Al-Messri and Hussein *Iraqi Journal of Science, 2022, Vol. 63, No. 12, pp: 5131-5138*
DOI: 10.24996/ijs.2022.63.12.4

ISSN: 0067-2904

Synthesis of Over-Based Magnesium Stearate Using Magnesium Oxide Nanoparticles and Evaluation as Multifunction Lubricating Oil Additives

Zainab A. K. Al-Messri*, Saba Zuhair Hussein
Department of Chemistry, College of Science, University of Baghdad, Iraq

Received: 7/9/2022 Accepted: 7/11/2022 Published: 30/12/2022

Abstract

The use of multifunction additives in the lubricant sector has attracted great interest due to their ability to simultaneously improve and add multiple functions. This work describes the preparation and evaluation of over-based magnesium stearate detergent as a multifunction additive by the reaction of stearic acid with carbon dioxide gas in the presence of magnesium oxide nanoparticles and ammonia. The prepared over-based magnesium stearate was evaluated as a multifunction additive through blending it in various concentrations of 1-5 wt/wt% with sixty stock lubricating oils. The American Society for Testing and Materials (ASTM) and the Institute of Petroleum (IP) were used to determine the total base number (TBN), viscosity index (VI), pour point (PP), rust prevention, copper corrosion inhibition, and oxidation stability. The over-based magnesium stearate detergent gave higher values for TBN and detergency efficiency. The blended oil with one percent of the prepared additive showed more rust, oxidation, and corrosion resistance than the standard antioxidant (hindered phenol HP). The VI values of the blended oils showed that the 5 wt/wt% over-based magnesium stearate, which has approximately the same VI values as the blend with 5% of the standard olefin copolymer (OCP), provides better performance.

Keywords: over-based detergent, lubricating oil, TBN, VI, PP, antirust, anticorrosion

تحضير ستيرات المغنيسيوم فوق القاعدية باستخدام جزيئات أوكسيد المغنيسيوم النانوية وتقييمها كمحسنات متعددة الوظائف لزيت التشحيم

زينب عبد الزهره خضير المصري* ، صبا زهير حسين
قسم الكيمياء، كلية العلوم، جامعة بغداد، بغداد، العراق

الخلاصة

اجتذب استخدام المحسنات متعددة الوظائف في قطاع زيوت التشحيم اهتمامًا كبيرًا نظرًا لقدرتها على تحسين وإضافة وظائف متعددة في نفس الوقت. يصف العمل الحالي تحضير وتقييم منظف ستيرات المغنيسيوم فوق القاعدي كمحسن متعدد الوظائف عن طريق تفاعل حامض الستيريك مع غاز ثاني أوكسيد الكربون بوجود أوكسيد المغنيسيوم النانوي والأمونيا. تم تقييم ستيرات المغنيسيوم فوق القاعدية المحضرة كمحسنات متعددة الوظائف عن طريق مزجها بتراكيز مختلفة تتراوح من 1 الى 5 نسبة مئوية وزنية مع زيت

*Email: zainababdulzahra@sc.uobaghdad.edu.iq

التشحيم الأساس. تم استخدام طرائق الجمعية الأمريكية للاختبار والمواد (ASTM) ومعهد البترول (IP) لمعرفة العدد القاعدي الكلي (TBN) و مؤشر اللزوجة (VI) ونقطة الانسكاب (PP) و مضاد الصدأ و تثبيط تآكل النحاس واستقرارية الأكسدة. أعطى منظف ستيرات المغنيسيوم فوق القاعدي قيمًا أعلى لـ TBN وكفاءة التنظيف. كما أظهر الزيت المخلوط مع واحد في المائة من المادة المحسنة المحضرة مقاومة للصدأ والأكسدة والتآكل أكثر من مضادات الأكسدة القياسية (HP). وأظهرت قيم VI للزيوت المخلوطة أن ستيرات المغنيسيوم فوق القاعدية بنسبة وزنية 5٪ (والتي لها نفس قيم VI تقريبًا مثل المزيج مع 5٪ من البوليمر المشترك الأوليفين القياسي (OCP)) تعطي أداءً أفضل.

1. Introduction

Lubricating oils are an important class of products in the refining industry. Lubrication, cooling, cleansing, suspending, and protecting metal surfaces against rust or corrosive damage are all activities that lubricating oils perform. They are made up of several additives and base oils. Additives are important compounds that increase the performance of lubricants by either adding new properties to the base oil (cleaning, anti-wear, and anti-corrosion performance) or increasing existing properties (viscosity index VI, pour point PP, and oxidation resistance are examples) [1]. Since the development of engines in the 1930s, additives have been used as a lot. Since then, both the additive production rate and applications have grown dramatically [2]. Multi-functional additives are substances with multiple functions, i.e., different characteristics. Zinc dialkyl-dithiophosphates (ZnDTPs) are commonly used as multi-functional additives as anti-wear, anti-oxidants, and corrosion inhibitors, depending on the structure of the alkyl group [3-6]. Polyacrylates are used as PP depressants, anti-wear AW agents, and VI improvers [7]. Different alkyl acrylate copolymers with jojoba oil [8], soybean oil [9], or rice bran oil [10] performed the best as PP depressants, VI improvers, and AW agents with good biodegradability [11]. In practice, other examples include over-based calcium sulfonates as detergents and anti-wear additives [12] and sodium dodecyl sulfate magnesium doped ZnO nanoparticles as efficient detergents and anti-wear lubricant additives [13]. Recently, new derivatives of Meldrum's acid [14] and pyranopyrazole [15,16] have been used as rust and corrosion inhibitors. This study examines the synthesis of an over-based magnesium stearate detergent and its performance as a multifunction lubricating oil additive (detergent, VI improver, PP depressant, antirust, anticorrosion, and antioxidant).

2. Experimental part

2.1. Chemicals

Octadecanoic (Stearic) acid (99%), ethanol (95%), and p-xylene (99%) were supplied by BDH, magnesium oxide (nanopowder) (99%) by Nanoshel, ammonium hydroxide (98%) by Fluka AG, and carbon dioxide gas (95%) by National Gas Company.

2.2. Base oil

The base oil was supplied by Midland Refineries Company/AL-Doura Refinery, Baghdad, Iraq. The properties of sixty-stock base lubricating oils are listed in Table 1.

Table 1: Properties of sixty-stock base oil

No.	Specification	Properties of base oil	Standard test method
1	Kinematic viscosity at 40°C	63.61 mm^2/s	ASTM (D445)
2	Kinematic viscosity at 100°C	8.35 mm^2/s	ASTM (D445)
3	Viscosity index (V.I)	100	ASTM (D2270)
4	Specific gravity	0.879	ASTM (D4052)
5	Pour point at °C	-6 °C	ASTM (D97)
6	Flash Point at °C	250	ASTM (D92)
7	Copper corrosion	2a	ASTM (D130)
8	Rust preventing	Fail	ASTM (D665)
9	Color	1.5	ASTM (D1500)

2.3 Preparation of an over-based magnesium stearate additive

Stearic acid (28 g, 0.1 mole) was dissolved in a mixture of ethanol and p-xylene (200 mL, 1:9 v/v) in a reactor consisting of a three-neck round-bottomed flask fitted with a condenser and gas dispersion tube. Magnesium oxide nanoparticles (12 g, 0.3 mole) were then added, and the reaction mixture was stirred for one hour at room temperature before being heated to 70 °C. Ammonium hydroxide (20 mL) was added, and carbon dioxide gas (60 mL/min.) was pumped into the reactor for three hours through a flow meter. Over-based magnesium stearate is produced by filtering the mixture and evaporating the filtrate [17].

2.4 Formulation of oil blends

Blends of the synthesized over-based magnesium stearate additive were prepared by dissolving and mixing various concentrations of 1, 2, 3, 4, and 5 wt/wt% in base oil at about 75 °C for two hours.

2.5 Measurements

The FT-IR spectrum was recorded on a Shimadzu FT-IR-8400S Spectrophotometer using the Cast Film technique. The TBN (mg of KOH/g of oil) was measured according to the standard method of the American Society of Testing and Materials (ASTM D4739), which is based on the potentiometric titration of the basic components in oil with hydrochloric acid to a fixed end-point [18]. Oxidation stability was evaluated according to the testing method of the Institute of Petroleum (IP280). The inhibited oil was blended with two catalysts, Fe and Cu, and a flow rate of 1 liter per hour of oxygen gas was pumped through the oil for seven days at 120 °C. The total oxidation products (TOP) were calculated by measuring the total acidity (T.A) and total sludge (T.S) of the oil [19]. The kinematic viscosity at two different temperatures; 40 and 100 °C, was determined according to ASTM D445, by measuring the time it takes for a volume of oil to flow at a steady rate *via* a capillary in a viscometer. ASTM D2270 was used to determine the oil viscosity index (VI) by comparing its kinematic viscosity to the oil viscosity index 100 and 0. The rust-preventing test (ASTM D-665) was used to measure the anti-rust ability of oil under the risk of water pollution. The test includes the mixing of the testing oil (300 mL) with water (30 mL) and a carbon steel rod being completely immersed in the test fluid at 60 °C for four hours. At the end of the test time, the rod is detached, washed with solvent, and rated for rust. This test is carried out in duplicate, and both test rods must be rust-free to be declared successful [20]. The copper corrosion test

(ASTM-D130) was utilized to determine the oil's anti-corrosion properties. A polished copper stripe is dipped in a 30 mL sample of blended oil for three hours at 100 °C. After the completion of the test, the copper strip is cleaned and tarnished-inspected. The stains on the copper strip were compared using a color scale that ranges from light orange (1a), which indicates slight tarnish, to black (4c), which indicates corrosion [21].

3. Results and discussion

Stearic acid, the most common saturated fatty acid found in animals and plants, is a good choice for lubricating oil detergent preparation because it is environmentally friendly and inexpensive. Al-Messri [17] and Yonglei [22,23] described the preparation of an over-based detergent, but nanoparticles of magnesium oxide replaced the active magnesium oxide. The preparation mechanism is a multiphase reaction consisting of a neutralization reaction (between stearic acid and magnesium oxide) and a carbonation reaction to produce magnesium carbonate ($nMgCO_3$), which is dispersed as sub-100 nm particles. The mechanism is depicted by the following three equations.

$$2CH_3(CH_2)_{16}COOH + MgO \rightarrow [CH_3(CH_2)_{16}COO]_2Mg + H_2O$$

$$MgO + H_2O \rightarrow Mg(OH)_2$$

$$[CH_3(CH_2)_{16}COO]_2Mg + nMg(OH)_2 + nCO_2 \rightarrow [CH_3(CH_2)_{16}COO]_2Mg.nMgCO_3$$

The structure of the synthesized additive was confirmed by FT-IR spectroscopy. The FT-IR spectrum of the prepared compound shows asymmetric stretching bands at 2955 cm^{-1} and 2920 cm^{-1} for the CH_3 and CH_2 groups, respectively, while the symmetric stretching band for the CH_2 group appeared at 2850 cm^{-1}. The scissoring vibration of the methylene groups appeared at 1455 cm^{-1}, while the rocking vibration of the straight chain appeared at 721 cm^{-1} [24]. The strong band at 1572 cm^{-1} refers to the asymmetric stretching of carboxylate ions [25]. The TBN of lubricating oil detergents is the most crucial indicator of quality. It is defined as the amount of KOH that would be equivalent to 1 gram of the material (mg of KOH/g). ASTM D4739 is the standard method for TBN measurement. The alkalinity of a detergent is proportional to the amount of $MgCO_3$ it contains, which indicates the detergent's ability to neutralize an acid. The effects of the molar ratio of stearic acid to magnesium oxide on the prepared additive TBN are shown in Table 2. The molar ratios of 1:3, 1:4, and 1:5, respectively, showed minor differences. In consideration of the cost savings, a 1:3 ratio was chosen as the optimal amount used.

Table 2: The effect of the stearic acid to MgO molar ratio on the TBN of the over-based Mg-stearate detergent

n(Stearic acid):n(MgO)	TBN (mg KOH/g)
1:1	128
1:2	231
1:3	443
1:4	451
1:5	450

According to ASTM D4739, the TBNs of the prepared additive and blended oils with different concentrations of 1-5 wt/wt% were measured. The detergent efficiency of the oil blends was also calculated and listed in Table 3, and Figure 1, which shows that the TBN and efficiency go up as the percentage of the prepared additive in the blended oil goes up. Additionally, the TBN values are higher than when using active magnesium oxide [17].

Table 3 : TBN, VI, and efficiency (%) of the over-based Mg-stearate detergent

Additive (%)	TBN	Detergent efficiency (%)	VI of the additive	Efficiency (%) of the additive	VI of the standard	Efficiency (%) of the standard
0	0.73	0.0	100	0.0	100	0.0
1	2.83	277	112	12	117	17
2	4.58	511	117	17	121	21
3	8.19	992	123	23	127	27
4	12.32	1409	131	31	132	32
5	21.48	2764	135	35	137	37

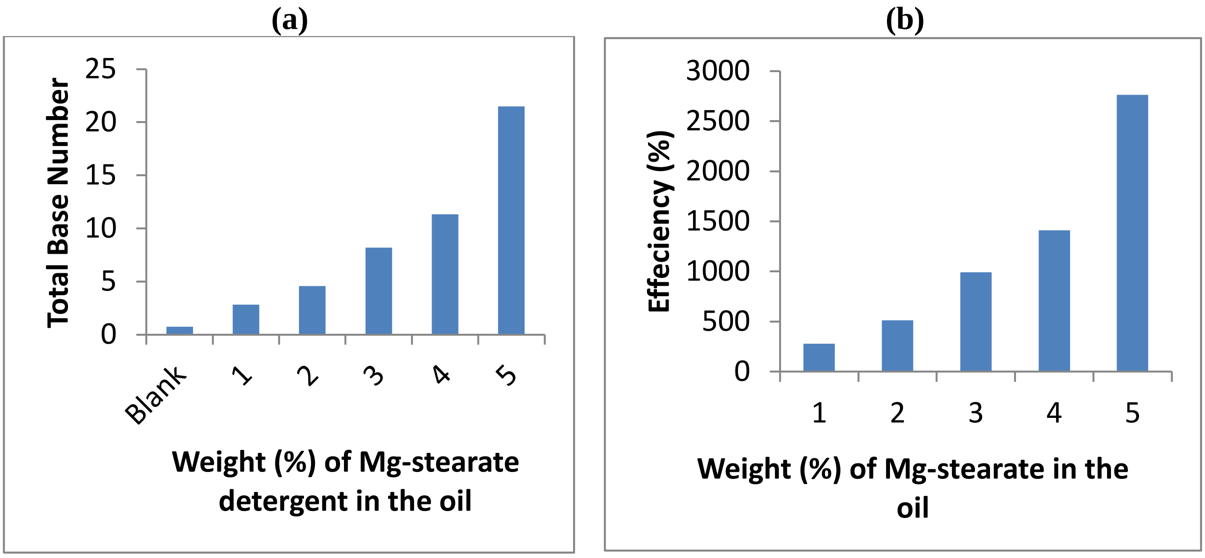

Figure 1: Oil blends with over-based magnesium stearate additive at different weight percentages: Total Base Number **(a)**; Detergent efficiency (%) **(b)**.

The oil blends with different concentrations of over-based magnesium stearate 1-5 wt/wt% were evaluated as VI improvers. The resultant values are listed in Table 3 and Figure 2. The VI values showed that better performance was obtained with the 4 and 5 wt/wt% over-based magnesium stearate. The viscosity index of these blends is about the same as the blends with 4 and 5 wt/wt% of the standard olefin copolymer (OCP). The long-chain *n*-paraffin has the highest viscosity index of oil. A possible explanation may be that as the temperature is elevated, the viscosity of the lubricating oil drops, increasing the micelle size. The decrease in oil viscosity was counterbalanced by the increase in micelle size, which reduced the viscosity change with temperature [26,27]. The efficiency of oil blends was calculated and the results are demonstrated in Figure 3, which shows that the over-based magnesium stearate additive in four and five percentage concentrations gives the highest efficiency.

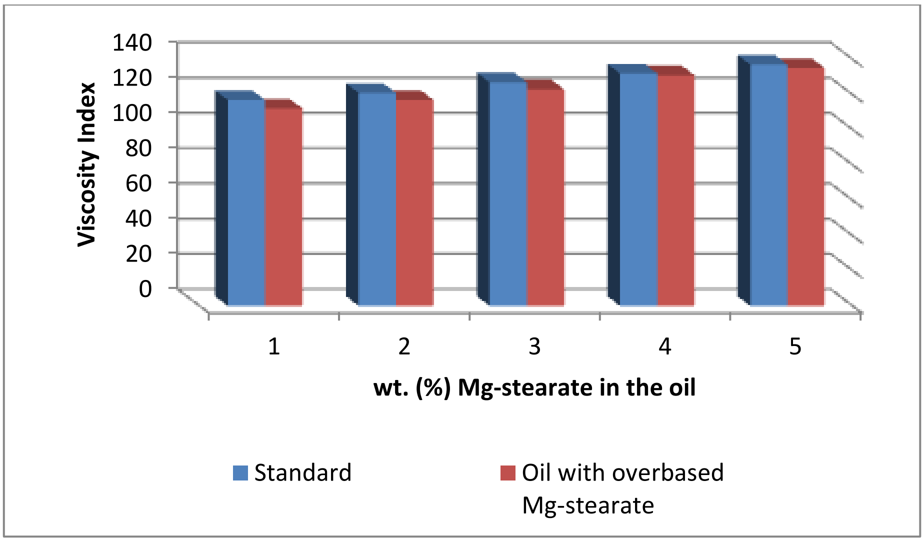

Figure 2 : The viscosity index of blended oil with over-based Mg-stearate and with OCP standard.

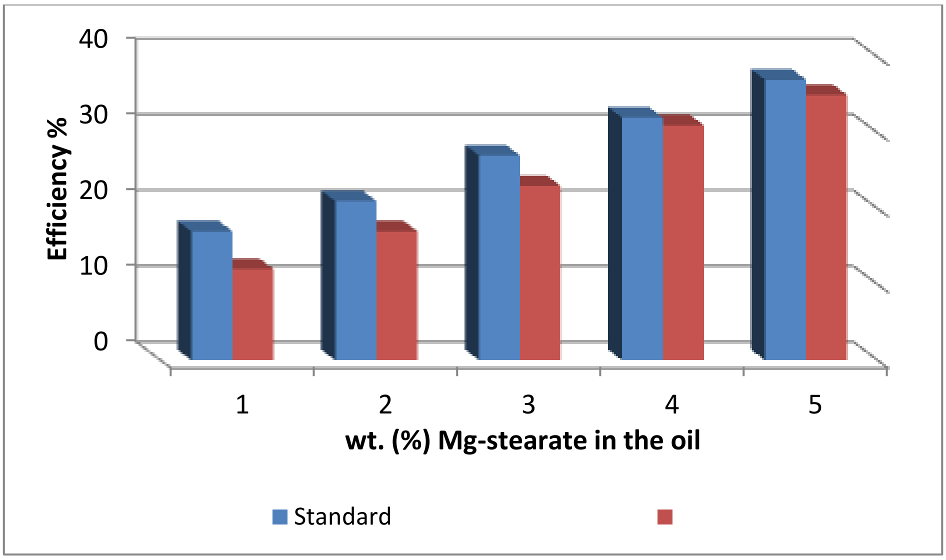

Figure 3: The efficiency of over-based Mg-stearate detergent as VI improvers.

The pour point (PP) of oil blends with over-based magnesium stearate was investigated. All additive concentrations depressed the oil pour point from -6 to -15 ^{o}C [28]. The oil blend containing 1% by weight of over-based magnesium stearate detergent was exposed to extreme oxidation conditions according to the IP280 method, and the results of total acidity (TA), total sludge (TS), and total oxidation products (TOP%) are given in Figure 4. These results show that blending oil with the prepared additive has better oxidation stability than conventional antioxidants. The over-based magnesium stearate detergent can act as an antioxidant because the carbonate in its structure neutralizes acids and the linear structure of the chain forms a protective coating on its surface. It is a kind of metal deactivator antioxidant that acts as a film-forming agent to cover the surface of the metal and prevent the entry of metal ions into lubricating oil.

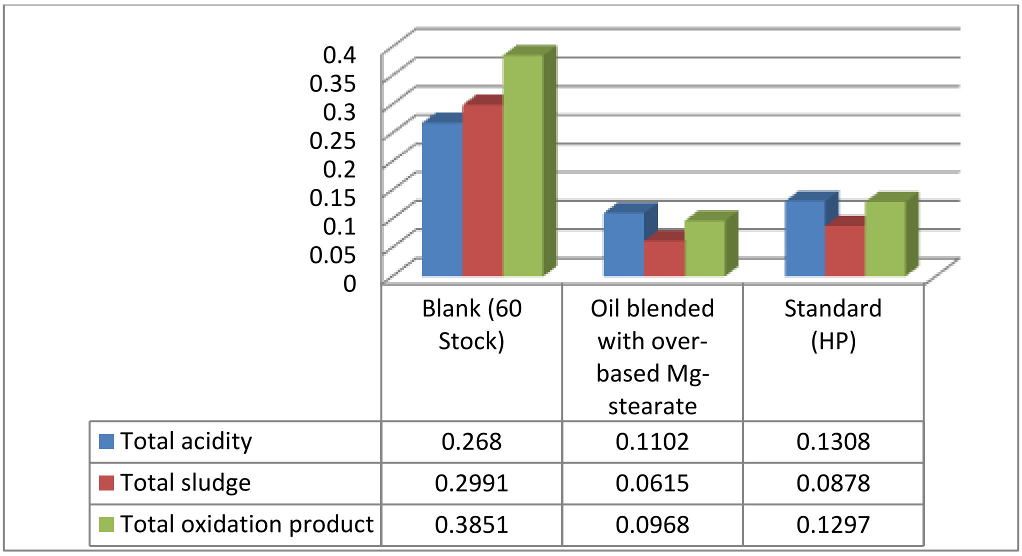

Figure 4: Total acidity, total sludge, and oxidation products of blended oils

The prepared over-based detergent was found to be an effective anti-corrosion additive, causing slight tarnishes (1b) in contrast to moderate tarnishes (2a) of the base oil. It reduces corrosive attacks to metal surfaces by physically limiting the access of corrosive species to the metal surface. Additionally, the blend of the prepared detergent has passed the duplicate rust-preventing test.

4. Conclusions

The over-based magnesium stearate detergent has been made successfully and shown to be multifunctional lubricating oil additive with antioxidant, anti-corrosion, anti-rust, viscosity index improver, and pour point depressant properties.

5. Acknowledgment

The researchers extend their thanks to the Iraqi Midland Refineries Company for providing the base oil and HP and OCP standards.

References

[1] R. Mortier, M. Fox, and S. Orszulik, *Chemistry and Technology of Lubricants, 3rd ed.; Dordrecht Holland: Springer*, 2010.

[2] L. Rudnick, *Lubricant Additives: Chemistry and Applications, 3rd ed.; Boca Raton, USA: CRC Press*, 2017.

[3] A. Barnes, K. Bartle, and V. Thibon, "A review of zinc dialkyl dithiophosphates (ZDDPs): characterization and role in the lubricating oil," *Tribology International*, vol. 34, no.6, pp. 389-395, 2001.

[4] D. Johnson, "The Tribology and Chemistry of Phosphorus Containing Lubricant Additives," *Advances in Tribology*, vol. 8, pp.175-195, 2016.

[5] I. Minami, "Molecular science of lubricant additives," *Applied Sciences*, vol. 7, no. 5, pp. 445, 2017.

[6] U. Abdulfatai, A. Uzairu, G. Shallangwa, and S. Uba, "In Silico Modeling, Prediction, and Designing of Some Anti-wear Lubricant Additives," *J. Bio- Tribo-Corrosion*, vol. 6, no.3, pp. 2198-4239, 2020.

[7] K. Dey, G. Karmakar, M. Upadhyay, and P. Ghosh, "Polyacrylate-magnetite nanocomposite as a potential multifunctional additive for lube oil," *Scientific reports*, vol. 10, pp. 19151, 2020.

[8] A. Nassar, N. Ahmed, and R. Nasser, "Jojoba polymers as lubricating oil additives," *Petroleum & Coal*, vol. 57, pp. 120-129, 2015.

[9] G. Karmakar and P. Ghosh, "Soybean oil as a biocompatible multifunctional additive for lubricating oil," *ACS Sustainable Chemistry & Engineering*, vol. 3, no. 1, pp. 19-25, 2015.
[10] M. Upadhyay, G. Karmakar, S. Kapur, and P. Ghosh, "Multifunctional greener additives for lubricating oil," *Polym. Eng. Sci.*, vol. 58, no. 5, pp. 810-815, 2018.
[11] G. Karmakar, K. Dey, P. Ghosh, B. Sharma, and S. Erhan, "A short review on polymeric biomaterials as additives for lubricants," *Polymers*, vol. 13, no. 8, pp. 1333, 2021.
[12] A. Richardson, M. Evans, L. Wang, M. Ingram, Z. Rowland, G. Llanos, and R. Wood, "The effect of over-based calcium sulfonate detergent additives on white etching crack (WEC) formation in rolling contact fatigue tested 100Cr6 steel," *Tribology International*, vol. 133, pp. 246-262, 2019.
[13] G. Kalyani, R. Rastogi, and D. Kumar, "Synthesis, Characterization, and Tribological Evaluation of SDS-Stabilized Magnesium-Doped Zinc Oxide Nanoparticles as Efficient Antiwear Lubricant Additives," *ACS Sustainable Chem. Eng.*, vol. 4, no.6, pp. 3420-3428, 2016.
[14] H. Hussien and Z. A. K. Al-Messri, "Synthesis, Characterization and Evaluation of 5-alkylidene Meldrum's acid derivatives as Multifunction Lubricating Oil Additives," *Eurasian Chem. Commun.*, vol. 3, no. 9, pp. 598-605, 2021.
[15] A. Salih and Z. A. K. Al-Messri, "Synthesis of pyranopyrazole and pyranopyrimidine derivatives using magnesium oxide nanoparticles and evaluation as corrosion inhibitors for lubricants," *Eurasian Chem. Commun.*, vol. 3, no. 8, pp. 533-541, 2021.
[16] A. Salih and Z. A. K. Al-Messri, "Synthesis, Characterization, and Evaluation of Some Pyranopyrazole Derivatives as Multifunction Additives for Medium Lubricating Oils," *Iraqi Journal of Science*, vol. 63, no. 7, pp. 2827-2838, 2022.
[17] A. Mohammed, M. Ahmad and Z. A. K. Al-Messri, "Synthesis, Characterization, and Evaluation of Overbased Magnesium Fatty Acids Detergent for Medium Lubricating Oil,' *Iraqi Journal of Chemical and Petroleum Engineering*, vol. 14, no. 3, pp. 1-9, 2013.
[18] Annual book of ASTM standards, Section 5; ASTM International: West Conshohocken, USA, 2002.
[19] A. Yano, S. Watanabe, Y. Miyazaki, M. Tsuchiya, and Y. Yamamoto, "Study on Sludge Formation during the Oxidation Process of Turbine Oils," *Tribology Transactions*, vol. 47, pp. 111-122, 2004.
[20] H. Ries, H. Cook, and C. Loane, "Monomolecular Films of Rust-Preventive Additives. Symposium on Steam Turbine Oils," in *Proceedings of the Second Pacific Area National Meeting*, Los Angeles, USA, 1956; ASTM International: West Conshohocken, USA, 1957.
[21] ASTM International, D130, Standard Test Method for Corrosiveness to Copper from Petroleum Products by Copper Strip Test. ASTM International: West Conshohocken, USA.
[22] W. Yonglei, E. Wumanjiang, L. Yuanfeng, and L. Laizao, "Synthesis of Environmentally Friendly Calcium Oleate Detergent," *Ind. Eng. Chem. Res*., vol. 47, no. 22, pp. 8561-8565, 2008.
[23] W. Yonglei and E. Wumanjiang, "Synthesis of Environmentally Friendly Overbased Magnesium Oleate Detergent and High Alkaline Dispersant/Magnesium Oleate Mixed Substrate Detergent," *Ind. Eng. Chem. Res.*, vol. 49, no. 19, pp. 8902-8907, 2010.
[24] R. Silverstein, F. Websters, and D. Kiemle, *Spectrometric identification of organic compounds, 7th ed.; New York, USA: John Wiley and Sons*, 2005.
[25] Y. Lu and J. Miller, "Carboxyl Stretching Vibrations of Spontaneously Adsorbed and LB-Transferred Calcium Carboxylates as Determined by FTIR Internal Reflection Spectroscopy," *J. Colloid Interface Sci*, vol. 256, pp.41-5, 2002.
[26] R. Moulian, J. Le Maître, H. Leroy, R. Rodgers, B. Bouyssiere, C. Afonso, P. Giusti, and C. Barrère-Mangote, "Chemical Characterization Using Different Analytical Techniques to Understand Processes: The Case of the Paraffinic Base Oil Production Line," *Processes*, vol. 8, pp. 1472-1492, 2020.
[27] A. Nassar, "The Behavior of Polymers as Viscosity Index Improvers," *Petrol. Sci. Technol*, vol. 26, no. 5, pp. 514-522, 2008.
[28] L. A. Abdulridha, T. M. Hameed, M. M. Khudhair, and S. K. Ghadeer, "Study the Effect of Friendly Environmental Materials Addition on Viscosity Index and Pour Point of Engine Diesel Lubricating Oil," *Iraqi Journal of Science, Special Issue*, pp. 75-83, 2019.