Scientific Contributions Oil & Gas, Vol. 46. No. 2, August: 37 - 44

SCIENTIFIC CONTRIBUTIONS OIL AND GAS

Testing Center for Oil and Gas

LEMIGAS

Journal Homepage:http://www.journal.lemigas.esdm.go.id

ISSN: 2089-3361, e-ISSN: 2541-0520

Synthesis and Evaluation of Sulphonyl Borate Ester as Grease Additive

Hassan Elsayed Ali[1], Mohammed Emad Azab[2], Nagy Soliman Sakr[1]

[1]MISR Petroleum Company
Cairo Governorate 11522, Egypt

[2]Chemistry department, Faculty of Science, Ain-shams University
Cairo Governorate 11522, Egypt

Corresponding author: hassanelsayedali@yahoo.com

Manuscript received: July 04st, 2023; Revised: July 31st, 2023
Approved: August 04st, 2023; Available online: August 21st, 2023

ABSTRACT - This study includes synthesis and evaluation of an additive to improve the two main properties of lubricating grease which are; “increasing the dropping point and improving the extreme pressure (EP) properties” of Lithium grease without any negative effect on the other characteristics of lubricating grease. Increasing the dropping point and extreme pressure (EP) properties are the most important factors to widen the application of lubricating grease. The additive is synthesized via two-steps condensation reactions of polyethylene glycol 400 and Boric acid followed by reacting the product with Dodecyl-benzene sulfonic acid in the presence of Xylene as azeotropic solvent. The structure of the synthesized Sulphonyl-Borate ester SPB is confirmed by using FT-IR. Evaluation of the synthesized additive is conducted by blending it with laboratory prepared Lithium grease sample in different ratios. Analysis were carried out to study the effect of additive on the lubricating grease properties, especialy grease consistency ASTM D217, dropping point ASTM D2265, oil separation ASTM D6184, and Four–Ball test ASTM D2783. The results showed that synthesized additive increased the dropping point by 65 % and extreme pressure properties by 66 % of the prepared grease grease sample.

Keywords: lubricating grease, extreme pressure, sulphonyl-borate ester, dropping point, friction modifier

© SCOG - 2023

How to cite this article:

Hassan Elsayed Ali, Mohammed Emad Azab, Nagy Soliman Sakr, 2023, Synthesis and Evaluation of Sulphonyl Borate Ester as Grease Additive, Scientific Contributions Oil and Gas, 46 (2) pp., 37-44, DOI.org/10.29017/SCOG.46.2.1553.

INTRODUCTION

Lubricants play an important role in decreasing friction between moving surfaces by forming thin film that pevent direct contact of metals (Wilfried Dresel & Theo Mang 2017). Greases are lubricants which consist of complex system of components mainly base oils and thickeners, and categorized as soap-type or non-soap type. In addition, chemical additives are used in small doses to improve the properties of grease (Spikes. H 2008). The additives are usually organic chemical substance; used in small doses to improve a property to decrease a disadvantage of grease to prevnt oxidation, prevent corrosion, modify friction, decrease wear and extend the application range of the grease like temperature range and operating loads range (He, Z.Y. et al. 2014). Extending the temperature range was achieved by increasing the dropping point which indicates the temperature at which the grease can be used safely and grease components (base oil and thickener) are not separated. The higher the dropping point of grease the higher the application temperature to which grease can be used safely. On the other hand extending the loads range is achieved by additive that decreases friction and eliminates wear at extreme pressure EP applications (Yan, J. et al. 2014). Such additives are referred to as friction modifier, anti-wear and extreme pressure additives.

Greases can be classified according to the used of base oil, thickener, and the applications where they be used as illustrated in Table I. These classification indicate the properties of grease and refer to the main components of grease. Base Oil is the main component of grease, up to 95 % depending on the required grease hardness or fluidity (Ratu Ulfiati 2016). Base oils may be mineral or synthetic and their properties control the performance of grease. Thickener is a component that acquires grease appearance. The hardness or softness of grease depends mainly on the thickener ratio (Sing, G.I.H. & Kuhn E. 1997). Thickener works as a sponge that carries base oil inside it. Thickener type varies according to its origin and preparation process whether saponification process or simply mechanical dispersion. Thickener properties controls the application temperature of grease. NLGI classified grease according to figures called "NLGI grades" as shown in Table 2 Those numbers indicate the consistency of grease which is evaluated by Cone-penetration test ASTM D217 (ASTM Book of Standards 2022).

The complex greases have higher temperature properties as indicated by its higher dropping point

Table 1
Classification of greases

Classification Item		
Base oi	**Thickener type**	**Application**
Mineral oil: -Paraffinic Naphtheni **Synthetic oil**: -PAOs -Ester oil -Silicon oil	**Organic thickener:** **Soap type**: -Simple -Complex **Non-soap type**: -Poly urea -Calcium sulphonate **Inorganic thickener:** -Bentonite (Clay) -Fumed silica	-Bearing grease -Coating grease -High Temp. /EP Grease -Conveyors Chain -Chassis, etc.

compared to simple soap grease (Fish et al. 2014). They are commonly specified for high-temperature industrial applications. Complex greases operating temperature are 100°F (56°C) higher than the simple soap greases. These high temperature properties of complex greases are due to high dropping point which is controlled by thickener type and the usage of complexing agent in thickener preparation. However, there are two difficulties facing complex greases; (i) rare and expensive raw materials and (ii) manufacturing requirements. For these reasons, the challenge is improving the properties of simple grease to achieve the properties of complex grease (Fagan & Gian, L. 2015).

The synthesized Sulphonyl-Borate SPB ester additive is very promising additive because of the

Table 2
Grades of greases according to NLGI

NLGI number	Penetration range
000	445 – 475
00	400 – 430
0	355 – 385
1	310 – 340
2	265 – 295
3	220 – 250
4	175 – 205
5	130 – 160
6	85 – 115

outstanding dropping point improver and friction-reducing properties with high degree of biodegradability. The raw materials are abundant and cheap, and the chemistry of the additive is simple and effective. It contains Sulfur and Boron elements, which were well known in extreme pressure applications. Boric acid esters are attractive because they contain many electronegative oxygen atoms which facilitate and increase the possibility of forming hydrogen-bonding channels formation.

To invistigate the effect of the synthesized additive on the properties of grease, the evaluations were carried out by testing the several parameters i.e Grease Consistency, oil separation, dropping point and four-ball test. Grease Consistency measures the depth (in tenths of a millimeter) to which a standard testing cone penetration of grease sample under prescribed condition. It indicates the hardness or softness of grease. Oil separation shows the percentage of oil separated from the grease under test conditions.

This property means the compatibility of thickener and base oil and the tendency of grease to bleed in storage. Dropping point is the temperature at which the thickener separated from base oil. It represents the high temperature application range of the grease. Four-ball "welding-load" manifest the load at which the balls weld together under the test conditions. This value exhibits the indication to the extreme pressure properties of grease.

The evaluation of the effect of SPB additive is carried out by mixing the additive with the prepared Lithium greasae sample and analyzing the mixture.

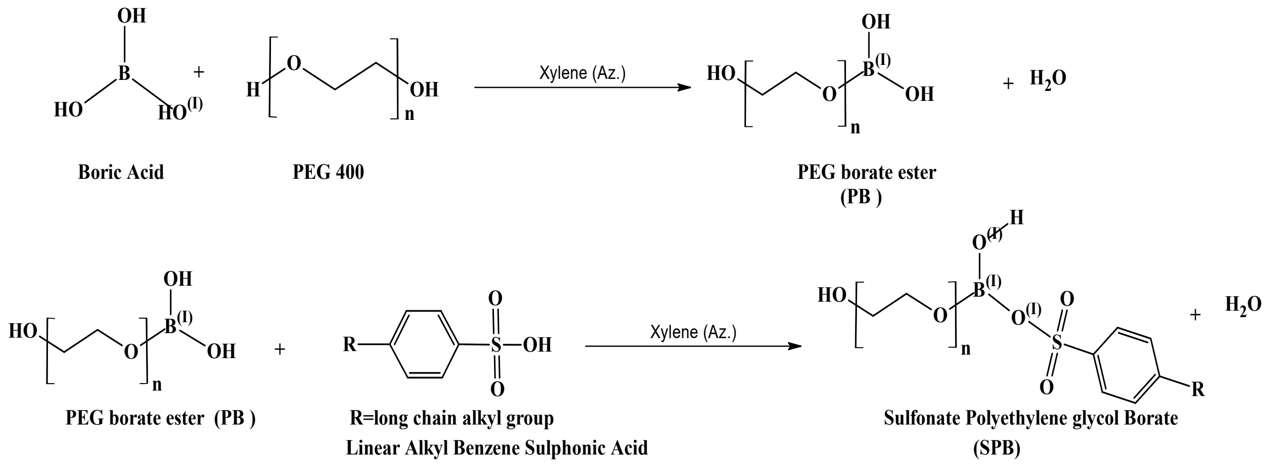
Experimental Procedures

Synthesis of the SPB ester additive

Synthesis of SPB additive is carried out by two consecutive esterification as illustrated in chemical equations in Scheme 1. First by reacting two Stoichiometric amounts of Boric acid and Polyethylene $Glycol_{400}$ in a 250 ml two-necked round bottom flask that connected through a separator water-trap. The thermometer is inserted into the other neck; adding 100 ml Xylene as azeotropic solvent. The reaction temperature is controled at about 180°C with stirring by magnetic stirrer. This reaction is performed as normal condensation-esterification reaction. Table III shows the conditions of reaction; after reaction completed the heating is stopped when the synthesized yellow viscous liquid ester cooled. In the second reaction we add 1 mole of Dodecyl benzene sulfonic acid to the Glycol borate GB then heat with the same system until reaction finish. The reaction product is extracted with petroleum ether, distilled under reduced pressure. The SPB ester was isolated as slight brown paste with yield about 80 %.

Preparation of *Lithium* grease

In order to evaluate the effect of the synthesized SPB ester as grease additive we prepared grease sample. In a glass beaker with mechanical agitator on a hot plate the mineral naphthenic base oil was weighed and heated at 90°C, then the fatty material of 12-hyroxystearic acid and hydrogenated castor oil are added to hot oil, after their melting, suspension of Li-OH in oil was added gradually to the mixture, then temperature is raised gradually the temperature to 200 °C, cool the temperature slowly to 180°C. Start adding the mineral heavy paraffinic base oil gradually, until the grease is completely formed and consistency is adjusted (Milda Fibria et al. 2015). The basic Lithium 12-hydroxy stearate grease sample without the synthesized SPB additive is analyzed and other grease samples are prepared adding the syn-



Scheme 1
Equation of SPB ester synthesis

Table 3
the optimum conditions for SPB ester additive synthesis

Item	Data
Temp., °C	Up to 180
Reaction time, hr	5
Stirring rate/rpm	150
Pressure	atmospheric pressure

thesized SPB ester additive with different doses and test them to evaluate the effectiveness of the additive.

Analysis of Lithium complex grease

Achieving the high temperature properties of complex grease is our target so an imported Lithium complex grease sample "HTG 2" supplied by Delta Logistics Company is analyzed to compare its results with the results of prepared Lithium grease and to evaluate the synthesized SPB ester additive as dropping point elevator additive.

Characterization and evaluation tools

For characterization of the synthesized additive and the functional evaluation we used the following instruments and standard methods; The Infra-Red (Nakamoto, K. 2009) spectra of the synthesized SPB ester were carried out on Brucker$_{USA}$ ALPHA series in "MISR Petroleum Company laboratory -Cairo-Egypt" to detect the esterification process and formation of synthesized additive. Grease Dropping point test ASTM D2265 this standard test was carried out on the prepared Lithium grease sample before and after mixing with the synthesized SPB ester with different doses to evaluate the effect of additive on the grease. Four–Ball test ASTM D2783 this standard test for the evaluation of the anti-wear and friction improving characteristics of lubricant and its ability to lubricate under extreme pressures and high loads. This test was carried out on the prepared Lithium grease sample and with the synthesized SPB ester with different doses to evaluate the effect of additive on the grease. Then the welding load is recorded for each measurement. Oil separation test ASTM D6184 this standard test method measures the amount of oil separated from grease under test conditions, the lower such number is, the better is the grease the more compatible the base oil with thickener. All these test methods are carried out in "MISR Petroleum Company laboratory - Cairo - Egypt";

RESULT AND DISCUSSION

Analysis of synthesized SPB ester additive:

Sulphonyl-borate of Polyethylene glycol ester SPB additive was synthesized by condensation reaction as illustrated in Scheme1 between Boric acid

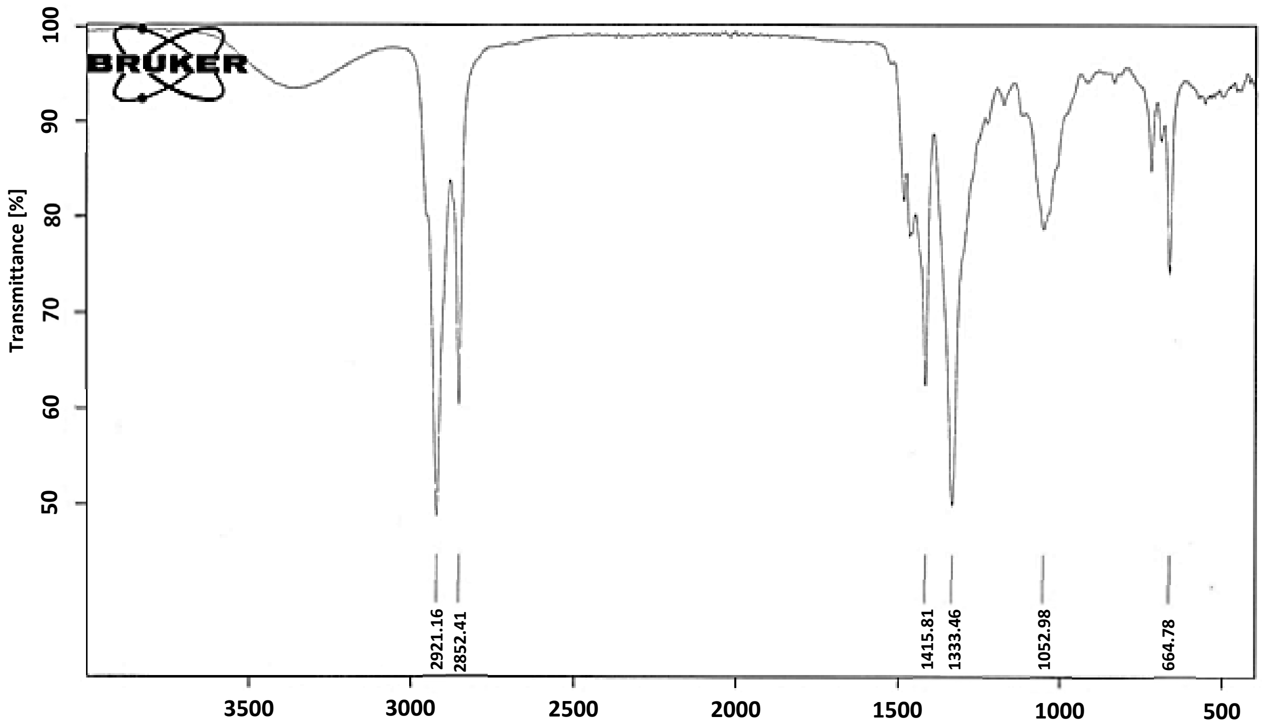


Figure 1
FT-IR Spectrum of GB ester

 | DOI.org/10.29017/SCOG.46.2.1553

and Polyethylene $glycol_{400}$, then reacting the product glycol borate ester with Dodecyl Benzene Sulfonic acid to give sulfonate Polyethylene glycol borate SPB ester additive.

Structure analysis

The FT-IR spectra [18] of Reactions products "Glycol-Borate GB ester of the first reaction and SPB ester of the second reaction" figure 1 and figure 2, Showed that the peak at 3373cm^{-1} in GB and at 3196 cm^{-1} in SPB are the absorption peak of the unreacted hydroxyl groups, the stretching vibration peaks at 2921.16, 2852.41cm^{-1} GB, 2510.64, 2358.81, 2259.35cm^{-1} SPB are the C-H bonds (CH_2 & CH- 2 or 3 bands), the B-O (belongs to B–O bonds of trigonal BO_3 units)asymmetric stretching vibration absorption peak is at 1415.81cm^{-1} GB, 1415.60cm^{-1} SPB, also spectrum peaks of SPB showed two absorption at 1192cm^{-1} corresponding to sulphonyl group and at 882.19cm^{-1} corresponding to S-OR sulphonate ester.

Evaluation of additives application

The effect of the synthesized additives on improvement the dropping point and extreme pressure EP properties of the laboratory prepared Li-12hydroxy stearate based grease sample at different doses Grease-B are illustrated in Table 4 which includes the analysis data of Grease-A the prepared grease

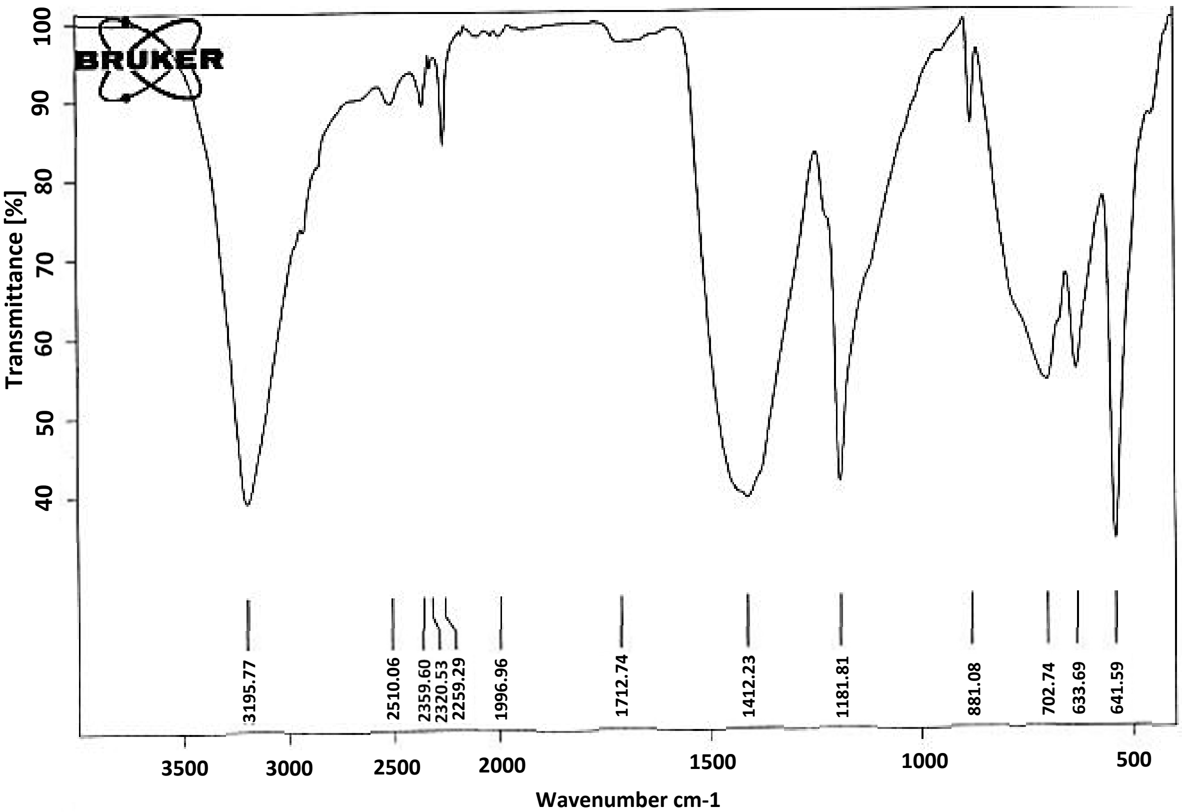


Figure 2
FT-IR Spectrum of SPB ester additive

sample without any additives. The results declare that with increasing the concentration of the additive SPB the dropping point and four ball welding load increases, and the results showed that 3% optimum concentration as shown in Figure 3 Fiure III Effect of SPB ester on Lithium 12- hydroxy stearate grease sample other characteristic functional properties for the title additive ester SPB at 3% concentration such as NLGI grease consistency grade and oil separation were estimated to find out if there's any negative effect of the used additive; and results declares that oil separation of grease is improved that prove the modification of the thickener after adding additive and the more compatibility between thickener and base oil.

We compared the results with imported Lithium complex grease Grease-C as a reference for the target data as shown in Table 5. The synthesized additive has a remarkable effect of raising the dropping point and EP properties of grease containing 12-hydroxystearic acid as thickener. The mechanism for the elevation of dropping point to the level of complex-

Table 4
Evaluation of Synthesized SPB additive doses

Grease-type	**Grease-A**	**Grease-B**			
Description	***Lithium*** **12-hydroxy stearate**	***Lithium*** **12-hydroxy stearate + SPB additive**			
Additive dose, %	0	1	2	3	4
Dropping point, °C	200	225	280	330	330
Four-ball, Welding load, Kg	150	180	210	250	250

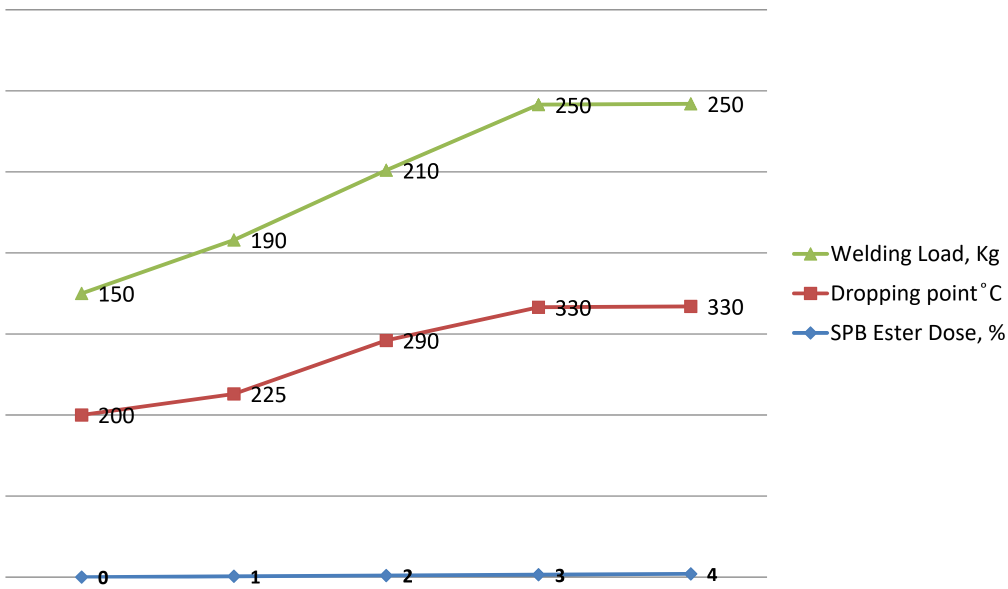


Figure 3
Effect of SPB ester on lithium 12- hydroxy stearate grease sample

soap grease results is presented by Siegart and Henry (Siegart et al. 1964); they explained this increase as result for formation of a coordinate-bonding and stable compound between the Boron atom of the borate ester compound and the hydroxyl group of the 12-hydroxystearic acid soap which lead to modification in the nature of soap acquiring it good thermal properties maintaining its consistency far beyond the melt point of simple soap grease (John J. & Lorimor 2009); (Riemenschneider W. 2019).

$$M\text{-}OOC\text{-}(CH_2)_5\text{-}CH(\ddot{O}H)\text{-}(CH_2)_{10}\text{-}CH_3 + \ddot{B}\text{-}(OR)_3$$

Where M is metal atom may be Lithium (Li^+) or Sodium (Na^{+}) or Calcium (Ca^{+2}) or Aluminum (Al^{+3}) and R is alkyl group from C_4 to C_{16}. And the mechanism of improving the Four-ball welding-load results "Extreme Pressure EP" properties is due to the presence of Sulfur element which is wee known on friction modification and anti-wear additives as it forms a of stable metal sulfide layer that coats the metal and prevent metal-metal contact (Deshmukh Vijay et al. 2016); (Setyo Widodo et al. 2016).

CONCLUSION

- The synthesized sulphonyl-borate ester SPB additive improved the Dropping point of the Lithium 12-hydroxy stearate laboratory prepared grease sample; this will increase the applications temperature range that satisfies and can replace the imported Lithium complex grease.

DOI.org/10.29017/SCOG.46.2.1553

Table 5
Results of Comparative tests.

Grease-type	Grease-A	Grease-B	Grease-C
Description	***Lithium*** **12- hydroxy stearate**	***Lithium*** **12-hydroxy stearate + 3 % SPB**	***Lithium*** **complex grease**
NLGI Grade	**2**	**2**	**2**
Dropping point, ^{o}C	200	330	275
Four-Ball, welding-load, Kg	150	250	200
Oil separation, %	0.5	0.2	0.3

- The synthesized sulphonyl-borate ester SPB additive improved the four ball "welding load" results of the Lithium 12-hydroxy stearate laboratory prepared grease sample; this acquired it extreme pressure EP properties.
- The synthesized sulphonyl-borate ester SPB additive has negative effect on the other properties of the grease sample.
- The synthesized SPB additive is very beneficial as it's easy to manufacture without special requirements, can be used with other 12-hydroxy-stearate grease such as, Sodium and Calcium and it's of low cost comparing with imported complex grease.

ACKNOWLEDGMENT

I would like to express my appreciation to all the staff of Research center - MISR prtoleum company who provided support to this study, and the staff of Ain-shams university for the supervision on this paper.

GLOSSARY OF TERMS

Symbol	Definition
EP	Extreme pressure
GB	Glycol borates
SPB	Sulphoyl Polyethylene glycol Borate
ASTM	American soscity for testing and materials

REFERENCES

ASTM (2022). Book of Standards – section 5.

Deshmukh, Vijay, et. al. (2016). "Evaluation of Boron Esters in Lithium Complex Greases Prepared with Hydrogenated Castor Oil"; NLGI Spokesman, 80(4), September-October, p 42.

Fagan, Gian L. (2015). "Continuous Lithium Complex Grease Manufacturing Process with a Borated Additive"; U.S. Patent No. 9,167,045.

Fish, Gareth, et. al., "Lubricating Grease Thickeners". (2014)**"**How to Navigate Your Way Through the Lithium Crisis"; NLGI 84th Annual Meeting, Olympic Valley, CA, June 12.

He, Z.Y.; Xiong; L.P., Qian, L.; Han, S.; Chen, A.X.; Qiu, J.W. and Fu, X.S. (2014). "Lubrication Science".

John J.; Lorimor. (2009). "An Investigation into the use of Boron Esters to improve the High-Temperature Capability of Lithium 12-Hydroxy-stearate Soap Thickened Grease", Presented at the NLGI 76th Annual Meeting Tucson, Arizona, USA June 13-16.

Kassman Rudolphi, Elisabet Kassfeldt, Marikta Torbacke (2014). “Lubricants Introducttion to properties and performance”.

Milda Fibria, Setyo Widodo, dan Endah Juwita M. (2015). “The Dissolution Ratio LiOH in Water and Their Effect to The Grease characteristics”, Scientific Contributions Oil and Gas **LEMIGAS J.** Vol. 49 No.1 April 2015.

Nakamoto, K. (2009). **;** “Infrared and Raman Spectra of Inorganic and Coordination Compounds”.

Pokhriyal, Vennampalli M., et. al. (2019) “Exploratory Studies on Borate Esters as Dropping Point Enhancers”; NLGI Spokesman, 83(2), May-June.

Ratu Ulfiati. (2016)“formulation of lubricating grease for agricultural equipment application”. Scientific Contributions Oil and Gas **LEMIGAS J.** Vol. 39, Number 1, April 2016.

Riemenschneider, W. (1987). “Organic Esters, in Ullmann’s Encyclopedia of Industrial Chemistry”.

Setyo Widodo, M. Hanifuddin, and Rona Malam Karina. (2016). Tribological properties of mineral base oils with tungsten disulphide (WS2) nanoparticles in boundary lubrication conditions, Scientific Contributions Oil and Gas, LEMIGAS J. Vol. 39, Number 2, August 2016.

Siegart, William R. and Henry, Clemence J., (1964). USP 3,125,526, March 16, (1964).

Sing, G.I.; H.; and Kuhn, E. (1997)“Systematic Effects on the Precision of Penetration Readings a Contribution to the Rheology of Lubricating Greases”, Eurogrease.

Spikes, H. (2008). ” Lubrication Science”.

Wilfried Dresel, Theo Mang. (2017)**“**Lubricant and Lubrication”**.**

Yan, J.; Zeng X.; Heide, E. and Ren, T. (2014)**“**Tribology International”.