Lubricant Additive Containing a Novel Nano Hybrid for improving Lithium Greases Extreme Pressure and Anti Wear Properties

Alaei, Mahshad[*+]
Catalyst Technology Development Division, Research Institute of Petroleum Industry, Tehran, I.R. IRAN

Zamen, Amir
Pars Oil Company, Tehran, I.R. IRAN

ABSTRACT: *A novel lubricating grease additive comprised of a new nanohybrid and A suitable base fluid has been proposed in this research. Addition of this nano additive (5 wt%) to the lithium grease improves 1.5 times the extreme pressure property and can reduce lithium grease wear scar diameter better than the other similar nanomaterials reported in the previous research. For preparing nanohybrid, during the hydrothermal synthesis reaction of nano metal borate, a suitable amount of nano transition metal dichalcogenides was added to the reaction vessel under the nitrogen atmosphere and high temperature for 18h. The base fluid comprises of fatty amines, fatty oils, fatty amides, fatty acid esters, and Zinc dialkyl dithiophosphate (ZDDP) with optimum ratios. Nano lubricant additive was prepared by adding the 0.1 wt% nano hybrid to the base fluid at 80 °C with mixing for 30 minutes.*

KEYWORDS: *Lubricating greases; Nano additives; Nanohydrids; Metal dichalcogenides; Fatty oils; Fatty amines.*

INTRODUCTION

Friction and wear are usually caused the energy consumption and material loss in mechanical systems. The application of a suitable lubricant in mechanical devices is necessary for reducing friction and wear. A lubricant is a layer of gas, liquid, or solid that is placed between two surfaces and improves the uniformity of movement of one surface on another and prevents damage to the surfaces. Lubricants have different applications depending on the type, amount of materials, and composition [1-6]. There are different lubrication methods and these methods are usually classified based on the method of film formation between the surfaces. This classification includes hydrostatic, elastohydrodynamic, and boundary Lubrication. In hydrostatic lubrication, the high pressure of the lubricant causes a layer of lubricant to form between the moving surfaces, thereby reducing friction. This type of lubrication is usually considered at the beginning of the movement. Hydrostatic lubrication is commonly used in cases where the relative velocity between surfaces is significant. As an example of

* *To whom correspondence should be addressed.*
+E-mail address: alaiem@ripi.ir
1021-9986/2023/4/1147-1153 7/$/5.07

this type of lubrication, we can mention sliding bearings. In this case, applying high-pressure lubricant is not necessary and only the volume of the lubricant and the speed of movement should be at an acceptable level. Elastohydrodynamic lubrication occurs in cases where the relative motion of the surfaces is of the rolling type with slip. This type of lubrication occurs in rollers, gears, cams, and roller bearings. In boundary lubrication, the thickness of the lubricant layer is very small and does not exceed a few molecules. Usually in this type of lubrication, the appropriate chemicals used in the lubricant react with the metal surface to form a thin protective layer on the metal surface or the lubricant contains lubricant solids that can provide a suitable protective layer between the two surfaces. This protective layer is also called the film. In cases where pressure and wear are discussed in addition to hydrostatic lubrication, boundary lubrication is of particular importance. Based on the type of additives in their structure, greases can be used for a variety of lubrication methods, especially boundary lubrication.

The lithium-based greases are widely used in aerospace, machinery, and other industrial fields because of their excellent properties such as high dropping point, suitable penetration, and effective applicability [7-12].

Since the last century, nanotechnology has been known as an important research field. This technology produced various types of nanoparticles. At least one dimension of nanomaterials is less than 100 nm. This nano size can influence the physiochemical properties of these materials. As a result, nanomaterials can show significantly better properties in comparison to the micro materials in various applications. This subject has been studied by researchers in different applications and the interesting properties of nanomaterials in improving the desired results have been confirmed [13-16]. In recent years, researchers have focused on the application of nanoparticles as additives in the lubricating grease structure in order to improve grease extreme pressure, anti-wear, and environment-friendly properties [17-21]. Nanoparticles can be added to the base fluid and form nano additives. Results show that nano additives have excellent tribological and environment-friendly properties compared with the traditional additives [22,23]. Therefore, nano additives can be widely used in the tribological field. *Zhao et al* [24] demonstrated that the addition of nano calcium borate to the lithium grease can improve anti-friction and extreme pressure properties and decrease the coefficient of friction of the lithium grease. Also, researchers showed that nano TiO_2/CuO and nano CeO_2 can improve the wear resistance of lithium grease and lower the COF [1,25,26].

In this research, a novel lubricating additive was proposed. The addition of this additive (5 wt%) to the lithium grease, improves 1.5 times the extreme pressure property and can reduce lithium grease Wear Scar Diameter (WSD) better than the other similar nano materials reported in the previous researches.

This nano additive is comprised of a base fluid and a new nano hybrid of nano transition metal dichalcogenides and nano metal borate. The base fluid consists of fatty oil, fatty amine, fatty amides, fatty acid esters and Zinc dialkyl dithiophosphate (ZDDP).

EXPERIMENTAL SECTION

Materials

Copper sulfide nano particles, Graphene oxide, Copper oxide nano particles, Tungsten disulfide nano particles were received from Research Institute of Petroleum Industry (RIPI).

$MgCl_2.6H_2O$ (99 %), ethanol, borax, oleic acid, 2-pentanol, diethylene tri amine, 1,4-Butanediol, Lithium hydroxide monohydrate, 12-hydroxystearic acid, Toluene and sulfuric acid were analytical grade from Merck Company. Therefore, these chemical materials were used without further purification.

Methods

Synthesis of Magnesium Borate nanoparticles

Solution 1 (containing borax that was dissolved in ethanol) and solution 2 (containing $MgCl_2.6H_2O$ that was dissolved in distilled water) with 400 mL ethanol are mixed in the steel autoclave at 200 ºC temperature, 15 bar pressure under N_2 gas atmosphere [27]. The heating rate was considered 5°C/min and the reaction was carried out for 18 hours. The product was removed from the autoclave, washed several times with distilled water and alcohol, and dried at 80 °C. Then the sample was annealed at a temperature of about 500 °C for 6 hours under N_2 gas atmosphere.

Synthesis of molybdenum disulfide nanoparticles using hydrothermal method

The reaction performed is somewhat different from the method presented in the reference [28]. Ammonium hepta molybdate was dissolved in 150 mL of distilled water

Table 1: Base fluid Composition

Base Fluid	Composition				
	Fatty acid ester (ester of 2-Pentanol and Oleic acid)	Fatty acid poly amine salt (reaction of diethylene tri amine and Oleic acid)	Fatty Oil (Castor Oil)	Fatty amine (Tallow amine)	ZDDP
wt%	11%	11%	43%	25%	10%

At 60 °C with 5 g of urea. Citric acid (3 g) was added and after complete dissolution of the material, 5.5 g of sodium sulfide was added. The sample was poured into a Teflon container placed in a steel autoclave and closed with a steel lid. The autoclave at 180 °C for 24 hours was placed under hydrothermal reaction conditions. After cooling the cell to reach room temperature, the sample was washed several times with distilled water and ethyl alcohol and dried inside the oven at 80 °C.

Synthesis of MoS_2/Magnesium Borate nanohybrid

The nanohybrid was prepared with the reaction of solution 1 (containing borax that was solved in ethanol) and solution 2 (containing $MgCl_2.6H_2O$ that was solved in distilled water) in steel autoclave at 200ºC temperature, 15 bar pressure under N_2 gas atmosphere. The molar ratio of borax to metal source is 1:2. Solution 1 was added to solution 2 and then 400 mL ethanol was added. In this step, 0.6 g MoS_2 nanoparticles were added to the mixture and the sample was mixed for 30 minutes for good mixing. The final solution was placed into an autoclave, which had a programmed heating rate of 5°C/min. The reaction was carried out for 18 hours. At the end of the process, the product was removed from the autoclave, washed several times with distilled water and alcohol, and dried at 80 °C. Then the product was annealed under inert gas for 6 hours at a temperature about 500 °C.

Preparation of the Nano additive

The novel nano package lubricant additive consists of the base fluid and a new nanohybrid structure. The as-prepared nanohybrid with an amount of about 0.1 wt% is added to the base fluid at 60℃ for 30 minutes and then placed in an ultrasonic probe for a few minutes.

The base fluid consists of several chemical compounds such as fatty oils, fatty amines, fatty acid esters fatty amine salts, and Zinc dithiophosphate (ZDDP) with optimum ratios.

Researchers have reported that fatty acid salts of polyamines, such as diethylenetriamine, provide good tribological properties when used together with fatty acid esters for improving the lubricity of water-based drilling fluids [29]. In this research, besides the mentioned chemical compounds, fatty oils or vegetable oils, fatty amines, and Zinc dithiophosphate (ZDDP) were used for the preparation of the base fluid, and the optimum weight percent of each component was determined (Table 1).

The fatty acid salts of polyamines are prepared by reacting fatty acids such as oleic acid with polyamines such as diethylenetriamine in the presence of xylene or Toluene as reaction solvents. For this purpose, oleic acid (50 mL) and diethylenetriamine (50 mL) with 100 mL xylene were added to 250 mL glass balloon and refluxed at 120 ºC for 12 h in the presence of toluene as the reaction solvent.

Fatty acid esters may be prepared by any conventional reaction such as acid-catalyzed esterification and may be generally prepared using a 1:1 stoichiometric ratio

of the fatty acid to the alcohol. Suitable alcohols, glycols, and polyols with 1 to 8 carbon atoms used to reactions such as 2-Pentanol. These esters may be generally prepared using a 1:1 stoichiometric ratio of the fatty acid to the alcohol functionality. The fatty acids may be the same as or different from the ones used to make the fatty acid salts of polyamines. For the esterification reaction, oleic acid (50 mL) and 2-Pentanol (50 mL) with several droplets of sulfuric acid as catalyst was added to 250 mL glass balloon and refluxed at 140 ºC for 18 h in the presence of toluene as a reaction solvent.

Preparation of the Lithium grease

In a suitable glass flask and under mechanical stirring, mineral oil (225g) and 12-hydroxystearic acid (48 g) were mixed and heated to 90℃. A solution of lithium hydroxide (7g of $LiOH{\cdot}H_2O$ in 70g of H_2O) was added to the mixture. The saponification reaction between lithium hydroxide and 12-hydroxystearic acid took place at 120°C for 5 h. After the mentioned reaction, the mixture was heated to 150°C for 3h to remove water from the grease. After that, 225g of the mineral oil was added. The reaction temperature was raised to 200°C at 16°C/h rate and kept for 10 min at 200°C. Then the sample was cooled down to room temperature [30].

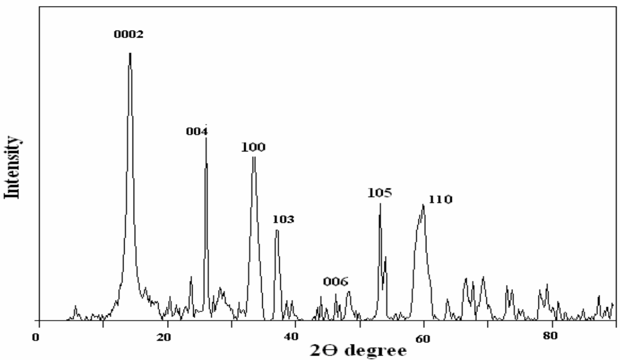

Fig. 1: XRD patterns of MoS_2 nano particles

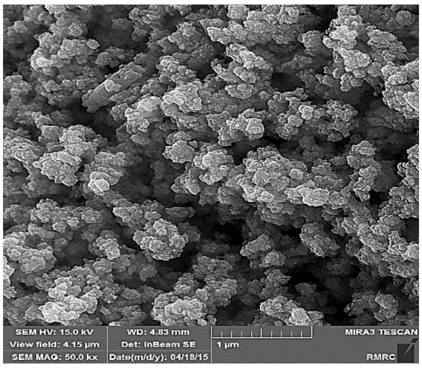

Fig. 2: SEM image of MoS_2 nanoparticles.

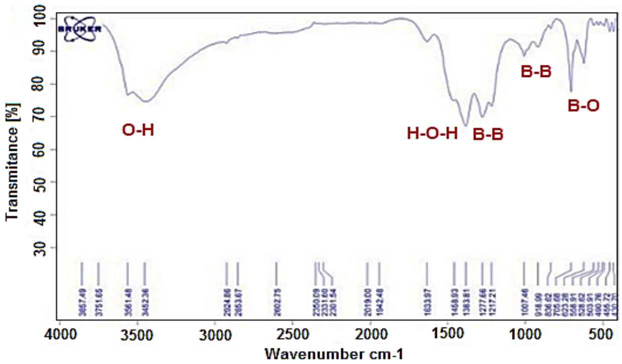

Fig. 3: FT-IR spectrum of Magnesium borate nano particles

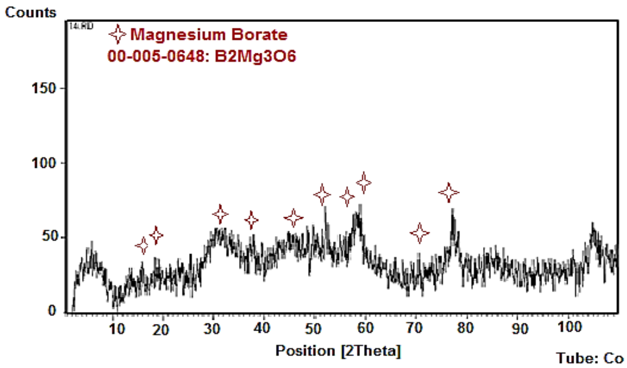

Fig. 4: XRD patterns of Magnesium borate nanoparticles

RESULTS AND DISCUSSIONS

MoS_2 nanoparticles characterization

The as-synthesized MoS_2 nanoparticles are spherical in shape with an average size of about 80 nm. The sample was characterized with X-ray diffraction (XRD) (Fig. 1) and SEM image (Fig. 2).

Fig. 1 illustrates XRD pattern of the as-prepared MoS_2 nanoparticles. The average particle size calculated with the Debye-Scherrer formula is about 80 nm (by using 0002 reflections). All the reflections can be indexed to the hexagonal MoS_2 cell (JCPDS card 37-1492 for MoS_2).

Fig. 2 presents the SEM image of the as-prepared MoS_2 nanoparticles. The sample with a semi-spherical structure was seen in the picture. The SEM image confirms the result that was obtained by using XRD pattern.

Magnesium Borate nanoparticle characterization

Fig. 3 shows FT-IR spectrum of the prepared Magnesium borate nanoparticles. This spectrum shows the formation of Magnesium borate structure according to the scientific literature [27].

The bond between 3250 and 3600 cm^{-1} is related to the stretching vibrations of O-H. The bending vibrations of H-O-H bond that can be seen between 1625 and 1650 cm^{-1} are due to the compound water crystals. The absorption peaks between 1210 and 1500 cm^{-1} are related to the three coordinated boron asymmetrical stretches [31,32]. The peak that exists between the peaks of 800 and 1080 cm^{-1} is related to the four coordinated boron asymmetrical stretches [31,32]. The peaks between 620 and 770 cm^{-1} are related to the in-plane bending vibrations of trihedral (BO_3) groups [32,33]. Therefore, FT-IR spectra of the sample confirmed that the borate compound had formed.

Fig. 4 presents the XRD pattern of the as-prepared Magnesium borate nanoparticles.

As can be seen in Fig. 4, the peaks have good agreement with the related standard card [27].

MoS_2/Magnesium Borate nanohybrid characterization

Fig. 5 shows the SEM image of the as-prepared nanohybrid sample.

As can be seen, the semi-spherical morphology of the nanohybrid creates a suitable layer and acts as a bearing when placed between adjacent moving surfaces. In other words, the as-prepared nanohybrid not only creates a suitable

Table 2: Four Ball Test Results

No.	Sample	Weld Point (kgf)	Pass Point (kgf)	Width of wear scar (mm)
1	Lithium grease	126	100	-
2	Lithium grease + 5%(Base fluid + WS_2/magnesium borate nanohybrid)	315	250	2.1914
3	Lithium grease + 5%(Base fluid + MoS_2/magnesium borate nanohybrid)	315	250	3.1770
4	Lithium grease + 5%(Base fluid + WS_2 nanoparticles)	250	200	1.2740
5	Lithium grease + 5%(Base fluid + MoS_2 nanoparticles)	250	200	2.2771
6	Lithium grease + 5%(Base fluid + nano magnesium borate)	250	200	2.3462
7	Lithium grease + 5%(Base fluid + nano Copper Oxide)	160	100	-

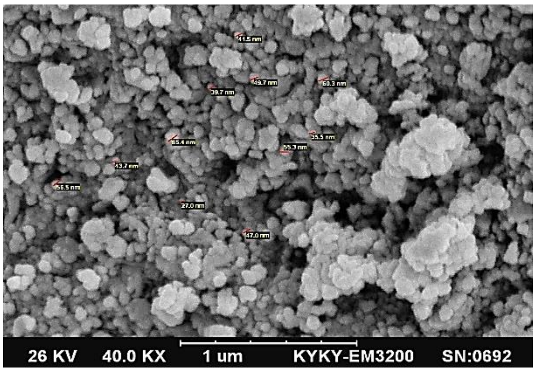

Fig. 5: SEM image of MoS_2/Magnesium borate nano hybrid

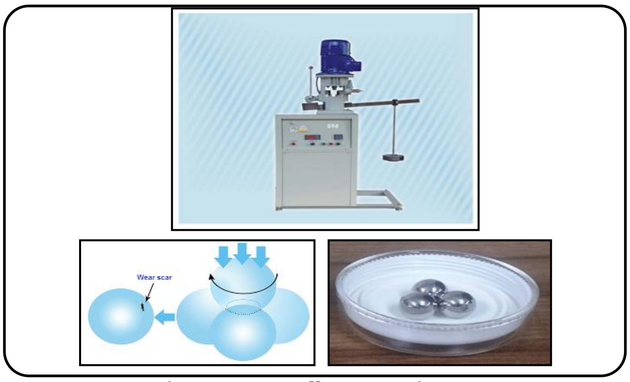

Fig. 6: Four Ball Test Equipment

layer, but also act as a bearing between adjacent moving surfaces and can dramatically reduce friction.

Evaluation of Lubricity and extreme pressure properties

Nano-structured materials (about 0.1 wt%) were mixed with the selected base fluid (Base fluid 1). These samples were used as nano lubricant additives for lubricating greases. Weld point, pass point, and width of wear scar were evaluated with a ball test tester machine (Fig. 6).

The nano package additive may contain suitable nanoparticles such as transition metal (group 6 of the periodic table such as Mo and W) dichalcogenides nanoparticles, nano metal borates, Copper sulfide nanoparticles, Copper oxide nanoparticles, Carbon nanostructures such as Graphene oxide and the as-prepared nanohybrid. In this research, several nano lubricant additives and the related Lithium greases were prepared and tribological properties of the samples were evaluated with a ball test machine (Fig. 6). The results are presented in Table 2.

As can be seen, the best nano package additive has been prepared with Base fluid together MoS_2/Magnesium borate nano hybrid. The tribological properties of the mentioned sample are 1.5 times better than the lithium base sample without this additive. Also, the results show that the as-prepared nano hybrid has a greater ability to reduce lithium grease Wear Scar Diameter (WSD) in comparison to other similar nano-structured materials.

CONCLUSIONS

The lithium-based greases are widely used in aerospace, machinery and other industrial fields because of their excellent properties such as high dropping point, suitable penetration and effective applicability. Nano materials can show significantly better properties with comparison to micro materials in various applications. In recent years, researchers are focused on the application of nanoparticles as additives in the lubricating grease structure in order to improve grease's extreme pressure, and anti-wear properties and decrease the coefficient of friction. Nanoparticles can be added to the base fluid and form nano additives. Results show that nano additives have excellent tribological properties with comparison to the traditional additives. Therefore, nano additives can be widely used in the tribological field.

In this research, a novel nano additive was proposed that is comprised of a base fluid and a new nanohybrid of nano transition metal dichalcogenides and nano metal borate. The base fluid consists of fatty oil, fatty amine, fatty amides, fatty acid esters, and Zinc dialkyl dithiophosphate (ZDDP). Results show that this nano additive improves the extreme pressure property (EP) of the lithium grease 1.5 times in comparison to the base grease and has a greater ability to reduce lithium grease Wear Scar Diameter (WSD) in comparison to similar nano structured materials.

Acknowledgment

The authors are grateful to the Research Institute of Petroleum Industry and Pars Oil Company for the support of this research.

Received: Jun. 22, 2022 ; Accepted: Sep. 26, 2022

References

[1] He Q., Li A., Guo Y., Liu S., Zhang Y., Kong L., Tribological Properties of Nanometer Cerium Oxide as Additives in Lithium Grease, *J. Rare Earths*, **36:** 209 (2018).

[2] Kumar N., Saini V., Bijwe J., Exploration of Talc Nanoparticles to Enhance the Performance of Lithium Grease, Tribo. Int., **162:** 107107 (2021).

[3] Menezes P.L., Nosonovsky M., Kailas S.V., Friction and Wear, *Tribol. Scien. Eng.*, 43 (2013).

[4] Jus A., Kaminski M., Radzikowska W., "Influence of Graphene Nanoflakes Addition on Grease Tribological Properties", *Proc 22th Int. Conf. App.l Phys. Condens Matter. Strbsk e Pleso Slovak*, 22 (2016).

[5] Novak C., Kingman D., Stern K., Zou Q., Gara L., Tribological Properties of Paraffinic Oil with Nanodiamond Particles, *Tribol. Lubr. Technol.*, **7:** 62 (2015).

[6] Spear J.C., Custer J.P., Batteas J.D., Frictional Properties of Graphene on Silica Surfaces with Nanoscale Roughness, *Tribol. Lubr. Technol.*, **6:** 40 (2015).

[7] Carpick R.W., Jackson A., Sawyer W.G., Argibay N., Lee P., Pachon A., Gresham R.W., The Tribology Opportunities Study: Can Tribology Save a Quad? *Tribol. Lubr. Technol.*, **5:** 44 (2016).

[8] He Q., Shen Y., Ren F.Z., Li A.L., Volinsky A.A., Numerical Simulation and Experimental Study of the Air-Cooled Motorized Spindle, *Proc. IMechE. Part C J. Mech. Eng. Sci.*, **6:** 2357 (2017).

[9] Wang L.B., Wang B., Wang X.B., Liu W.M., Tribological Investigation of CaF_2 Nano Crystals as Grease Additives, *Tribol. Int.*, **40:** 1170 (2007).

[10] Mohamed A., Osman T.A., Khattab A., Zaki M., Tribological Behavior of Carbon Nano Tubes as an Additive on Lithium Grease, *J. Tribol.*, **137:** 011801 (2015).

[11] Radulescu A.V., Radulescu I., Rheological Models for Lithium and Calcium Greases, *Mechanics*, **59:** 67 (2016).

[12] Krawiec S., On the Mechanism of the Synergistic Effect of PTFE and Copper in a Lithium Grease Lubricant, *Ind. Lub. Tribol.*, **63:** 171 (2011).

[13] Asadikia A., Agha Mirjalily S.A., Nasirizadeh N., Kargarsharifabad H., Characterization of Thermal and Electrical Properties of Hybrid Nanofluids Prepared with Multi-Walled Carbon Nanotubes and Fe_2O_3 Nanoparticles, *International Communications in Heat and Mass Transfer*, **117:** 104603 (2020).

[14] Asadikia A., Agha Mirjalily S.A., Nasirizadeh N., Kargarsharifabad H., Hybrid Nanofluid based on CuO Nanoparticles and Singlewalled Carbon Nanotubes: Optimization, Thermal, and Electrical Properties, *Int. J. Nano Dimens.*, **11(3):** 277 (2020).

[15] Alaei M., Torkian S., Shams M.H., Rashidi A.M., Simple Method for the Preparation of Fe_3O_4/MWCNT Nanohybrid as Radar Absorbing Material (RAM), *Iran. J. Chem. Chem. Eng. (IJCCE)*, **37(6):** 9-14 (2018).

[16] Alaei M., Rashidi A.M., Mahjoub A., Two Suitable Methods for the Preparation of Inorganic Fullerene-Like (IF) WS_2 Nanoparticles, *Iran. J. Chem. Chem. Eng. (IJCCE)*, **28(2):** 91-98 (2009).

[17] Jiang M.J., Guo X.C., Dong J.X., Chen G.X., Study on the Lithium Complex Grease, *Lubr. Eng.*, **5:** 009 (2000).

[18] Liu H.T., Ji H.M., Hong H.P., Younes H., Tribological Properties of Carbon Nano Tube Grease, *Ind. Lubr. Tribol.*, **66:** 579 (2014).

[19] Nan F., Xu Y., Xu B.S., Gao F., Wu Y.X., Li Z.G., Effect of Cu Nano Particles on the Tribological Performance of Attapulgite base Grease, *Tribol. Trans.*, **58:** 1031 (2015).

[20] Ji X.B., Chen Y.X., Zhao G.Q., Wang X., Liu W.M., Tribological Properties of $CaCO_3$ Nano Particles as an Additive in Lithium Grease, *Tribol. Lett.*, **41:** 113 (2011).

[21] Chang L., Zhang Z., Breidt C., Friedrich K., Tribological Properties of Epoxy Nano Composites: I. Enhancement of the Wear Resistance by Nano-TiO_2 Particles, *Wear*, **25:** 141 (2005).

[22] He Q., Li A.L., Shen Y., Design and Application on Experimental Platform for High Speed Bearing with Grease Lubrication, *Adv. Mech. Eng.*, **7:** 1 (2015).

[23] Salehi Z., Zinatloo-Ajabshir S., Salavati-Niasari M., Dysprosium Cerate Nano Structures: Facile Synthesis, Characterization, Optical and Photocatalytic Properties, *J. Rare Earths*, **35:** 805 (2017).

[24] Zhao G.Q., Zhao Q., Li M.W.,Wang X.B., Liu W.M., Tribological Properties of Nano Calcium Borate as Lithium Grease Additive, *Lubr. Sci.*, **26:** 43 (2014).

[25] Chang H., Lan C.W., Chen C.H., Kao M.I., Guo J.B., Anti-Wear and Friction Properties of Nano Particles as Additives in the Lithium Greases, *Int. J. Precis. Eng. Manuf.*, **15:** 2059 (2014).

[26] Luo T., Wein X., Zhao H., Cai G., Zheng X., Tribology Properties of Al_2O_3/TiO_2 Nanocomposites as Lubricant Additives, *Ceramics Inter*., **40:** 10103 (2014).

[27] Saffari H.R.M., Soltani R., Alaei M., Soleymani M., Tribological Properties of Water-based Drilling Fluids with Borate Nanoparticles as Lubricant Additives, *Journal of Petroleum Science and Engineering*, **171:** 253 (2018).

[28] Nagaraju G., Tharamani C.N., Chandrappa G.T., Livage J., Hydrothermal synthesis of MoS_2 nanofiber bundles via acidification of ammonium heptamolybdate tetrahydrate, *Nanoscale Res. Lett.*, **2:** 461 (2007).

[29] Xiang T., Amin R., Lumpur K., Water-based Mud Lubricant using Fatty Acid Polyamine Salts and Fatty Acid Esters, *US Patent* 9340722 B2, (2016).

[30] Zhang J., Wang A., Yin H., Preparation of Graphite Nanosheets in Different Solvents by Sand Milling and their Enhancement on Tribological Properties of Lithium-based Grease, *Chinese Journal of Chemical Engineering*, **28:** 1177 (2020).

[31] Jun L., Shupping X., Shiyang G., FT-IR and Raman Spectroscopic Study of Hydrated Borates, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, **51:** 519 (1995).

[32] Goa Y.H., Liu Z.H., Wang X.L., Hydrothermal Synthesis and Thermodynamic Properties of $2ZnO.3B_2O_3.3H_2O$, *Chemical Thermodynamic*, **41:** 775 (2009).

[33] Zhao C., Chen Y.K., Jiao Y., Loya A., Ren G.G., The Preparation and Tribological Properties of Surface Modified Zinc Borate Ultra Fine Powder as a Lubricant Additive in Liquid Paraffin, *Tribology International*, **70:** 155 (2014).