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Preparation of Additive Package for Gear Lubricants and Determination of Tribological Properties[1]

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Abstract—In this study an extreme pressure and anti-corrosion additive package for gear oils has been created. In this context three different organic molecules were synthesized. Methylene-bis (dibutyldithiocarbamate), Sulfured oleic acid and o,o-Dialkyldithio Phosphate. Mass spectrums and Elemental analyses were carried out for these three molecules. For each molecule 4-ball weld points (WP), 4-ball Wear Scar Diameter (WSD), Copper corrosion (CC) and salt spray tests (SS) were carried out. Antioxidant properties of synthesized molecules were determined. According to the test results eight different additive packages were prepared and WP, WSD, CC and SS tests were applied to each package to determine a suitable package content. The highest yield was obtained in the five and six additive package with 250, 300 kg weld point and 0.41, 0.53 mm scar diameter respectively. For all additive packages the extreme pressure and corrosion resistance properties of gear oil increase by increasing the percentage of Methylene-bis (dibutyldithiocarbamate). o,o-Dialkyldithio Phosphate showed the highest antioxidant activity and it has been obtained bets corrosion protection with Sulfured oleic acid.

Keywords: Additive package, extreme pressure, 4-ball, gear oil, synthesis

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A lubricant performs some of important functions. These include lubrication, cooling, cleaning and suspending, protection against corrosion, wear and friction. Lubricant include a base fluid and an additive package. Base fluid's mainly duty is lubricating and carry to additives. The function of additives is either to enhance an already-existing properties or to add a new property [1]. As a result lubricants have varies properties differs from one to the other depending on the intended use. Like Hydraulic, Slide way, Turbine, Quenching, Gear and Motor oils.

An additive package should have anti-wear, corrosion protection, cleaning, anti-foam and lubrication properties within. Especially the mechanical efficiency by reducing the friction further results in decreased fuel consumption and results in energy savings. These depend on the content of additive package with various extreme pressure (EP) and anti-wear (AW) additives [2]. The distinction between AW and EP additives is not clear. Some are classed as AW in one application and EP in another, and some have both AW, EP and Antioxidant properties. This additives classified by their element contents, sulfur additives are probably the earliest known, widely used EP compounds in lubricants. Sulfurization by addition of elemental sulfur to fatty acids known as sulfurized fatty acid esters [3] and to olefins known as sulfurized olefins [4, 5]. Phosphate esters have been using as lubricant additives earliest of 1920s. Selection of substituents considerable in phosphate esters to give optimum performance to lubricant [6]. There is many study on the use of phosphorodithioic acid esters in lubricating oils. Alkyl esters of phosphorodithioic acids, amine dithiophosphates and other novel dithiophosphate esters are reported as AW and EP additives [7, 8]. Sulfur and Nitrogen containing are used to provide protection against moderate to high pressure, metal to metal contacts in boundary lubrication, open chained and heterocyclic compounds have been studied in many research to found their AW properties. Dithiocarbamates are most widely used near organic sulfonic acid ammonium salts [9] and alkyl amine salts of thiocyanic acid [10].

In the present work it has been synthesized three organic molecule; Methylene-bis (dibutyldithiocarbamate), Sulfured oleic acid and o,o-Dialkyldithio Phosphate. Using H NMR, C^{13}, P^{31} and Elemental analysis chemical structure of molecules were determined. After that AW, EP, Antioxidant and Anti-corrosion properties for each molecule were determined. According to the obtained results eight additive packages created which have different rates of this molecules. Finally performance tests were applied for each package to determine true additive package.

[1] The article is published in the original.

Table 1. Physical properties of used additives

Additives *Synthesized*	Yield (%)	Elemental analysis (%)				Solubility[a]
		C	N	H	S	
Methylene-bis(dibutyldithiocarbamate)	78.6	54.42	7.43	8.73	NA	Sol
o,o-Dialkyldithio Phosphate	82.35	46.67	<1	7.31	NA	Sol
Sulphurised oleic acid	94.25	NA	NA	NA	30.26	Sol
Commercial						
Methylene-bis (dibutyldithiocarbamate)	NA	54.55	7.09	8.82	NA	So l
o,o-Dialkyldithio Phosphate	NA	51.25	<1	7.88	NA	Sol
Sulphurised oleic acid	NA	NA	NA	NA	29.81	Sol

[a] Solubility at a concentration of 3 wt % in base oil.
NA: Not Analysed.

1. SYNTHESIS OF MOLECULES

1.1. Materials

Commercial Metylene-bis(dibutyldithiocarbamate), o,o-Dialkyldithio Phosphate and Sulfured oleic acid purchased from Vanderbilt Chemicals, LLC. For the synthesis of equivalent molecules Phosphorus sequisulphide and sulfur purchased from Sigma-Aldrich, *n*-butanol, diethyl fumarate, hydroquinone, benzene, sodium carbonate, sodium sulfate, sodium hydroxide, dibutyl amine, carbon disulfide, methylene dichloride, oleic acid and Sodium chloride purchased from Merck. Group I base oils purchased from local refinery Turkish Petroleum Refineries Co. For the determination antioxidant properties of synthesized commercial molecules, DPPH, methanol and n-butanol purchased from Merck.

1.2. Synthesis Procedures

O,O-dibutyldithiophosphate synthesized in two step, first O,O-dibutyl dithiophosphoric acid synthesized according to the Colclough et al. (1997) [11] briefly modifications. Phosphorus sequisulphide and sulfur were heated in refluxing n-butanol for 2 hours at 110°C. Second step, O,O-dibutyl dithiophosphate synthesized according to the Cassaday et al. (1950) [12] briefly modifications. A mixture of O,O-dibutyl diyhiophosphoric acid, diethyl fumarate and hydroquinone was heated at 65°C for 24 hours, than allowed to cool the room temperature. The reaction mixture was taken up in 300 cc. benzene, washed with 10% sodium carbonate solution and with water. The organic layer was dried over anhydrous sodium sulfate, filtered and concentrated in vacuo.

Methylene-bis (dibutyldithiocarbamate) synthesized according to the Jover et al. (1998) [13] briefly modifications. Sodium hydroxide, dibutyl amine and water were mixed in an autoclave and the mixture was cooled to 5°C. Maintaining stirring Carbon disulfide was slowly added to the cooled mixture. The temperature was controlled by an effecting cooling system and it was not allowed to raise above 15°C. Then Methylene dichloride were added and the mixture slowly heated. After alkylation the excess of Methylene dichloride was distilled off at normal pressure. After that mixture cooled to the 40°C which resulted separation of a mixture in to an aqueous and organic phase. The organic phase was further distilled in vacuum and organic phase was washed with water three times.

Sulfured oleic acid was synthesized according to the Horodysky et al. (1985) [14] briefly modifications. Oleic acid and sulfur were charged to a glass reactor. Mixture was heated to 180°C under nitrogen atmosphere for 2 hours. The temperature was lowered to 145°C and air replaced the nitrogen atmosphere. And filtered through diatomaceous earth at 100°C.

1.3. Base oil and Additives Properties

The base stock used in the test is a paraffin base oil (Group I, SN 150; Kinematic viscosity 5.35 at 100°C and 31.25 at 40°C, SN 500; Kinematic viscosity 10.5 at 100°C and 96.54 at 40°C). Three different additives were synthesized and their commercial equivalents were analyzed together to compare their activities in base oil.

1.4. Preparation of Tested Gear Oil Formulations

Base oil, synthesized molecules and commercial molecules analyzed concentrate to determine antiwear properties content of additive package. According to the test results it has been decided to rate of using additives in package. Eight different packages created by using additives in different concentrations

Table 2. Content of the created additive packages

Additives %	Package 1	Package 2	Package 3	Package 4	Package 5	Package 6	Package 7	Package 8
Base oil (SN 150)	25	25	25	25	25	25	25	25
Synthesized								
Methylenebis dibutyldiyhio carbamate	35	–	20	–	30	–	5	–
o,o-Dialkyldithio Phosphate	10	–	30	–	40	–	35	–
Sulphurised oleic acid	30	–	25	–	5	–	35	–
Commercial								
Methylenebis dibutyldiyhio carbamate	–	35		20	–	30	–	5
o,o-Dialkyldithio Phosphate	–	10		30	–	40	–	35
Sulphurised oleic acid	–	30		25	–	5	–	35

(Table 2). The gear oils in SAE 80W-90 grade created by using this additive packages,

pour point depressant and viscosity index modifier were analyzed according to the Turkish Standard TS ISO 11485 [15]. Finished SAE 80W-90 grade oil has 133 cSt viscosity at 40°C, 14.6 cSt at 100°C, 105 viscosity index, –27°C pour point, 215°C flash point.

1.5. Tribological Properties

The anti-wear properties of synthesized molecules, commercial molecules and additive packages were analyzed by 4-ball Wear Scar Diameter (ASTM D4172) [16] and 4-ball Welding Points (ASTM D2783) [17] which were examined on a 4-ball tester (SETA-Shell 4-ball test machine) in room temperature, at 1600 rpm rotating speed, at 50 kgf load and steel balls with diameter of 12.7 mm.

1.6. Antioxidant Properties

2,2-diphenyl-picrylhydrazyl (DPPH) free radical scavenging activities of synthesized molecules were determined according to the Ferreira et al. (2009) [18]. An aliquot (1 mL) of appropriately diluted solutions of molecules were mixed with 2.7 mL 6.10^{-5} M DPPH solution. Samples were kept for 1 h at room temperature and then the absorbance was measured at 517 nm. The percentage of absorbance inhibition (I %) at 517 nm was calculated using the equation of: $I\,\% = [(A_{blank} - A_{sample})/A_{blank}] \times 100$.

1.7. Anti-corrosion Performances

All additives and packages tested according to the ASTM B 117 [19] standard (Salt Spray Test) for 120 hours at 35+ 1.1 – 1.7°C with a CW Salt Spray Model SF/100 test machine. Salt solution prepared by dissolving 5 ± 1 parts by mass of sodium chloride in 95 parts of water. The compressed air supply to the nozzle for atomizing the salt solution maintained between 69 and 172 kPa/m^2. The test specimens consist of steel meeting the requirements of ASTM D 609 washed with sample and dried in room temperature before the test.

Copper corrosion test, according to the ASTM D 130 [20] for 3 hours at 100°C, applied to the all additives and packages. The test carried out with a SETA Copper/Silver Corrosion Bath 11400-6 model test machine.

2. RESULTS

Physical properties of synthesized and commercial additives shown on Table 1. It can be seen clearly that synthetic additives yields ranged from 78.6% to 94.25%. All additives have different rate of elements because of their structural natures. Commercial additives and synthetic ones have the similar values of elemental % contents. All additives can soluble in paraffinic base oil.

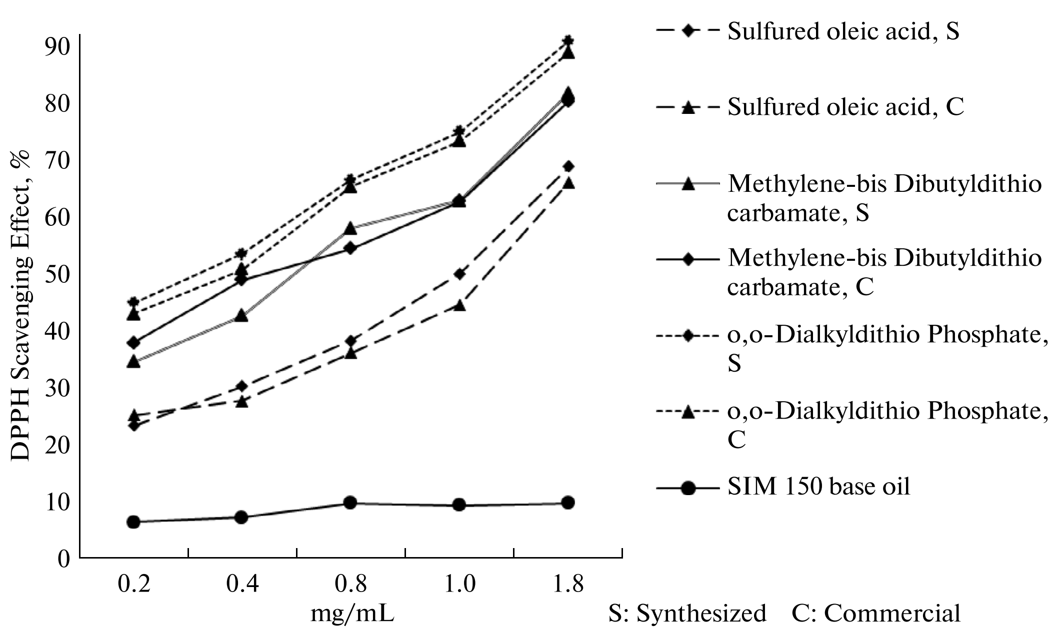
It has been shown on Table 2 content of the created packages. Created SAE 80W-90 grade samples tested to determine tribological properties of the synthesized, commercial additives and created packages. For each sample it has been used two different rate from additive package 1% and 1.8 % to determine 4-ball WSD and 4-ball WP values. According to the results for both synthesized and commercial additives, the best values obtained with Methylene-bis (dibutyldithiocarbamate) 0.59 mm WSD value and 300 kgf WP value for 1.8% addition of synthesized product and 0.54 mm WSD value and 250 kgf WP value for 1.8% addition of commercial product. Second best

Table 3. Friction values from standard 4-ball WSD and 4-ball WP of additives and additives packages in SAE 80W-90 grade lubricant

Additives	4-Ball WSD (mm)		4-Ball Welding Additives (kgf)	
Synthesized	1 wt %	1.8 wt %	1 wt %	1.8 wt %
Methylenebis dibutyldiyhio carbamate	0.67	0.59	250	300
o,o-Dialkyldithio Phosphate	0.78	0.66	200	250
Sülphürised oleic acid	0.82	0.76	<200	<200
Commerical				
Methylenebis dibutyldiyhio carbamate	0.62	0.54	250	250
o,o-Dialkyldithio Phosphate	0.66	0.58	200	250
Sülphürised oleic acid	0.83	0.74	200	200
Packages				
Package 1	0.54	0.48	250	300
Package 2	0.51	0.49	250	300
Package 3	0.68	0.68	200	200
Package 4	0.58	0.51	<200	200
Package 5	0.53	0.53	250	300
Package 6	0.43	0.46	250	250
Package 7	0.86	0.78	<200	<200
Package 8	0.84	0.81	<200	<200
SN 150 base oil (without additives)	0.88		150	

value obtained with synthesized and commercial o,o-Dialkyldithio Phosphate and last one with Sulfured oleic acid.

Results which are obtained with additive packages showed that, best value was obtained with package 6 which created with commercial additives for 1.8 addi-



DPPH scavenging activity (% Inhibition) of synthesized and commercial Additives.

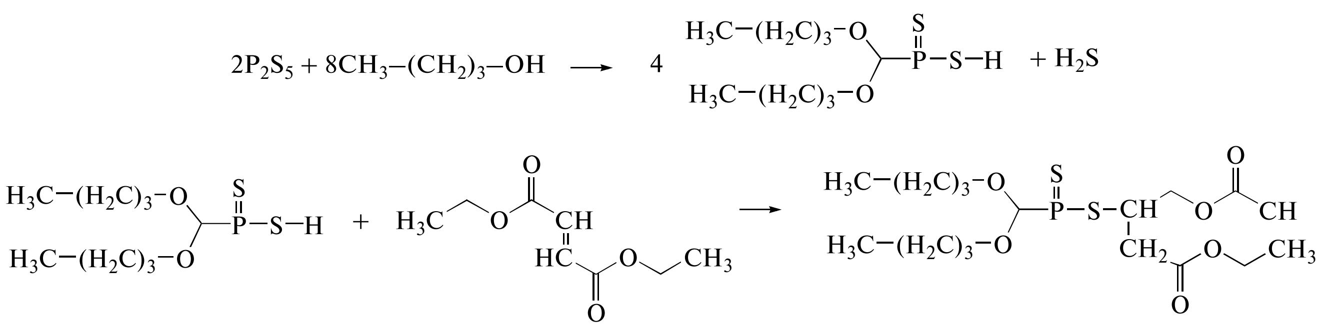
tion of package to the SAE 80W-90 grade product, with 0.43 mm WSD value and package 1, 2, 4, 5, 3, 7, 8 respectively, followed it. The results showed that highest Methylene-bis (dibutyldithiocarbamate) content effected the results mainly and highest o,o-Dialkyldithio Phosphate content secondly. For the Welding results for both packages 1, 2 and 5 obtained 300 kgf Welding value. It is clearly seen on this results Methylene-bis (dibutyldithiocarbamate) has more effect on WP results than the others additives (Table 3).

Antioxidant properties of synthesized and commercial additives were determined in different concentrations. Among both synthesized and commercial additives the highest DPPH Scavenging effect was obtained with 91.09% and 89,05% at 1.8 mg/mL concentration for o,o-Dialkyldithio Phosphate. Methylene-bis (dibutyldithiocarbamate) showed better antioxidant activity than Sulphurised oleic acid for both synthesized and commercial additives (figure).

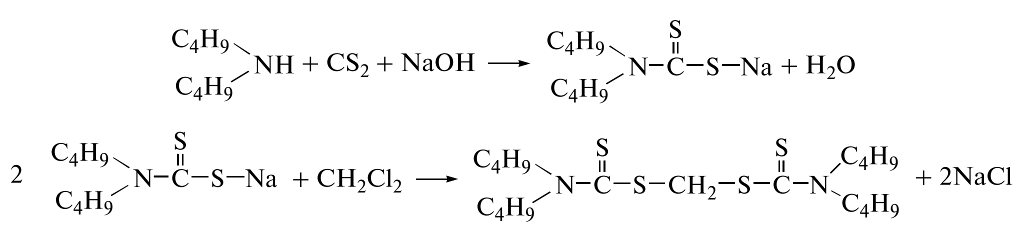
According to the ASTM B 117 test results without Sulfured oleic acid all samples failed the test. Only Sulfured oleic acid passed the test for both synthesized and commercial samples. Sulfur is an important component of the anti-corrosion additive packages for many years in lubricants and these results once again revealed the same truth. On the other hand all samples passed the Copper Corrosion test without Sulfured oleic acid synthesized and commercial samples because of the high active sulfur content.

4. CONCLUSIONS

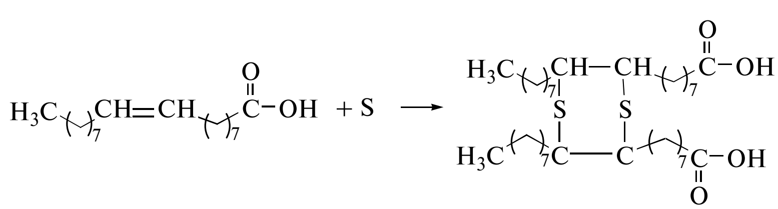
In this study it has been investigated tribological, anti-corrosion performances and antioxidant activities of three synthesized additives and their commercial equivalent additives. According to the results it has been created eight different additive packages which are obtained from a mixture of these three contributions. All packages tested according to the ASTM standards do determine their effects as a gear oil additive. These test results showed that, Methylene-bis (dibutyldithiocarbamate) is the best AW and EP additive alone, o,o-Dialkyldithio Phosphate has the highest antioxidant activity and Sulfured oleic acid is the best anti-corrosion agent for gear lubricants. On the other hand, eight different additive packages because of their different rates of additives contents showed different results. Package six and five showed very good AW and EP properties in the gear lubricant with their high Methylene-bis (Dibutyldithiocarbamate) and o,o-Dialkyldithio Phosphate content.



Schema 1. Synthesize mechanism of O,O-Dibutyldithio Phosphate.



Schema 2. Synthesize mechanism of Methylene-bis(dibutyldithiocarbamate)



Schema 3. Synthesize mechanism of sulfured oleic acid.

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