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Synthesis of Oil Soluble Boron Esters and Obtaining Lubricant Additive Packages with Anti-wear and Extreme Pressure Properties

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Abstract

The purpose of this work is synthesis and characterization of pryridin-yl-borate esters and investigation of tribological performance as additive. The synthesis of dialkyl-(2-(pyridin-2-yl) ethyl) borate esters both in the literature and the novel synthesis of dialkyl 2-(methyl (pyridin-2-yl) borate esters and dialkyl 2- (5-ethylpyridin-2-yl) ethyl borate esters were carried out. The boron esters to be obtained were characterized by using IR, 1H NMR,13C NMR spectroscopic methods as well as physical methods such as TAN and corrosion tests. The friction-reducing and anti-wear properties of the synthesized lubricant additives were measured with a four-ball friction and wear tester. As a result of these studies, it has been shown that the friction coefficient is reduced by about 30-40 % compared to the base oil and the wear is also reduced. In the tribological analysis performed using synthesized four molecules within the scope of the study, it was found that resistance to oxidation is increased when the synthesized molecules were added to group I base oil at 0.5 % and 1% w/w concentration. The novel synthesis of dialkyl 2-(methyl (pyridin-2-yl) borate esters and dialkyl 2- (5-ethylpyridin-2-yl) ethyl borate esters were carried out and tribological performances in base oil were analysed first time.

Keywords: Anti-wear; Borate esters; Friction; Green additives; Lubricants

Research Article

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1. Introduction

Lubricants are materials that are needed in industrial machinery, motor vehicles, the metalworking industry, furniture, construction, medicine and wherever metal is present due to their preventive properties against wearing problems [1]. However, base oils alone may not provide adequate protection, so additives that improve tribological properties are added to the lubricants. It is an undeniable fact that investing in better performing lubricants protects equipment used in industry, thus making the facilities more reliable by running longer and more efficiently [2]. Almost all of the lubricants that are used in the automotive and manufacturing sectors are oil or grease-based [3]. These lubricants contain harmful components that are not readily biodegradable and can therefore bring about a significant number of contaminants into the waste stream for the environment [4]. In addition to designing economical and durable products, the interest in the made products that are proper for environmentally friendly approaches has continuously increased in the last ten decades [5]. Long-term impacts of lubricants are cumulative and ultimately harmful for humans, plants, animals, and the ecosystem [6]. Hence, Environmental Protection and Government agencies in many countries of the world are putting increasingly stringent legislation and regulations regarding the use, storage and disposal of oil and grease-based lubricants [7,8]. Tremendous efforts have been made to develop new generation friction-reducing and anti-wear lubricant additives with low-toxicity. Recently, there has been a significant interest in research related to boron-based additives due to their environmentally safe and inexpensive profiles [9]. Unlike the traditional lubricant additives that contain health risks to the ecosystem, organic borate esters which possess excellent wear resistance, unique oxidation inhibition and biocompatibility, have been received great attention [10].

The heterocyclic compounds containing the N element are reported to have excellent extreme pressure and anti-wear properties in the lubricating oil [11]. The number of N atoms is the main factor influencing tribological performance. N-containing heterocyclic compounds contain N atoms with a pair of lone electrons in the p orbital that will form a complex with the empty 2p orbital of

the B atom against the attack of nucleophiles to increase the resistance of boron esters to hydrolysis [12].

Boron is known as one of the least abundant elements naturally on earth since it is a metalloid that is found chemically combined with other elements [13,14]. Hence, several allotropes present naturally, there are many forms of boron such as brown powder amorphous, silvery to black crystalline and extremely hard material forms [15]. Nevertheless, it is hard to believe that it could be soluble in oil and even exhibit unique tribological properties since boron is generally recognized as a metalloid [16]. Boron additives, displaying tremendous properties different from their macroscopic counterparts, have been synthesized with emerging and rapidly expanding chemistry points of view [17,18]. Besides, among the lubricant additives, boron gained importance not only due to its emerging properties but also because of its diverse and nonpareil potentials in the lubricant industry [19].

In this study, novel heterocyclics borate esters that containing N element were synthesized. Tribological properties, such as oxidation stability, anti-wear, extreme pressure, were determined. According to the tribological activities, synthesized molecules formulated at different concentrations to create additive packages. Created additive packages tribological properties were also studied.

2. Methods and Materials

2.1 Materials

The Hydrocarbon base oil which is commercially known as Heavy Neutral used in all experiments was purchased from Tüpraş, Turkey. This base oil was also used without further treatment, and its typical characteristic is shown in Table 1. Boric acid (H3BO3), sodium bicarbonate, diethyl ether, toluene, and sodium sulfate were purchased from Merck (Darmstadt,Germany). 1-Octanol ($C_8H_{18}O$), 1-Dodecanol ($C_{12}H_{26}O$), 2-(2-hydroxylethyl)pyridine (C_7H_9NO) and 2-(Methyl (pyridin-2-yl) amino) ethanol ($C_8H_{12}N_2O$) were supplied from Sigma-Aldrich (St. Louis, MO, USA), pure water was obtained from Merck (LC-MS grade, Germany). All the experiment reagents purchased from the following companies were analytical-grade without further purification. The commercial extreme pressure additive package commercially named as Hitec® 343 (purchased from Afton Chemical Co., Ltd., Singapore), which is widely used as an anti-wear agent to improve the tribological performance of lubricating oils, was used as a comparison to evaluate the anti-wear properties of prepared additive packages.

2.2 Synthesis of molecules

In this study, four novel boron esters were synthesized in the laboratory and their tribological properties were characterized. Figure 1. shows the synthetic pathway of borate esters. According to the synthesizing pathway, 2-pyridine ethanol (0.1 mol), N-methyl-2-(2-pyridylaminoethanol) (0.1 mol), 1-dodecanol (0.2 mol), 1-octanol (0.3 mol) and boric acid (0.1 mol) were added into a three-neck round flask with a thermometer. The reactant mixture was uniformly dispersed in 250 mL toluene at room temperature then heated to 110–125 °C and refluxed for 16 h under stirring, meanwhile the water formed during the reaction was separated using dean–stark trap. After the completion of the reaction, the oil phase was separated from the water phase by repeatedly extracting the water with ether. Then, the reaction mixture was filtered, and rotary evaporated to remove solvent residues under the vacuum conditions. The final product was distilled under vacuum to remove toluene and water. A colorless liquid was obtained as the final product.

Table 1. Typical physical properties of base oil.

Tests	Standards	HN base oil
Appearance	-	Clear&Bright
Colour	ASTM D 6045	L1.5
Density, 15 °C, gr/cm^3	ASTM D 4052	0.885
Refractive Index, 20 °C	ASTM D 1218	1.4852
Viscosity, 40°C, cSt	ASTM D 445	96.69
Viscosity, 100°C, cSt	ASTM D 445	10.82
Viscosity Index	ASTM D 2270	95
Pour Point, °C	ASTM D 6749	-3
Water content, mg/kg	ASTM D 6304	31
Total acid number, mgKOH/gr	ASTM D 664	<0.1
Flash point, °C	ASTM D 92	262

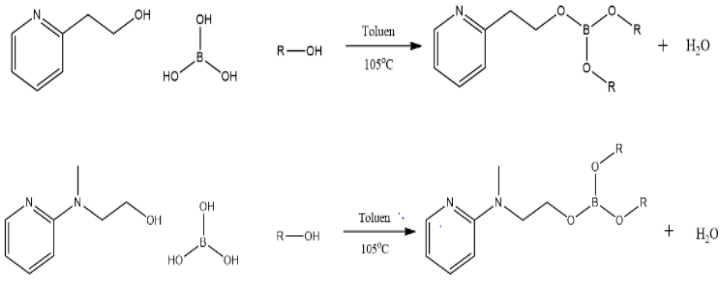
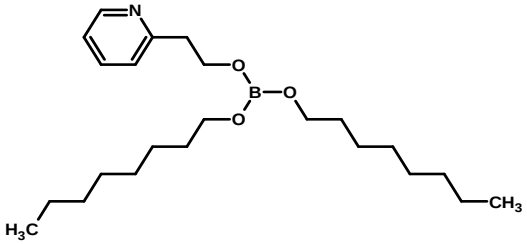
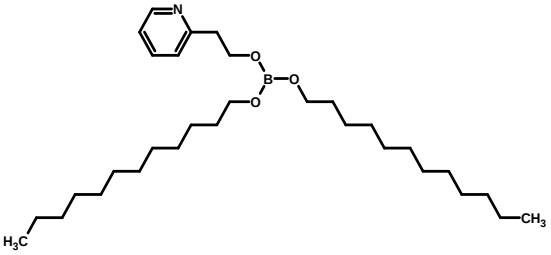
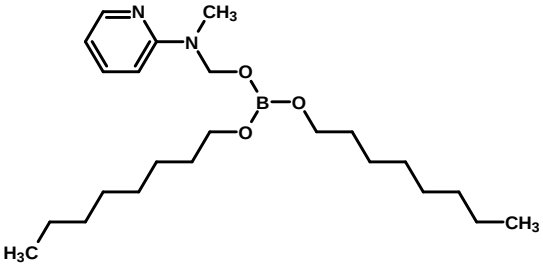
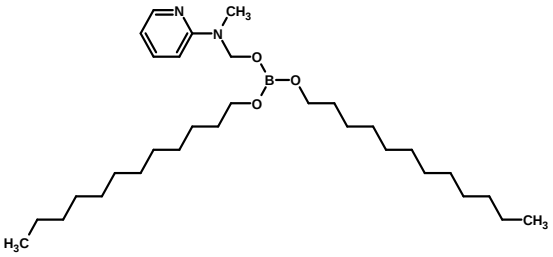


Fig. 1. Boron esters synthesized by the reaction procedure described above are shown.

The synthesized boron esters were dissolved in diethyl ether and extracted with 50 mL 1 M sodium bicarbonate solution three times, then the product was washed twice with deionized water. The organic phase was dried over sodium sulfate and the solvent was removed under the vacuum at 130 °C at 10 mbar. The chemical structures of the synthesized molecules and the codes given to them are shown in Table 2.

Table 2. The synthesized boron esters and their chemical structures are indicated by the given code.

Chemical structure	Boron esters	Code	Yield %
	Dicapryl(2-(pyridin-2-yl)ethyl)borate	1a	79.93
	Didodecyl(2-(pyridin-2-yl)ethyl) borate	1b	63.9
	Dioctyl(2-(methyl(pyridin-2-yl)amino) ethyl) borate	2a	67.64
	Didodecyl (2-(methyl(pyridin-2-yl) amino ethyl borate	2b	55.6

2.3 Characterization of synthesized molecules

^{1}H NMR experiments were performed in the Faculty of Chemistry at the Bolu İzzet Baysal University using JEOL -ECS 400 MHz spectrometer. Each sample (10–20 mg in CDCl3; ~0.7 mL) was analyzed at 25 C° and chemical shift values are given in ppm relative to TMS for ^{1}H NMR and ^{13}C NMR. JEOL-ECS NMR spectrometer was operated to different functional groups at 75.46 MHz for ^{13}C and 400.09 MHz for proton NMR. All ^{1}H-NMR data were processed using zero filling and exponential apodization of FIDs prior to Fourier transformation, phasing and baseline correction. Signal calibration was referenced to TMS at δ <0.00 ppm, and relevant signals have been collected and integrated. It is important that sidebands are not included to ensure the accuracy of subsequent quantification, so special attention has been paid to the integral limit of the signals. The main functional groups of synthesized molecules were characterized by Fourier transform infrared (FTIR) spectroscopy. The FTIR spectra were obtained using a Spectrum-Two FT-IR (Perkin Elmer) spectrophotometer with a resolution of 0.1 cm^{-1}. FTIR experiments were performed to confirm the chemical structure of prepared borate esters and the spectra were collected in the range of 400–4000 cm^{1}.

2.4 Measurement of the tribological properties

The tribological properties of the synthesized molecules within the scope of the study were determined in two steps. Firstly, it was determined in which tribological activity the synthesized molecules were active. In this context, the tribological activities of the synthesized molecules were determined by dissolving in base oil Heavy Neutral (HN) (Table 3) in certain proportions. In the second step, additive packages were formed by preparing mixtures of different proportions from the synthesized molecules and their tribological activities were determined.

Firstly, for the determination of tribological activities of synthesized molecules; each molecule was added into the base oil at 0.5 and 1 % concentrations. Molecules and base oil mixtures were prepared by stirring for 30 min. at 40 °C. The prepared sample's formulations were shown in Table 3.

Table 3. Samples preparation for determining tribological properties

%	HN	1a	1b	2a	2b	Hıtec 343
FH1	100	-	-	-	-	-
FH2	99.5	0.5	-	-	-	-
FH3	99.5	-	0.5	-	-	-
FH4	99.5	-	-	0.5	-	-
FH5	99.5	-	-	-	0.5	-
FH6	99.5	-	-	-	-	0.5
FH7	99.5	1	-	-	-	-
FH8	99.5	-	1	-	-	-
FH9	99.5	-	-	1	-	-
FH10	99.5	-	-	-	1	-
FH11	99.5	-	-	-	-	1

FH, Formulations prepared with HN

The tribological activities of synthesized boron esters in HN base oil were tested with a four-ball tester. The wear scar diameter (WSD) with an accuracy ±0.01 mm and weld load were measured using a seta-shell fourball tribometer according to ASTM D 4172 and ASTM D 2783 standards. Before each test, the balls were ultrasonically cleaned with acetone in a beaker for 10 minutes, and then oven-dried at 37 °C. The friction reduction and anti-wear capacities of the additives were evaluated with a four-ball tribometer under the following conditions: 1200 rpm/min at 392 N load for 60 minutes at 75 °C. The steel balls used in tribological tests were 12.7 mm in diameter made from GCr 15 bearing steel with 59-61 hardness HRC (Rockwell hardness). An optical microscope was used to measure the wear scar diameters (WSD) on the three bottom balls. Copper strip corrosion test was conducted at 100 °C for 3 h, according to ASTM D-130, by immersing the polished electrolyzed copper strip in a vessel. To determine the oxidation stability, 24-hour aging tests were carried out under sunlight simulation on the prepared samples. Then, at the end of the 24-hours aging test, the Total Acid Number (TAN) values were measured according to the ASTM D 664 standard by using an automatic titrator system (Mettler Toledo).

In the second step, additive packages were created considering the tribological activity results of the synthesized molecules (Table 4). Hitec 343 (Afton Chemicals) were used as the positive control. In all performed tribological and performance tests additive packages were added HN base oil at 2.5 % concentration.

Physical tests of additive packages in HN base oil were performed by using copper-corrosion test, oil-solubility, oxidation stability included total acid number test and 24 h ageing test. The tribological performance of additive packages in HN base oil was measured by a four-ball tribometer. Wear scar diameter (WSD) of the test balls was used to evaluate- the anti-wear performance of the additives. Each test was repeated three times, and the mean value was recorded as the final WSD result.

Table 4. Formulation of created additive packages

	% Concentration of synthesized molecules and control					
	1a	**1b**	**2a**	**2b**	**HN**	**Hitec 343**
Package 1	5	5	5	5	80	-
Package 2	5	10	5	10	70	-
Package 3	5	15	5	5	70	-
Package 4	5	5	5	15	70	-
Package 5	5	5	10	10	70	-
Package 6	5	5	15	15	60	-
Package 7	5	5	20	5	65	-
Package 8	25	25	15	15	20	-
Package 9	20	20	10	10	40	-
Package 10	15	15	15	5	50	-
Package 11	-	-	-	-	-	100

The oil solubility and hydrolytic stability of the borate esters were evaluated by the standard method presented in [20] and were tested as follows. The hydrolytic stability of created additive packages was evaluated by accelerated hydrolysis method by wet heating treatment as follows 150 g oil sample 0.5 wt % was added into a 200 mL beaker and then placed in a hot and humid oven (temperature at 50±2 °C, relative humidity more than 95%). The sample was monitored every hour and the time was recorded. If precipitation was observed in the sample or the sample was no longer transparent, it means that the additives have been hydrolyzed.

3. Results and Discussion

3.1 Characterization of Synthesized esters

The FTIR spectra of boron esters are shown in Fig. 2, the signal at approximately 1337-1381 cm^{-1} corresponds to peak of the O-B-O bonding, and the peaks located at 2955-2845 cm^{-1} are assigned to $–CH_2$ and $–CH_3$ groups, and O-H bonding located at 3224 cm^{-1}, respectively. The signal at around 1463 cm^{-1} is indicative of the bending vibration of the $-CH_2$ group.

The peak located at 1601 cm^{-1} corresponds to benzene ring. According to FTIR results; hydroxyl peaks in the synthesized molecules were caused by the amount of fatty alcohols remaining. Thus, the IR results confirm that various functional groups and elements were incorporated into the borate esters.

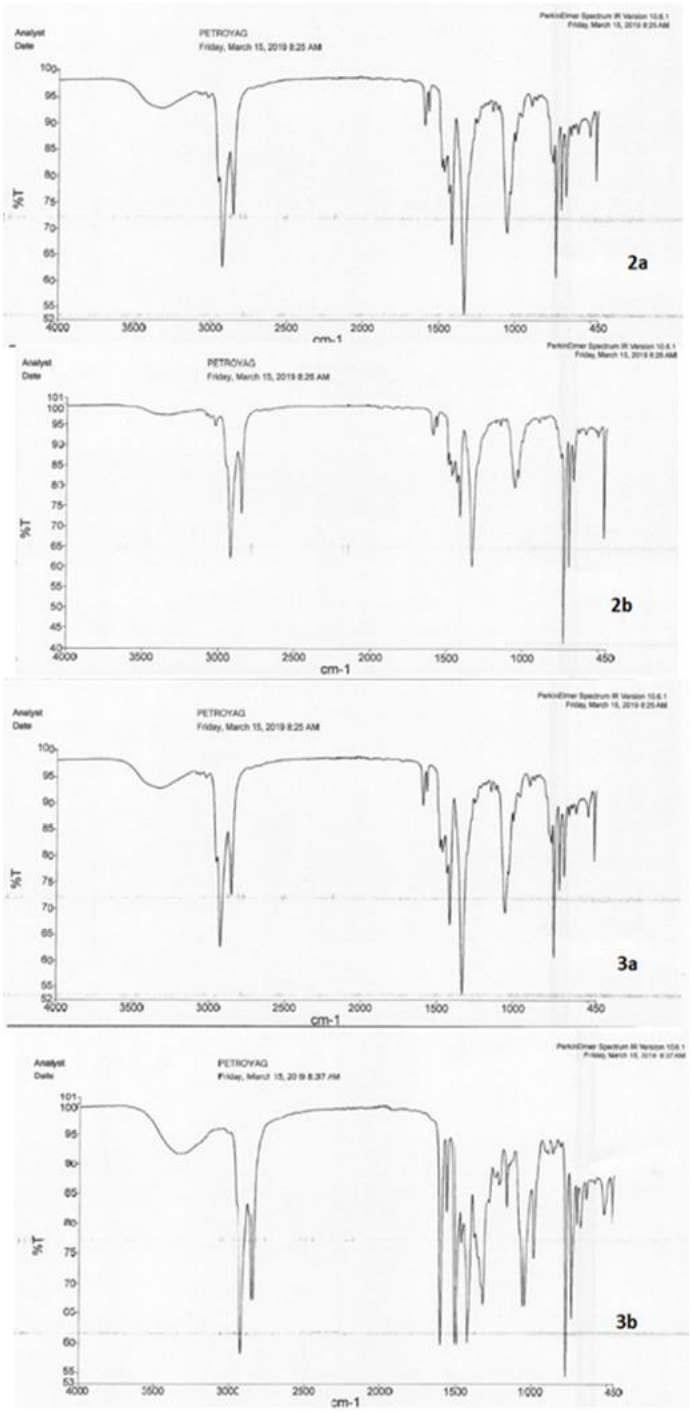


Fig. 2. FTIR spectra of synthesized molecules (1a,1b,2a,2b)

1a: Dicapryl(2-(pyridin-2-yl)ethyl)borate; Color: white liquid; Solubility: Hexane, Toluene; Yield: 79.93%
1H NMR: δ 0.87 (6H, t, J = 7.0 Hz), 1.19-1.39 (16H, 1.27 (quint, J = 7.0 Hz), 1.28 (h, J = 7.0 Hz), 1.23 (quint, J = 7.0 Hz), 1.35 (tt, J = 7.0, 6.7 Hz)), 1.24 (4H, quint, J = 7.0 Hz), 1.73 (4H, tt, J = 6.9, 6.7 Hz), 3.18 (2H, t, J = 6.5 Hz), 3.56 (4H, t, J = 6.9 Hz), 3.72 (2H, t, J = 6.5 Hz), 7.17 (1H, ddd, J = 7.4, 4.6, 1.2 Hz), 7.26 (1H, ddd, J = 7.6, 1.2, 0.5 Hz), 7.64 (1H, ddd, J = 7.6, 7.4, 1.9 Hz), 8.48 (1H, ddd, J = 4.6, 1.9, 0.5 Hz).

1b: Didodecyl(2-(pyridin-2-yl)ethyl) borate; Color: colorless liquid, Solubility; Hexane, Toluene, Yield: 63.9 %
1H NMR: δ 0.87 (6H, t, J = 7.0 Hz), 1.19-1.32 (28H, 1.28 (tt, J = 7.1, 7.0 Hz), 1.28 (h, J = 7.0 Hz), 1.23 (quint, J = 7.0 Hz), 1.23 (quint, J = 7.0 Hz), 1.23 (quint, J = 7.0 Hz), 1.23 (quint, J = 7.0 Hz), 1.23 (quint, J = 7.0 Hz)), 1.24 (4H, quint, J = 7.0 Hz), 1.39 (4H, tt, J = 7.1, 6.7 Hz), 1.73 (4H, tt, J = 6.9, 6.7 Hz), 3.18 (2H, t, J = 6.5 Hz), 3.56 (4H, t, J = 6.9 Hz), 3.72 (2H, t, J = 6.5 Hz), 7.17 (1H, ddd, J = 7.4, 4.6, 1.2 Hz), 7.26 (1H, ddd, J = 7.6, 1.2, 0.5 Hz), 7.64 (1H, ddd, J = 7.6, 7.4, 1.9 Hz), 8.48 (1H, ddd, J = 4.6, 1.9, 0.5 Hz).

2b: Didodecyl (2-(methyl(pyridin-2-yl) amino ethyl borate, Color; light brown liquid, Solubility; Hexane, Toluene, Yield: 55.6%
1H NMR: δ 0.87 (6H, t, J = 7.0 Hz), 1.19-1.32 (28H, 1.28 (tt, J = 7.1, 7.0 Hz), 1.28 (h, J = 7.0 Hz), 1.23 (quint, J = 7.0 Hz), 1.23 (quint, J = 7.0 Hz), 1.23 (quint, J = 7.0 Hz), 1.23 (quint, J = 7.0 Hz), 1.23 (quint, J = 7.0 Hz)), 1.24 (4H, quint, J = 7.0 Hz), 1.39 (4H, tt, J = 7.1, 6.7 Hz), 1.73 (4H, tt, J = 6.9, 6.7 Hz), 2.62 (3H, s), 3.56 (4H, t, J = 6.9 Hz), 4.77 (2H, s), 6.98 (1H, ddd, J = 7.9, 4.8, 1.3 Hz), 7.21 (1H, ddd, J = 8.1, 1.3, 0.5 Hz), 7.63 (1H, ddd, J = 8.1, 7.9, 1.9 Hz), 8.27 (1H, ddd, J = 4.8, 1.9, 0.5 Hz.

To further determine the content of C, N and B in the synthesized molecules, elemental analysis was conducted, and the results are listed in Table 5. The theoretical value of each element was calculated based on the chemical formulas. The experimental values of C, N and B are in good agreement with the theoretical values within the limits and experimental error.

Table 5. The elemental analysis of the synthesized compounds.

	C (wt%)	H (wt%)	B (wt%)	N (wt%)
1a	71.02(70.58)[a]	10.19 (10.82) [a]	2.84 (2.76) [a]	3.39 (3.58) [a]
1b	73.44(73.93) [a]	10.03 (11.61) [a]	2.06 (2.15) [a]	2.91 (2.78) [a]
2a	68.09(67.97) [a]	10.44 (10.66) [a]	2.57 (2.66) [a]	5.99 (6.89) [a]
2b	71.27(71.79) [a]	11.05 (11.47) [a]	2.19 (2.08) [a]	5.67 (5.40) [a]

[a]Calculated value (balanced by oxygen).

3.2 Tribological performance of synthesized molecules

The tribological activities of the synthesized molecules were evaluated by measuring the weld load capacities and wear scar diameters of the prepared samples with base oil at 0.5 and 1 % concentrations (Table 6).

Table 6. Four ball test results of synthesized molecules.

		Weld Load (kg)		
Molecule	**Base oil**	0 % additive	0.5 % additive	1 % additive
1a	HN	<250	<250	<250
1b	HN	<250	<250	<250
2a	HN	<250	<250	<250
2b	HN	<250	<250	ND
		Wear Scar Diameter (mm)		
1a	HN	>0.6	>0.6	0.54
1b	HN	>0.6	>0.6	>0.6
2a	HN	>0.6	>0.6	>0.6
2b	HN	>0.6	0.51	0.46

The potentiality of boron esters as EP (extreme pressure) additive in HN base oil was investigated on a four-ball tester and the variation of weld load and WSD (wear scar diameter) with different concentrations in HN base oil were investigated. The concentration increasing of the molecule 2a and 2b in the formulations, increased the weld load capacity and decreased the WSD values. The increasing in concentration of molecule 2a and 2b did not affect the extreme pressure properties of formulations prepared with HN. The highest weld load capacity and lowest WSD values were observed with 2a and 2b molecules at 1% concentration in the base oil.

Oxidation stabilities of the synthesized molecules were investigated by measuring the T.A.N (Total acid value-ASTMD 664) value of prepared formulations before and after sunlight simulation aging tests (Table 7).

Table 7. Oxidation test results of the synthesized molecules.

		0.5 % additive		
Molecule	**Base oil**	0 hours	24 hours	change
1a	HN	0.2355	0.2457	0.0102
1b	HN	0.2126	0.2403	0.0277
2a	HN	0.133	0.2618	0.1288
2b	HN	0.1327	0.16	0.0273
Hıtec 343	HN	0.0111	0.0526	0.0415
		1 % additive		
1a	HN	0.471	0.543	0.072
1b	HN	0.3783	0.3901	0.0118
2a	HN	0.2649	0.3724	0.1075
2b	HN	0.2372	0.2534	0.0162
Hitec 343	HN	0.459	0.611	0.152

By measuring the T.A.N. values of the synthesized molecules before and after the sunlight simulation aging test, the change that occurred was evaluated as an indicator of oxidation measurement. The samples formulated with HN which are containing 1b and 2b molecules showed higher antioxidant activity than containg 1a and 2a molecules. In general, all prepared samples in HN base oil are showed similar antioxidant activity when compared the positive control Hitec 343. This method is widely used to determine the oxidation performance of lubricants. It was used to determine the oxidation stability of mineral white oils under both light and heat exposure [21].

Copper strip tests of the synthesized molecules were evaluated by using ASTM D 130 standard. All samples prepared in HN base oils resulted as 1b max. with the synthesized molecules and positive control Hitec 343 [22].

3.3 Tribological performance of created additive package

Additive packages were created according to the results obtained from synthesized molecules' tribological activity results. 11 additive packages were created in the study. In all packages, HN used as base oil and Hitec 343 used as a positive control.

The copper strip corrosion test is designed to assess the relative degree of corrosiveness of a petroleum product. Crude petroleum can contain a variety of sulfur compounds and most of these are removed during refining. Because copper strip corrosion caused by sulfur compounds in petroleum naphthas generally present very thin layers, it is necessary to use specific methods of surface analysis and microanalysis to determine the sulfur concentration on the copper strip surface [23]. When the additive packages obtained with the molecules synthesized were added to the base oil, the copper corrosion strip tests values came close to the copper corrosion strip test values created by the base oil alone. This situation can be explained by the absence of sulfur in the structure of the synthesized molecules [24]. All created Additive packages were analyzed according to the ASTM D 130 for their copper strip corrosion effects and all tests resulted as 1b max (Table 8-9).

Table 8. Formulations of created additive packages.

	% concentration of synthesized molecules and control					
	1a	1b	2a	2b	HN	Hitec 343
Pack. 1	5	5	5	5	80	-
Pack. 2	5	10	5	10	70	-
Pack. 3	5	15	5	5	70	-
Pack. 4	5	5	5	15	70	-
Pack. 5	5	5	10	10	70	-
Pack. 6	5	5	15	15	60	-
Pack. 7	5	5	20	5	65	-
Pack. 8	25	25	15	15	20	-
Pack. 9	20	20	10	10	40	-
Pack. 10	15	15	15	5	50	-
Pack. 11	-	-	-	-	-	100

Pack.: Package

According to test results, all packages indicated good performance for the copper-corrosion test. Hence, all packages show good anti-corrosion properties.

24 hours aging test were performed on additive packages using sun light simulator. Total acid number was measured to determine.

Table 9. Tribological and performance test results of created additive packages.

	Copper corrosion test	T.A.N mgKOH/gr 24h ageing test	Weld point, kg	Wear scar diameter (mm)
Pack. 1	1a	1.81 ± 0.03	< 250	>0.6
Pack. 2	1a	0.86 ± 1.12	<250	>0.6
Pack. 3	1a	0.72 ± 0.14	<250	>0.6
Pack. 4	1a	0.43 ± 0.09	<250	>0.6
Pack. 5	1b	0.91 ± 0.02	350	>0.6
Pack. 6	1b	0.54 ± 0.16	400	0.48
Pack. 7	1a	0.84 ± 0.08	400	0.46
Pack. 8	1b	0.21 ± 0.01	350	0.56
Pack. 9	1b	0.31 ± 0.21	350	0.47
Pack. 10	1a	0.35 ± 0.04	400	0.42
Pack. 11	1b	0.48 ± 0.05	400	0.44

the oxidation stability of all additive packages. According to test results, package 8, package 9 and package 10 showed better oxidation resistance than other additive packages. Furthermore, packages 4 and 6 demonstrate good performance for oxidation stability due to having lower acid number values. Nevertheless, package 1, package 2 and package 5 had the highest acid number compared to other additive packages. Therefore, these packages were not sufficient in terms of antioxidant performance when compared to Hitec 343 named as package 11.

Four-ball test was performed on additive packages. Four ball test results of additive packages compared with Hitec 343 which was included in package 11. On the analysis results, weld load and WSD values indicated significantly good anti-wear and friction properties for package 6, package 7, package 8, package 9 and package 10. Hence, 2a and 2b molecules can be used in this package's EP and anti-wear additives because of having high tribological activity. Amino ethyl groups linked pyridine ring get increased EP, friction and anti-wear properties in the presence of these additive molecules [25, 26].

Package 7 and 10 showed good performance and WSD get significantly reduced. In addition to this the weld load values increased with package 10 and package 6. However, package 1, package 2, package 3, package 4 and package 5 showed poor performance compared to packages and Hitec 343 (package 11).

According to tribological and performance test results of created additive packages; Package 9 and package 10 showed effective and positive impact in all packages. Furthermore, this package exhibits superior tribological characters indicating potentiality of replacing Hitec 343 in the anti-wear and EP field.

4. Conclusion

In summary, novel borate esters (1a,1b,2a,2b) were synthesized by the esterification process and were characterized using NMR, FTIR, and elemental analysis. The Anti-wear and friction-reducing performances of synthesized molecules added into the HN base oil were studied. Based on the conducted studies, these conclusions were drawn.

The structure of novel borate esters was characterized by FT-IR and NMR spectroscopy, which indicated that functional groups were incorporated into novel esters that possessed an excellent thermal and hydrolytic stability properties. Hydrolytic stability of the synthesized borate esters mainly due to the electron-donating performance of the π-bond in the aromatic ring.

The chemical structure of the synthesized molecules with a B-containing benzene ring allowed S and P to inhibit its high reactivity to some extent and therefore reduced excessive S and P consumption in the oil. This is one reason why these molecules have superior tribological performance than other conventional S and/or P-containing additives.

According to analyses results of additive packages; package 9 and package 10 were suitable and showed good performance similar to Hitec 343. In general, boron esters synthesized have the potential to be widely used in many lubricating oils applications which will be considered as the future perspective of this research.

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Nomenclature

cSt : Centistoke (mm^2/s)

Conflict of Interest Statement

The authors declare that there is no conflict of interest in the study.

CRediT Author Statement

Mustafa Akın: Tribological analysis**,**
Mehmet C. Durmuş: Writing-original draft, Validation,
İmren Meydan and Emel Atılal: Synthesis and characterization of molecules

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