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Research Paper

Synthesis and Tribological Properties of Oleic Acid-Modified Magnesium-Aluminum Nanoparticles as Lubricating in the SN500HVI Paraffinic Base Oil

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ABSTRACT

The study focused on the performance enhancement of SN500HVI base oil by incorporation of the oleic acid modified $MgAl_2O_4$ nanoparticles synthesized using combined of hydrothermal and sol-gel processes. The properties of the nanoparticles were studied by Fourier transform infrared (FTIR) spectroscopy, field emission scanning electron microscope (FESEM), and X-ray diffraction spectroscopy (XRD) techniques. Nano particles with different contents were added into the oil, and a Pin-on-Disk apparatus was employed to investigate tribological behaviors of the oil. Subsequently, wear and friction tests were performed. The addition of nanoparticles to the oil improved its tribological properties, and decreased the friction coefficient by 15%, 59%, and 27%, using 0.25, 0.5, and 1 wt.% of nano particle content, respectively, in comparison with unloaded oil. The mean friction coefficients improved with increasing the nanoparticles in the base oil, and this value decreased to 0.071 at the optimal concentration of 0.5 wt.%. The results showed that the synthesized nanoparticles can act as an effective additive for improving the quality of lubricating oil due to their high flexibility, high malleability, and low hardness.

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1. Introduction

In general, nanoparticle-containing fluids (e.g., base oils), called as nanofluids, are novel oil alternatives with a proven efficiency [1]. Concerning nanoparticles' unique nature, the similarity of their physical and chemical properties to the base fluids can lead to the establishment of suspensions with high stability [2]. Furthermore, since nanoscales materials are lightweight, gravity-induced sedimentation occurs at slower rates than particles with milli and micro in size [3]. The advantage of nanoparticles as lubricating additives over other organic additives may be due to their tiny size and faster entry into the contact area between surfaces [4-8].

Numerous researchers investigated the effects of nanoparticles in improving the friction and wear properties of different oils. In the meantime, some studies were performed on magnesium oxides, aluminum oxides. Song et al. investigated oleic acid-modified surface $ZnAl_2O_4$ spinel nanoparticles, and their results indicated that applying this compound improved the tribological properties of the lubricant [9]. Nabhan et al. also examined the tribological and rheological properties of Al_2O_3 nanoparticles as lithium grease additives and showed that the addition of Al_2O_3 nanoparticles reduced COF by approximately 57.9% [10]. The study performed by Chen and Zhu on copper nanotubes in liquid paraffin (L.P) lubricant confirmed that employed oleic acid to stabilize the nanoparticle had notable influences in improving its tribological properties [11]. Chang et al. synthesized and introduced a new compound, called MSH (magnesium silicon hydroxide), and stated that this compound played a critical role in reducing sliding friction coefficient [12]. Wang et al. investigated the tribological properties of liquid-phase exfoliated graphene as an additive in SAE 10W-30 lubricating oil and illustrated the effectiveness of tribological properties generated for concentrations below 0.1 wt.% [13]. Guo et al. also examined different effects of Cu nanoparticles in the presence of additives used in ester base oils and their tribological properties [14]. The results reported by the latter researchers revealed that despite the reduction of some additive properties, Cu nanoparticles and most additives have synergy on oil tribological performance. It is generally observed that the positive effects of using nanoparticles on oils' properties and lubricants' tribological behaviors are confirmed by all the above studies.

There were numerous methods for synthesizing $MgAl_2O_4$ spinel (MAS) nanoparticles [15-19]. In this study, a combination of sol-gel and hydrothermal processes (sol-gel-hydrothermal process) was selected to control the size, shape distribution, and degree of MAS nanoparticle crystallinity. Also, the effects of MAS nanoparticles were studied on improving the friction and wear properties of base oil and its stability on the LAB scale. It is noteworthy that some criteria, such as low specific gravity and a high strength-to-weight ratio, were considered in the selection of these nanoparticles [20]. Magnesium metal is one of the lightest metal elements in the engineering industry that has anti-friction effects. Hence, it can play positive roles in increasing stability and improving dispersion into base oils [21]. Other causes of its choosing for lubrication applications were involved stability at high temperatures and oxidation processes, good hardness/flexibility degree, acid-cleaning properties (especially under oils' high functions), high environmental compatibility, high thermal coefficients [22,23] to improve the heat transfer property of the nanofluid oils, engine cooling property, and its relative bright color (dark nanoparticles change the color of lubricant and have unfavorable marketability). Numerous studies have been conducted on the effects of different nanoparticles in the fabrication of nanofluids without considering the suitable base oil as another component of nanofluid. Therefore, carefully selecting the base oils as the main component of a nanofluid was considered the innovation of this research by examining different paraffinic base oils of SN600HVI, SN500, SN600LVI, and SN500HVI. In choosing oil type, we tried to use base oils with fewer impurities, including sulfur (sulfur content of group 1 oils is more than 300 ppm), toward improving MAS nanoparticles' dispersion and inhibit sediment formation induced by mixing impurities with MAS nanoparticles. It should be emphasized that the rheological testing was practiced to select the base oil with fewer impurities and Shear Stress to prevent their combinations with MAS nanoparticles and decrease the deposition process [24].

2. Materials and methods

2.1. Materials

The base oil used in the present study was SN500HVI (High Viscosity Index) paraffinic base oil, which is one of the most practiced and widely used base oils produced by Sepahan Oil company, Iran. This base oil is obtained from the Dewaxing unit following solvent extraction and is classified in group No. 1. Low volatility and oxidation stability are the advantages of this base oil. Some of the characteristics of this product are presented in Table 1.

Table 1. Characteristics of SN500HVI base oil

Test	Result	ASTM
Kinematic viscosity@100°C(c.St)	10.5-11.2	D-7042
KinematicViscosity@ 40°C(c.St)	85-102	D-7042
Viscosity Index (min)	90	D-2270
Density@ 15°C	0.885-0.896	D-4052
Pour point (°C) (max)	-6	D-5950
Flash point (°C) (min)	245	D-92
Color (max)	1	D-1500
Demulsibility@ 82°C	40/37β(15min)	D-1401
Noack volatility(wt%)(max)	4	D-5800
Foam	10/0,30/0,10/0	D-892

Also, all materials used for synthesis and surface modification were provided by the Merck company, Germany.

2.2. Methods

2.2.1. Synthesis of MAS nanoparticles

In general, magnesium chloride solution and sodium hydroxide are required for the synthesis of MAS. Accordingly, 100 ml of magnesium chloride solution was first dissolved in 400 ml of sodium hydroxide solution to increase the pH (pH= 9) and to inform magnesium hydroxide precipitates. Then, aluminum nitrate solution (equal to 100 ml) was added to the above solution. After complete dissolution of the above substances, 5g urea (99.5%) was added to this solution and stirred perfectly. The resulting solution was transferred to a sand bath and heated at 150 °C for seven hours and the sand bath was then cooled to room temperature. In the next step, the obtained milky solution was centrifuged, and the white sediments were washed in two stages with distilled water. Then, in order to dry the resulting product, it was heated at 65 °C for 7 hours. After hydrothermal treatment, gel was formed. In order to achieve MAS nanoparticles with a suitable crystal structure, secondary heat treatment was required. For this purpose, the prepared gel was placed in a furnace (at room temperature) and then increased to a temperature of 1000 °C at a rate of 6 ° C per min. The product was placed at this temperature for 5 hours to calcination, and then cooled naturally to obtain MAS less than 50 nm in size. Eventually, FESM, FTIR, and XRD techniques were employed to confirm the performed processes and the synthesized nanoparticles.

2.2.2. Surface modification of MAS nanoparticle

In the present study, the surface of MAS nanoparticles was modified using oleic acid to enhance its stability and dispersion into the base oil. Accordingly, 2 g of the examined nanoparticles were first dispersed into 80 g of n-heptane, and 10 g of oleic acid was suddenly added to the obtained compound and stirred magnetically for 30 minutes. The mentioned step was repeated with 20 g of oleic acid, and samples were then stirred in ultrasonic at 80 ° C, and a frequency of 44 kHz for 60 min. At this temperature, heptane evaporated, and oleic acid was deposited on the nanoparticles' surfaces. Next, the solution containing surface-modified nanoparticles was centrifuged at 4000 rpm for 60 min. Again, samples were washed several times with 1 mL heptane and centrifuged. Next, the heptane collected on the falcons' surface was excluded, and finally, the mixture was placed in an oven at 80 ° C for 120 min to dry the samples, evaporate the heptane, and remove the excess oleic acid. Eventually, two modified surface nanoparticles with 10 and 20 g of oleic acid were prepared (named S1 and S2 samples), respectively. Then FESEM test was performed on two samples of S1 and S2, and the product with more suitable morphological characteristics was determined and selected for other tests.

2.2.3. Preparing SN500 HVI nano fluid using surface modified nanoparticles of $MgAl_2O_4$

In this study, the different amounts of the nanoparticles with 0.25 %wt., 0.5 %wt., 1 %wt., and 5 %wt. were first added to the SN500HVI base oil. In this regard, ultrasonic and magnetic stirrer devices were also applied to achieve product suspension stability. Accordingly, the samples were first stirred with a Jet-Mixer (at 1000 rpm for 30 min) to obtain a good dispersion of the nanoparticles in the base oil. The nano-lubricants were then stirred with an ultrasonic vibrator for 120 min to ensure uniform dispersion and good stability of the prepared nanofluid.

2.2.4. Characterization tests of synthesized nanoparticles

FESEM (MIRA 3 model, manufactured by TE-SCAN Co., The Czech Republic) equipped with energy-dispersive X-ray spectroscopy (EDX) was employed to observe the morphology, and the size of the prepared MAS nanoparticles. Also, XRD (Explorer model, manufactured by GNR Co., Italy) was used to perform tests related to structural characterization and identify crystallographic forms of the synthesized nanoparticles. All XRD technique peaks were evaluated according to the JCPDS standard card (00721-0307), and the approximate nanoparticle sizes of the examined samples were obtained using the Scherrer equation.

$$D = \frac{0.9\,\lambda}{\mathrm{B}\cos\theta} \quad (1)$$

in which, D, B, θ, and λ represent mean particle size, line broadening at half the maximum intensity for nanoparticle crystal plates, Bragg angle, and X-ray wavelength parameters, respectively.

In addition, the functional groups of the prepared nanoparticles were characterized by a Fourier transform infrared spectrometer (model UV1800, manufactured by Shimadzu Co., Japan), using the potassium bromide (KBr) pellet method to prepare the sesame sample. The zeta potential technique and the ZS90 nanopotentimeter (manufactured by Malvern, UK) were used to assess the stability of MAS nanoparticles.

2.2.5. Rheological test

The MCR301 viscometer (manufactured by Brookfield Co., USA) equipped with integrated temperature control with low to high shear rates was used for this test. The dynamic viscosity of different base oils was measured under applied shear stress ranging from 0.01 Pa to 1000 Pa at the room temperature of 28.5 °C, to select appropriate base oil for tribological test.

2.2.6. Tribological test

Pin-on-disk wear testing (Model 03 TSN-WTC, manufactured by Tajhiz Sanat Nasr Co., Iran), which is performed to sliding contact measuring, was used to perform the above test. It is noteworthy that ST37 and 52100 plates of steel (with harnesses of 250HV and 64 HRC) were respectively employed to prepare the applied discs and pins in this study. The further data about pin and disk studied in the present study are detailed in Table 2. The disks were prepared with a diameter of 40 mm, rotated at a constant speed of 600 rpm with a load of 10 N and 30N.

Table 2. Specifications of the examined discs and pins

	material	Diameter	hardness
Pin specifications	Steel 52100	6mm	HRC 64
Disk specifications	Steel ST37	40mm	HV 250

3. Results and discussion

3.1. Stability of modified nanoparticles and mechanisms of surface modification

In general, nanoparticles larger than 1-2 mm in size are considered large particles that agglomerate in oil due to their significant chemical activity and strong gravitational forces [2]. However, the nanoparticle sizes synthesized in the present study are about 50 nm, but also, they must be well dispersed in the solvent; otherwise, these synthesized particles may adhere together after a short time, leading to increase mass, reduced surface tension, and increased sediment. Phan and Haes reported that nanoparticles' stability was changed under different aqueous conditions, and oxide nanoparticles may have more stability than the other materials [25]. However, limited evidence was observed regarding the non-oxide nanoparticles' stability over 30 days [24]. The non-modified MAS nanoparticles cannot be dispersed in non-polar organic solvents. According to the evidence, because oxides have a large hydroxyl group on their surface, it is possible to modify their surface with oleic acid [6,26]. Surface-modified MAS nanoparticles using oleic acid can be evenly distributed in paraffin oil. Fig. 1 displays the oil containing oleic acid-modified surface spinel nanoparticles after 30 days. The stability/ instability and the deposition rate of the synthesized nanoparticles in the present study evaluated by investigating the retention time, and results showed that agglomerates and flakes not formed for nanoparticles smaller than 1 wt. %. So that, the maximum value of 1 wt.% was selected to incorporate nano particles into the base oil, and the nano particles loading into the oil was varied from 0.1 wt. %. to 1 wt. %. In conclusion, the results showed relatively good dispersion and stability of nanoparticles dispersed into the base oil.

Fig 1. The oil containing different weight percentages of nanoparticles after 30 days (0.25, 0.5, 1, and 5% respectively from left to right).

A quantitative examination of the colloidal stability of nanoparticles was also carried out using a zeta potential test that was compatible with the precipitation method. The absolute potential value of nanoparticles without surface modification was increased from 17.5 mV to 28.2 mV after surface modification. An increase in the absolute value of the zeta potential implies that the produced colloid is more stable. Oleic acid, a monounsaturated fatty acid, has an active group and about 18 carbon atoms in the alkyl chain length [27,28] and was employed for the modification of nanoparticle in this study. The interaction between nanoparticles with different modifying agents can create several modification mechanisms. Metal oxides are known to have reactive hydroxyl groups present on their surface [29]. In this regard, carboxylic acid groups of the oleic acid can be linked with nanoparticles' surface hydroxyl groups by hydrogen bonding and then adsorbed on nanoparticles' surfaces [30]. It is worth noting that the long-chain in oleic acid causes the formation of nanostructures in the form of micelles in the oil (Fig. 2). On the other hand, nonpolar long-chains of oleic acid cover the surface of MAS particles and create an electrostatic repulsion force between MAS particles that prevents them from accumulating [31]. Organic acid-modified samples can easily distribute in different organic solvents, such as toluene, benzene, and paraffinic oils. Also, since oleic acid plays a critical role in reducing friction, its consumption should be careful that during the process of surface modification, the excess oleic acid does not remain on the surface of the nanoparticles and does not lead to create the error in the result. The heptane was also employed to increase the surface tension of nanoparticles' surface and improve oleic acid absorption on the nanoparticles. In other words, heptane, as a wetting agent, facilitates and accelerates the loading of carboxylic functional groups in oleic acid on nanoparticles' surface [29].

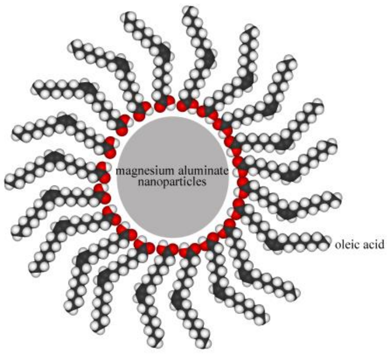
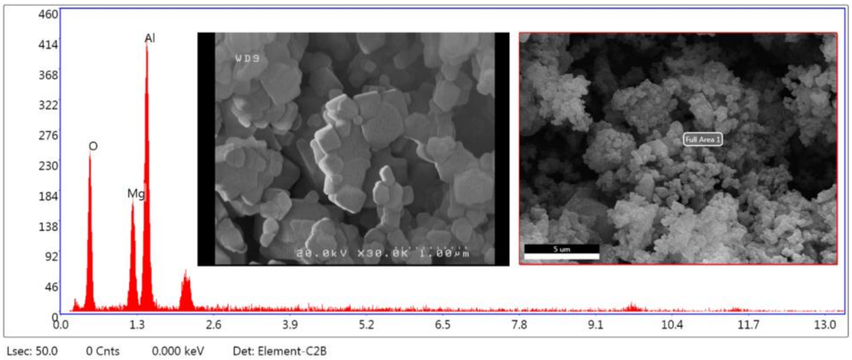


Fig. 2. Image of the modified $MgAl_2O_4$ nanoparticle.

3.2. Surface morphological analysis of MAS nanoparticles by FESEM

FESEM images of MAS nanoparticles and unmodified nanoparticles in two magnifications of 30.0 k, and 60.0 k are shown in Fig. 3. In addition, the nanoparticle composition is qualitatively demonstrated by EDX, in which, the constituent elements of the nanoparticles are presented before and after surface modification.

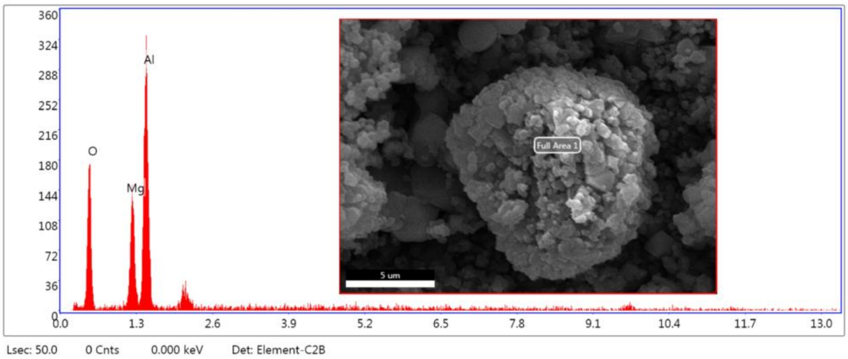
The uniform dimensional distribution of nanoparticles (Fig. 3(b)) indicated that the synthesized nanoparticles have almost blooming flower-like structures, and their forming layers are visible through magnification. MAS nanoparticles consist of plate-shaped structures with similar thicknesses, which eventually converted into almost cubic structure nanoparticles. The average size of the MAS nanoparticles was assessed equal to 50 nm. Moreover, The EDX spectroscopy result of MAS nanoparticles in comparison with that of modified nanoparticles revealed that surface modification of magnesium-aluminum nanoparticles by oleic acid resulted in increasing carbon levels.



eZAF Smart Quant Results

Element	Weight %	Atomic %	Net Int.	Error %	Kratio	Z	A	F
O K	38.3	50.5	34.5	10.0	0.1636	1.0646	0.4008	1.0000
MgK	16.0	13.8	29.1	7.9	0.1073	0.9843	0.6785	1.0063
AlK	45.7	35.7	73.8	6.9	0.2719	0.9480	0.6272	1.0003

(a)



eZAF Smart Quant Results

Element	Weight %	Atomic %	Net Int.	Error %	Kratio	Z	A	F
O K	36.8	48.8	24.8	10.6	0.1551	1.0661	0.3952	1.0000
MgK	17.0	14.9	23.9	8.1	0.1161	0.9857	0.6873	1.0062
AlK	46.2	36.3	56.2	7.3	0.2727	0.9493	0.6220	1.0003

(b)

Fig. 3. EDX-FESEM for the synthesized $MgAl_2O_4$ nanoparticles (a) after and (b) before surface modification.

As mentioned, two types of surface-modified nanoparticles (named S1, and S2) were prepared by using the amount of 10 g, and 20 g of the oleic acid, respectively. The formed morphology of two samples is shown in Fig. 4.

It has been reported that the nanoparticles with smaller sizes, more spherical shapes, and lower density can better penetrate and transfer between surfaces [32]. In this study, despite no significant differences in nanoparticle size caused by varying the consumed amount of oleic acid, the S2 sample had a more spherical and uniform shape with longer dispersion time in the base oil (Fig. 4(b)).

Accordingly, the S2 sample was preferred compared to another sample to use through subsequent experiments.

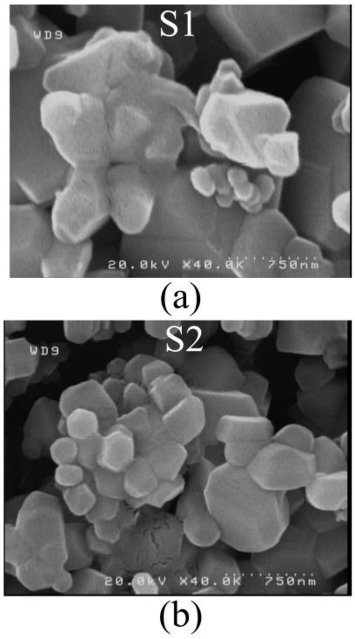


Fig. 4. EDX-FESEM for the synthesized $MgAl_2O_4$ nanoparticles using (a) 10 g, and (b) 20 g of oleic acid, respectively.

3.3. XRD analysis of MAS nanoparticles

The XRD technique was employed to identify the prepared MAS compound (Fig. 5). According to Fig. 5, the average particle sizes evaluated about 50 nm using the Scherer equation. In general, all peaks corresponding to the synthesized samples had an orthorhombic shape that was in complete agreement with the standard data of MAS (JCPDS no. 00-021-1307). Fig. 5 also showed that no diffraction peaks from impurities were detected in the XRD patterns of the synthesized nanoparticles. In other words, the XRD pattern of the synthesized sample was characterized by sharp and well-defined peaks, which indicates the crystallinity of the synthesized nanoparticles. In this regards, unmodified and oleic acid-modified CuS nanorods were prepared by water bath and hydrothermal method, and the same XRD results was reported [11].

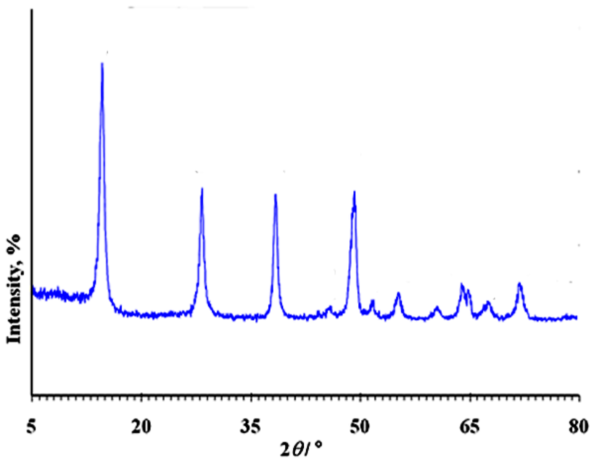


Fig. 5. The XRD pattern related to the synthesized spinel nanoparticles.

3.4. FTIR analysis of MAS nanoparticles

Fig. 6 shows the FTIR spectrum of synthetic MAS nanoparticles, before and after surface modification. Comparison of FTIR test for two samples was performed to evaluate the modified surface and to ensure oleic acid immobilization on the primary nanoparticles.

Absorption bands for MAS nanoparticles were appeared in wavelength ranges of 1300-400 cm^{-1} and were mainly related to the fingerprint regions. For example, the absorption band in the wavelength range of 540 cm^{-1} was associated with the MAS phase, especially ALO_6 groups. It has also been reported that the absorption bands for Mg-O (metal-oxygen) appear at 530 cm^{-1} and 709 cm^{-1} wavelength, which are associated with lattice vibrations of tetra and octahedral coordinated metal ions [33].

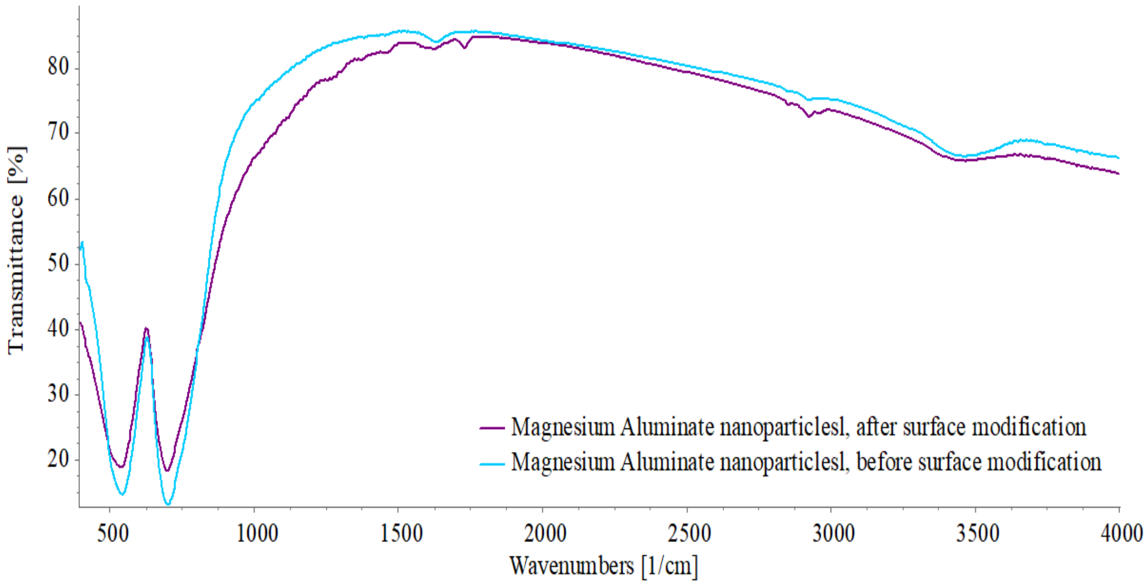


Fig. 6. The FTIR pattern related to the synthesized spinel nanoparticles.

FTIR analysis were performed to interpret the absorption spectra added after surface modification, confirm the surface modification, and recognize oleic acid on the surface of synthesized nanoparticles, too. After the surface modification process, a new absorption band, which is relevant to stretching vibrations of the C=O oleic acid bonded on the sample surface, was added to the pre-surface modification spectrum with weak intensity at 1710 cm^{-1} [34]. The aforementioned is considered the most prominent peak in the data and indicates that surface-modified nanoparticles were successfully fabricated. The 1717 cm^{-1} peak for the MAS sample is related to water adsorbed on the nanoparticle surface and the O-H bond on the nanoparticle. In Fig. 6, this peak appears weaker than usual, which could be due to the hydrogen bonding of oleic acid with some OH groups on the nanoparticle surface [35]. Peaks related to oleic acid are visible in two regions, where weak absorption bands close to 2855 cm^{-1} and 2925 cm^{-1} assigned to asymmetric stretching vibrations of the C-H [36], and strong band at 1710 cm^{-1} corresponded to C=O stretching vibrations in the carboxylic acid.

3.5. Analysis of rheological test of base oil

The rheological test is one of the most important tests for the measurement of the base oil suitable for the stability of MAS nanoparticles. As shown in Fig. 7, the value of the viscosity was constant where the shear rate changes varied from 0.1 s^{-1} to 1000 s^{-1} for vertically oscillating non-Newtonian fluids. The peak at a shear rate of about 10 s^{-1} was probably due to the change of flow regimes from laminar to turbulent and indicated that the fluids were non-Newtonian under high shear stresses.

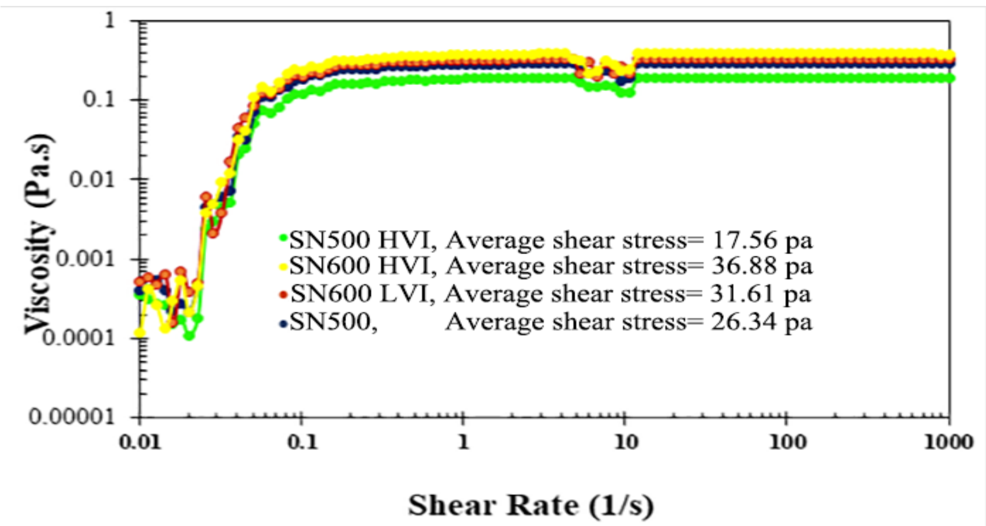


Fig 7. Rheological test of some base oils of SN500HVIO, SN500O, SN600HVIO, and SN600LVIO produced by Sepahan Oil Company (SOC).

In this study, the SN500HVI base oil was selected to investigate the effects of metal nanoparticles based on its more reliable rheological properties than the other mineral and paraffin oils. Accordingly, the SN500HVI paraffinic base oil produced by Sepahan oil company was selected after comparison with several other base oils, including SN500Generic, SN600HVI, and SN600LVI. The results of Fig. 7 indicated that the graph related to base oils at a low shear rate has a linear deviation, which can be due to the impurity of the oil and some contaminants such as sulfur compounds. The most Suitable selection in terms of rheological properties has fewer shear stress. Therefore, SN500HVI base oil was selected with fewer fluctuations in the diagram, fewer shear stress (17.56 Pa) and more prominent non-Newtonian behaviors than the other base oils. [37] Also, less pollution of sulfur and other impurities in SN500HVI than other base oils can be considered one of the main criteria for the base oil selection. Suitable base oil in terms of rheological properties has fewer impurities and contaminants, which, in turn, reduced the possibility of agglomeration of impurities with the used nanoparticles, and could consequently, disperse nanoparticles more efficiently. It is worth to mention that some properties of SN500HVI base oil were presented in Table 1.

3.6. Friction surface analysis of wear tests

The tribological effectiveness is measured by their ability to reduce the friction coefficient and surface wear features. Accordingly, both of which were investigated in this study. Fig. 8 displays the morphologies of disk surfaces after the friction and wear tests, in the presence of SN500HVI oil at different weight percentages of magnesium nanoparticles and absence of nanoparticles. It should be noted that all images were captured at a load of 10 Nm.

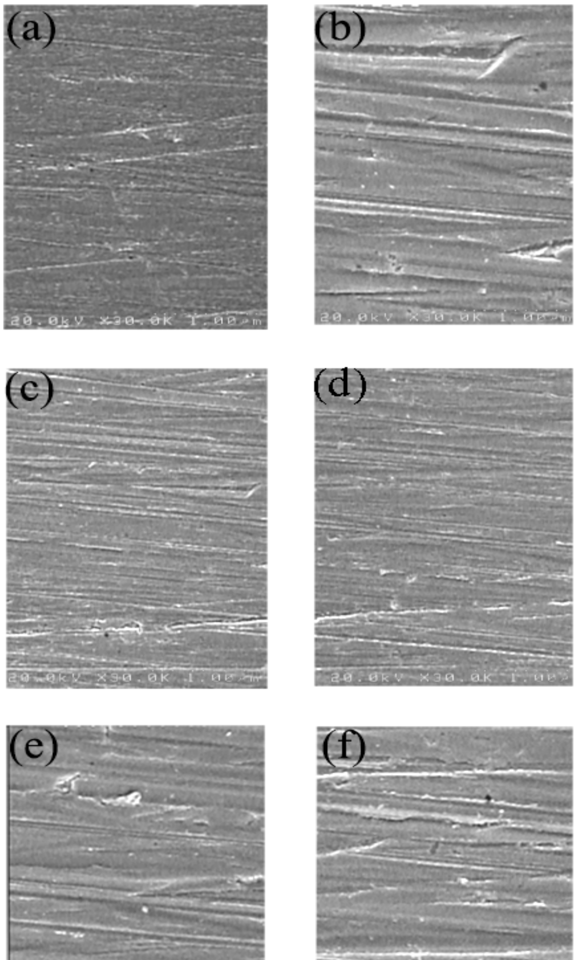


Fig. 8. (a) Disk surface before the test; (b) in the presence of base oil and absence of nanoparticles after wear test under 10 N loading; (c) in the presence of $MgAl_2O_4$ nanoparticles at weight rates of 0.25, (d) 0.5, (e) 1, and (f) 5٪

The morphology of the disk surface before the test is shown in Fig. 8(a). Fig. 8(b) explains that the wear surface lubricated by pure paraffinic oil had a rough appearance with large pores and a large number of thick and deep channels that may have been due to adhesive wear. As shown in Fig. 8 (e), the wear surface created by paraffin oil containing 1 wt.% of nanoparticles with wear lines up to 585 nm was rougher; however, the covered surface in Fig. 8 (c) using 0.25 wt.% of nanoparticles had a less harsh degree. The wear surface lubricated by paraffinic oil containing 0.5 wt.% of nanoparticle, with an average thickness of wear lines up to 57 nm (see Fig. 8(d)) was softer and were formed smoother grooves.

According to the delamination theory of wear, Hence, the increase in nanoparticles could lead to more nanoparticles being exposed to friction, increasing the weight percentage of nanoparticles led to improve wear properties [38-40]. Therefore, direct contact between friction surfaces was prevented and led to an enhanced performance at high pressures and increased force capacity on the lubricating oil [41].

Reciprocally, excessive increase of nanoparticles can also cause agglomeration and reverse results. According to Fig. 8 (e, f), it was also observed that increasing MAS nanoparticles at high concentration may simply cause the agglomeration and can have the opposite effect. There are some possible explanations for this result. Hence, the optimal percentage of nanoparticles and their stability are the main parameters affecting the tribological properties of paraffin oils.

Overall, according to Fig. 8, it was concluded that the anti-wear properties of the applied fluid improved following the addition of modified nanoparticles.

3.7. Friction surface analysis of wear tests under high loads

Analysis of the SEM technique on rubbing surfaces lubricated by pure SN500HVI base oil (with and without nanoparticles), are shown in Fig. 9. It should be noted that all images were captured at a load of 30 Nm and a speed of 600 rpm. Gradually, increasing the weight percentage of nanoparticle concentrations led to the penetration of MAS nanoparticles between the joints and grooves and improved the tribological properties by reducing the surfaces exposed to direct contact. In general, slight wear occurred in the contact area at high loads due to the hardness between nanoparticles and the contacting surfaces. It should be noted that the accurate measurement of wear degree is very complex and depends on many variables, including particle properties (e.g., size, degree of hardness, and shape) and environmental properties (e.g., surface, topographic conditions, type of working oil, and the amount of load applied) [42]. Accordingly, comprehensive studies on these factors and their interactions can offer complete descriptions regarding nanoparticles' roles and their effects on friction and wear processes.

3.8. Friction surface analysis of friction tests

The average friction coefficient of SN500HVI base oil at different weight percentages of nanoparticles and absence of nanoparticles in the absence of nanoparticles and are shown in Fig. 10. It should be noted that all results were obtained at a load of 10 Nm, at the velocity of 0.6 m/s with the radius of 4 cm, and a speed of 600 rpm.

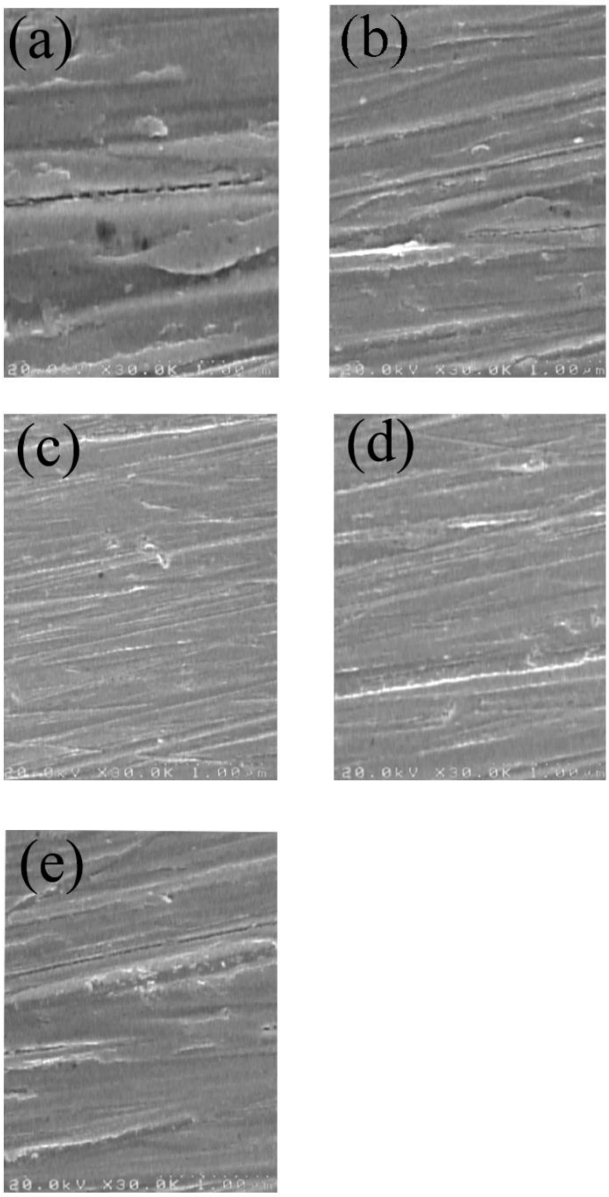


Fig. 9. Disk surface after wear testing under 30 Nm loading. a) at the presence and absence of the synthesized $MgAl_2O_4$ nanoparticles; b) concentration of 0.25 wt%; c) concentration of 0.5 wt%; d) concentration of 1 wt%; and e) concentration of 5 wt%

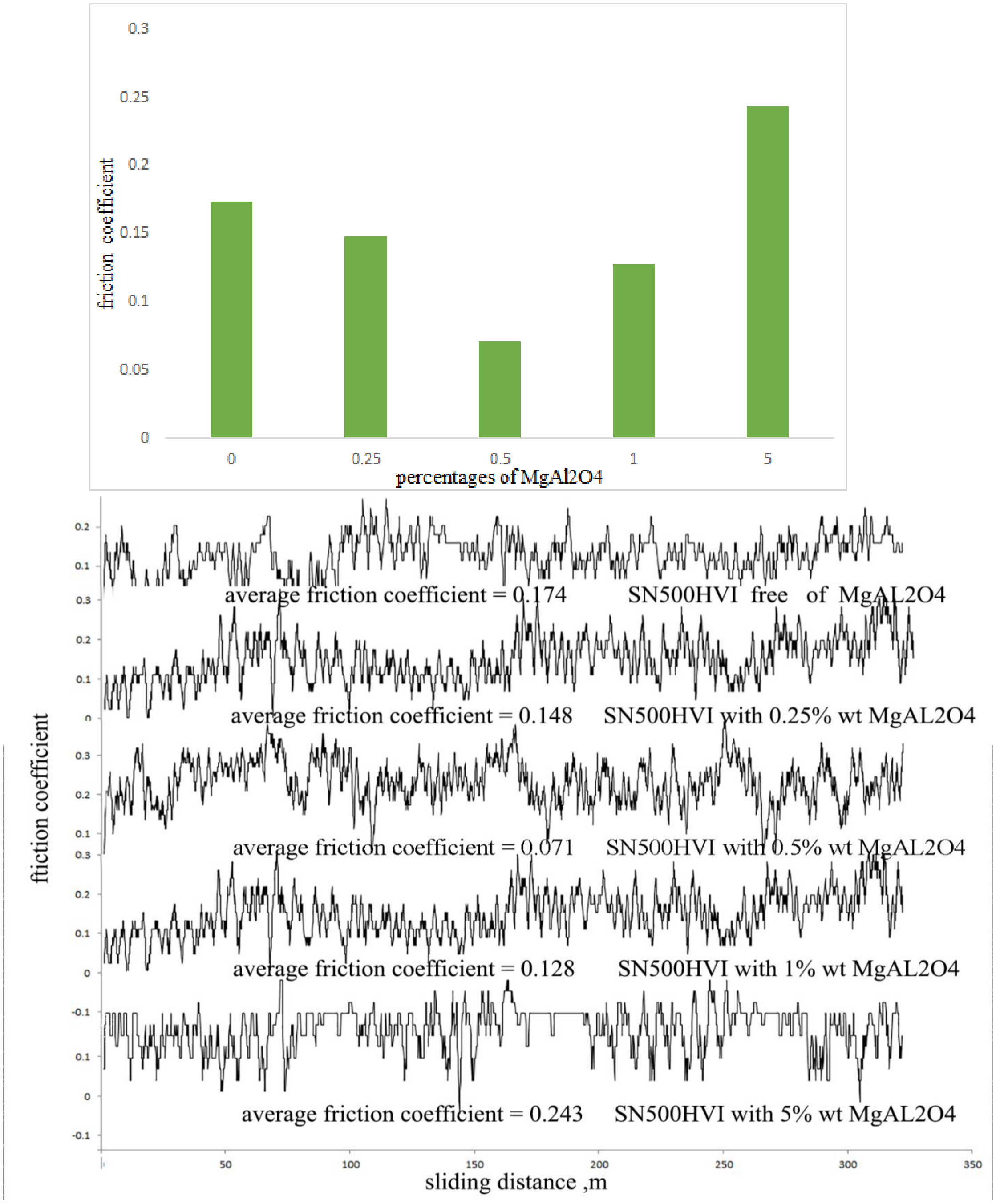


Fig. 10. SN500HVI base oil friction coefficient data in the absence of surface-modified $MgAl_2O_4$ nanoparticles in different concentrations.

As shown in Fig. 10 the average friction coefficient was estimated equal to 0.174, which was considered a suitable criterion for other concentrations and laboratory outcomes. In general, it was observed that the coefficient of friction of nanoparticles was concentration-dependent, but it did not fully follow this trend. In other words, the coefficient of friction was first decreased by increasing MAS nanoparticles' concentration up to 0.5 wt. %, and then increased with further increasing nanoparticles. Fig. 10 displays that the mean friction coefficients improved with increasing weight percentages of nanoparticles in the base oil, and this value decreased to 0.071 at the optimal concentration of 0.5 wt.%. The results also revealed that the reduction percentage of average friction coefficient for base oil with concentrations of 0.25 wt.%, 0.5 wt.%, and 0.75 wt.% compared to that for base oil without nanoparticles were found to be 15 %, 59 %, and 27%, respectively. According to the above results, a reason for the performance improvement of reducing the friction of MAS nanoparticles could be attributed to their small size at a scale of less than 50 nm, excellent dispersion in the base lubricant, and high hardness. These properties facilitate the entrance of synthesized nanoparticles at optimal concentration to the desired surfaces, resistance to stresses and surfaces' loads, and ultimately prevent direct contact with rough surfaces. In addition, the results of the analysis of Fig. 10 (along with wear surfaces) showed that increasing concentration of nanoparticles increased the deposition and adhesion of nanoparticles on the surfaces and significantly improved the wear and tribological properties of the SN500HVI base oil. In contrast, the average friction coefficient of 1 wt.% of MAS nanoparticles was slightly higher than that in the pure base oil. Furthermore, MAS nanoparticles at concentrations higher than the optimum concentration had tended to accumulate in the base oil. The tendency to form irreversible agglomerates in MAS achieved by adding excess concentration of MAS to the base lubricant, and the agglomerates between the contact surfaces increased the average friction coefficient. Therefore, since high concentrations of nanoparticles could have adverse effects, sufficient care must be taken in choosing the optimal concentration and should be avoided from the use of nanoparticles in high concentrations.

3.9. Comparing the results with others' findings

The obtained results of the present study were separately compared with different similar studies based on the type of nanoparticles, synthesis technique, base oil, surface modification, and the testing method. Results displayed in Table 3 showed that the nanoparticles used in this work, have the effective and the desirable results compared to other nanoparticles used in other studies.

Table 3. Comparison of the present study with other similar researches

Type of nanoparticles	Size (nm)	synthesis method	Type of oil used	Dispersion method	Optimal percentage of nanoparticles	Test method	fiction coefficient of base oil	Friction coefficient of nanofluid	Percentage reduction of friction	Ref.
$MgAl_2O_4$	50	sol-gel-hydro thermal	Base oil (SAE-30)	Surfactant (oleic acid)	0.5	Pin on disc	0.174	0.071	59	present study
$MgAl_2O_4$	30	Hydro thermal method	Base oil (SAE-20)	-	0.5	ball-on-disc	0,144	0,125	14	[43]
ZnO/Al_2O_3 composite	53,66,124	Sol–gel method	mechanical oil	Surfactant (oleic acid)	١	four-ball	-	-	37.5	[44]
CuO	5	-	engine oil API-SF	-	0.1	reciprocating sliding friction	-	-	18.4	[44]
TiO_2	80	-	engine oil API-SF	-	0.1	reciprocating sliding friction	-	-	Not improved	[45]
CuO	30–50	-	PAO 6	-	١١	block-on-ring	-	-	20	[46]
MSH		Hydrothermal methods	PAO	-	0.3	block-on-ring	0.08	0.06@t=0 0.02@t=60 min	25 75	[12]
CuS	-	hydrothermal methods	liquid paraffin	Surfactant (oleic acid)	0.5	Pin on disc	0.09	0.0345	62	[11]

This outcome could greatly depend on the type of nanoparticles, synthesis method, selected percentages, hardness of nanoparticles (MAS nanoparticle had a mohs hardness of 8-9 [23]) and the surface modification method. Therefore, several parameters could be affected in the results. The most similar study to the present study was conducted by Leitans et al. [43].

Despite the similarity of nanoparticles in both studies, the results of two studies were significantly different. One of the most important reasons for the difference between the results of two mentioned studies was related to the surface modification factor. It was appeared that the type of the surface modifier in the present study led to improve tribological properties, increase stability, and improve efficiency of MAS nanoparticles in displacement and impact on wear surfaces. Other differences between both studies were differences in nanoparticle size and geometric shape, base oil type, and nanoparticle synthesis method. These cases determine that the choice of nanoparticles alone is not important and various other physical and chemical factors can be effective in tribological discussion and affect the properties of wear and friction.

4. Conclusion

The tribological properties of oleic acid surface-modified $MgAl_2O_4$ nanoparticles in a lubricant were examined and the following results were obtained based on tribological tests and wear surface analysis. $MgAl_2O_4$ nanoparticles with an average diameter of less than 50 nm can be prepared by blending hydrothermal and sol-gel techniques. Rheological testing was performed on several different base oils of group one, and SN500HVI base oil was selected among them based on the occurrence of obvious non-Newtonian behaviors. Also, oleic acid-modified nanoparticles showed a good dispersion and stability in the SN500HVI base oil.

The integration of modified oleic acid improved additive particles' stability in the lubricant, and produced a complete and uniform liquid with the anti-wear property .

The properties of tribology, load tolerance, anti-wear, and friction in the SN500HVI base oil were enhanced by surface-modified $MgAl_2O_4$ nanoparticle integration. The sphere-like $MgAl_2O_4$ nanoparticles might result in rolling effect between the rubbing surfaces, and the situation of friction is reformed from sliding to rolling. So, the friction coefficient can be decreased. Also, the anti-wear mechanism is related to the deposition of $MgAl_2O_4$ nanoparticles on the worn surface, consequently improving the tribological properties. The optimum concentration of these nanoparticles in SN500HVI base oil was selected equal to 0.5 wt.%.

Conflict of Interest

The authors declare that they have no conflict of interest.

All authors have participated in (a) conception and design, or analysis and interpretation of the data; (b) drafting the article or revising it critically for important intellectual content; and (c) approval of the final version.

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