study, two different borate ester additives were added to engine oil at various ratios, and the tribological properties of the additives were investigated. The results obtained are summarized below.

- Two different borate esters containing Di-n-dodecylamine groups and Didecylamine groups were synthesized.
- The lowest wear quantities in the additive oils were obtained in 0.2 wt.% additive oils in experiments with low speed and contact pressure.

- It was observed that both borate ester additives synthesized had no significant effect on wear and friction. It is interpreted that the most important reason for this is that the selected engine oil is additive.
- The use of borate ester synthesized additives in additive motor oils affects wear adversely. For this reason, borate ester additives should not be used in additive motor oils.
- Increasing the additive ratio in high additive borate ester additive oils increases the amount of wear, COF, and contact zone temperature.
- In the oils without additives, micro-pits occur with abrasive wear, while in the oils with Di-n-dodecylamine and Didecylamine additives, macro-pits and mechanical ruptures occur with abrasive and adhesive wear.

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