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TRIBOLOGICAL PROPERTIES OF MINERAL BASE OILS WITH TUNGSTEN DISULPHIDE (WS_2) NANOPARTICLES IN BOUNDARY LUBRICATION CONDITIONS

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ABSTRAK

Gesekan antar komponen mempengaruhi efisinsi dalam sistem mekanik. Paper ini mempelajari pengaruh aditif nano jenis Tungsten Disulphide (WS_2) sebagai pemodifikasi gesekan friction modifier (FM). Karakteristik gesekan dan keausan pada penambahan aditif WS_2 0.1% dan 0.5% berat ke dalam base oil dipelajari menggunakan uji HFRR dan uji FourBall. Penyiapan sampel dilakukan dengan menggunakan pengaduk magnetik pada temperatur 50^{o}C selama 60 menit, dilanjutkan proses homogenisasi selama 1 jam. Hasil penelitian menunjukkan bahwa penambahan aditif WS_2 mampu meningkatkan ketahanan anti aus dari sampel base oil group I hingga 40%, sedangkan untuk base oil dari Group II dan Group III hanya 12%. Koefisien gesekan meningkat dalam kisaran 7,5% sampai 35% lebih tinggi sebagai hasil dari penambahan aditif.

Kata Kunci*: aditif, gesekan, keausan, tungsten disulfida, four-ball*

ABSTRACT

Friction affects the efficiency of a mechanical system. This paper discusses the influence of Tungsten Disulphide (WS_2) as a friction modifier (FM). Friction and wear characteristics of base oil as a result of the addition of 0.1% and 0.5 % weight of WS_2 were studied. WS_2 nanoparticles were mixed with base oil using magnetic stirrer at 50^{o}C for 60 minutes, then were homogenized in an ultrasonic homogenizer for 1 hour. Friction and wear characteristic of these mixtures were tested using four-ball and HFRR test-rig. The results show that the addition of both 0.1% and 0.5% WS_2 nanoparticles increased by around 40% the anti-wear characteristic of mineral base oil group I and 12% for other groups of base oils. The increase in friction coefficients was in a range of 7.5% to 35% as a result of the addition of additives.

Keywords: additive, friction, wear, tungten disulfide, four-ball.

I. INTRODUCTION

The main source of energy loss in a mechanical system is friction, but this can be reduced by lubrication. The combination of base oil and additives, such as antioxidants, detergents, dispersants, extreme-pressure (EP) and antiwear (AW) improve lubricants' properties. Three types of traditional EP and AW additives are sulphur, chlorine, and phosphorus. They cover surfaces by forming easily sheared layers of sulphides, chlorines or phosphides, preventing severe wear and seizure (Choyet al. 2009,Yu et al. 2008, Peng et al. 2009). (Choi et al. 2009, Yu et al.

2008, Peng et al. 2009). The use of chlorine and phosphorus compounds as lubricant additives are restricted because of environmental reasons. Due to the outstanding tribological and environmental properties, nanoparticles are regarded as excellent candidates to replace those traditional EP and AW additives. Nanoparticles are relatively insensitive to temperature and limited tribochemical reactions. These are the main advantages of using nano materials, compared to traditional additives (Battez et al. 2010). Another advantage of nanoparticles in lube oils is that they cannot be retained by the filters (Tarasov et al. 2002).

The antiwear mechanism of nanoparticulate additives can follow three different processes: nanoparticles may be melted and welded on the rubbing surface, reacted with the specimen to form a protective layer or tribo-sintered on the surface (Chou et al. 2010). However, nanoparticles can also act as nano-bearings on the rubbing surfaces (Chou et al. 2010). The above mentioned deposition mechanisms take place only under mixed and boundary lubrication. Several study reporting that the depositon of nanoparticles on to the rubbing surface, improve the tribological properties of the base oil, displaying good friction and wear reduction characteristics even at concentrations below 2 wt% (Battez et al. 2010). There are four mechanisms of addition of nanoparticles to the base oil (Peng et al. 2009), (i) smaller nanoparticles are more likely to interact with the surfaces to form a surface protective film; (ii) small spherical nanoparticles are more likely to roll between the surfaces and change the sliding friction for a mixing of sliding and rolling friction; (iii) compressive stress concentrations associated with high contact pressure can be reduced by many nanoparticles, which bear the compressive force, and (iv) nanoparticles are deposited on the surface forming a physical tribofilm that compensates for the loss of mass, this effect is called “mending effect”. A combination of four effects explain the good friction and wear properties of nanoparticles in base oil.

Several studies have been carried out on applications of nanoparticles in the field of lubrication. The reduction of friction and wear are dependent on the characteristics of nanoparticles such as size, shape, and concentration. Numerous nanoparticles used as oil additives have been investigated in recent years (Choi et al. 2009, Yu et al. 2008, Peng et al. 2009, Battez et al. 2010, Tarasov et al. 2002, Chou et al. 2010, Peng et al. 2009, Jiao et al. 2011, Kalina et al. 2012, Kogovsek et al. 2013, Luo et al. 2011, Mukesh et al. 2013, Krishna et al. 2012, Hernandez et al. 2008, Pawlak et al. 2009, Sudeep et al. 2013, Kimura et al. 1999). Da Jiao et al. prepared alumina/silica (Al_2O_3/SiO_2) composite of 70 nm nanoparticles, added to lube oil (Jiao et al. 2011). The tribological properties of modified Al_2O_3/SiO_2 composite nanoparticles as lube oil additives were investigated by four-ball and thrust-ring tests in terms of wear scar diameter, friction coefficient, and the morphology of thrust-ring. The results show that their anti-wear and anti-friction performances are better than those of pure Al_2O_3 or SiO_2 nanoparticles. The diameters of wear scar and friction coefficients are smallest when the concentration of nanoparticle additives are around 0.5 %-wt.

The mechanism and performance of lubricants using nanotubes MoS_2 aaditive resulted in the lower friction coefficient of lubricant in two-fold and wear decreased 5-9 times (Kalina et al. 2012). Coating nanotubes MoS_2 on the steel surface resulted in a lower friction coefficient of around 40-65%, depending on surface roughness of the steel (Kogovsek 2013). This paper investigates the effect of the addition of nanoparticles WS_2 in mineral base oil. The antiwear behavior was studied using a HFRR testing-rig and four-ball machine.

II. METHODOLOGY

Materials used in this research were base oil and WS_2 powder as a friction modifier. Characteristics of the mixtures were compared with commercial friction modifiers additives such as Nano Energizer, Xado, and Can WS_2. Mineral oil used as the base oil including group I (HVI 60, HVI 95, HVI 160, SN 150, and BS 150), group II (N 300 and N 500), and group III (Dubase 4, Dubase 6, and Yubase 8). WS_2 powder derived from M.K. Impex Corp., a particle size of 90 nm and 99%-purity. The size, shape and chemical composition of nanomaterials were characterized using SEM, EDX and TEM. Mineral base oils were mixed with 0.1% and 0.5 %-weight of WS_2 using magnetic stirrer at 50oC and for 60 minutes and homogenized in an ultrasonic homogenizer for 1 hour. EP properties were characterized using 4-ball test apparatus at 1200±60 rpm, 75±2oC, for 60±1 minute, and load 40±0.2 kgf. Balls test used in this study were chromium-steel alloy, which meets the AISI standard E-52100, 12.7 mm (0.5 inches) in diameter, 25 EP (Extra Polish) grade and Rockwell C hardness of 64-66. The scratch of test balls measure identifies that the greater the scratches mean the lower the protection is against wear. The AW/EP test was performed in accordance with the ASTM D4172 standard.

The high-frequency reciprocating test rig (HFRR) was applied to investigate the friction and wear performances of lubricants. The HFRR system consists of a ball-on-disk test to measure the friction and wear under boundary lubrication conditions using a highly stressed ball-on-disk contact. A hard steel ball (58-66 HRC) of 6.0 mm diameter reciprocates on a softer steel disk (190-210 HV) of 10 mm diameter under the fully submerged oil condition at a normal load of 10 N and 1 mm stroke length at 50 Hz for 75 min. Both ball and disk were made of AISI 52100 steel. The lubricant temperature was kept at 50°C. The friction coefficient was measured by a piezoelectric force transducer and the formation of electrically insulating films at the sliding contact was measured by the ECR (Electrical Contact Resistance) technique.

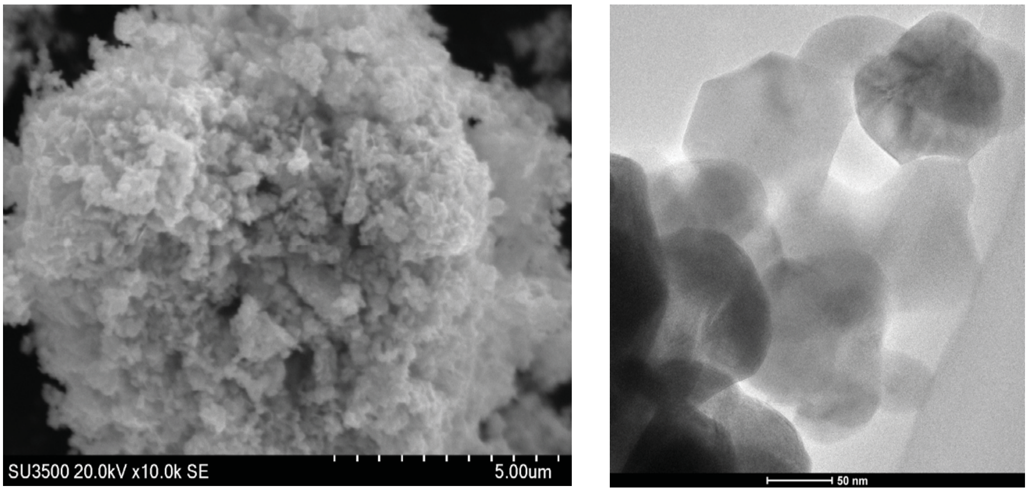
The main properties of the nanoparticles and lubricant used in the experiments are listed in Table 1, Table 2 and Figure 1.

Table 1
Material properties WS_2 (Lower Friction.com 2015)

Properties	Value
Colour	Silver Gray
Appearance	Crystalline Solid
morphology	nearly spherical
purity	99%
APS	90 nm
SSA	30 m^2/g
Melting Point	1250° C, 1260°C (decomposes)
Density	7500 $Kg.m^{-3}$
Molecular Weight	248
Coefficient of Friction (COF)	0.03 Dynamic; 0.07 Static
Thermal Stability in air	COF <0.1 till 1100°F (594°C)
Load bearing ability	400,000 psi for coated film COF:0.044@ 20,000 psi COF reduces to 0.024 between 200,000 to 400,000 psi
Lubrication Temperature Range	Ambient: from -273° C to 650° C
Chemical Durability	Inert Substance, Non-Toxic
Magnetism	Non-Magnetic
Compatibility	Oil, Solvent, Paint, Fuel

Table 2
Material properties of base oils

No	Characteristics	Test Method ASTM	HVI 60	N300	Yubase-8
1	Color	D1500	L 3.5	L 2.5	L0.5
2	Density @ 15°C, [g/cm³]	D 1298	0.8647	0.847	0.8449
3	Flash Point COC, [°C]	D 92	222	247	260
4	Kinematic Visc., [cSt] :	D 445			
	@ 40°C		23.69	43.89	44.23
	@ 100°C		4.523	7.234	7.375
5	Visc. Index	D 2270	103	127	131



(a) (b)

Figure 1
SEM (a) and TEM (b) micrographs of WS_2.

Table 3
Average scar diameter of ball test

Material	Group	Scar diameter (μm)		
		Base Oil	weight of WS_2	
			0,1%	0,5%
HVI 60	I	721,37	457,08	451,19
HVI 95		725,35	431,4	441,11
HVI 160		727,58	451,08	438,12
SN 150		724,38	423,11	441,57
BS 150		726,11	445,15	432,86
N 300	II	488,35	364,53	397,11
N 500		491,24	420,55	421,99
Dubase-4	III	471,26	400,34	404,22
Dubase-6		463,11	401,34	409,11
Yubase-8		466,35	405,42	410,62

Table 4
Anti-Wear properties of Base Oil by the addition of commercial friction modifier additives

Base Oil	% Improvement of anti-wear characteristic		
	Nano Energiser	Can WS_2	Xado
HVI 60	7.20	7.21	7.21
N300	4.87	4.88	4.88
Yubase-8	4.65	4.65	4.65

III. RESULT AND DISCUSSION

A. Wear Protection Characteristic

Wear protection characteristics based on the size of scratches (scar diameter) of ball-test, reported as average value, are presented in Table 3.

The addition of WS_2 into group I of base oil shoThe addition of WS_2 into group I of base oil shows a significant reduction in the scar of ball-test compared to both Group II and Group III. These results are due to the initial characteristics of Group II and Group III which have better wear protection, consequently, the additive has only a slight effect. The increase in of the anti-wear characteristic of several base oil is the result of additives presented in Figure 2 and Figure 3.

A comparison of the addition of WS_2 to commercial friction modifier additives exhibited in Table 3 shows that most of them have similar characteristics in terms of increasing the anti-wear properties, however, nanoparticles WS_2 additive has a stronger effect. The addition of nanoparticle WS_2 up to 0.1% improves 40% of anti-wear characteristic of HVI 60, on the other hand, nano energizer was only 7.20%.

B. Friction Characteristic

Tests were carried out on the base oil representing each group with a similar range of viscosity grades, such as HVI 60 (Group I), N 300 (Group II) and Yubase 8 (Group III). The performance of lubricant with and without additives was evaluated. Figure 4a shows that the friction coefficient of HVI 60 tends to decrease when approaching the end of the test. Slow formation of the lubricant layer on the surface of the test specimen produces a high friction coefficient at

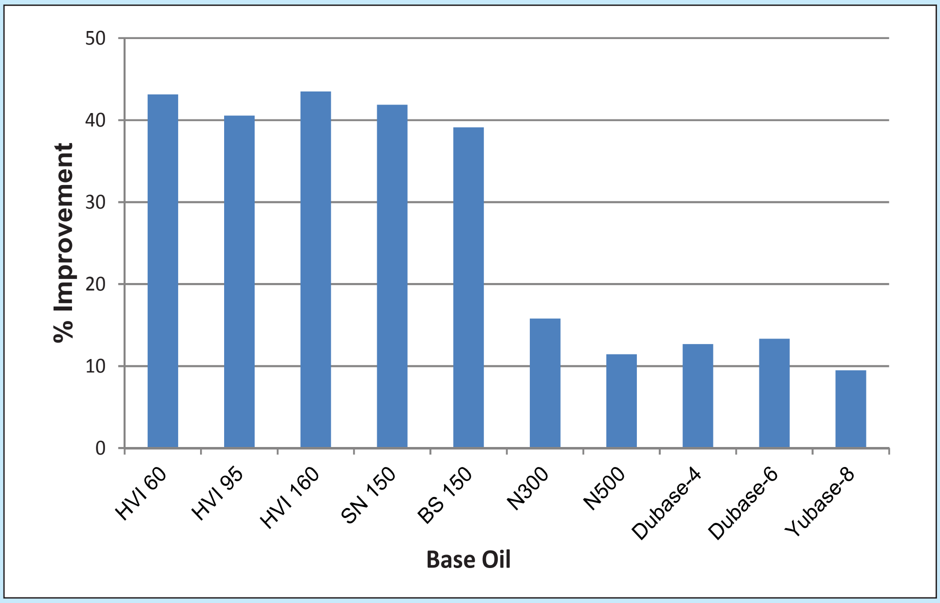


Figure 2
Anti-Wear properties of samples by the addition of 0.1%-wt of WS_2.

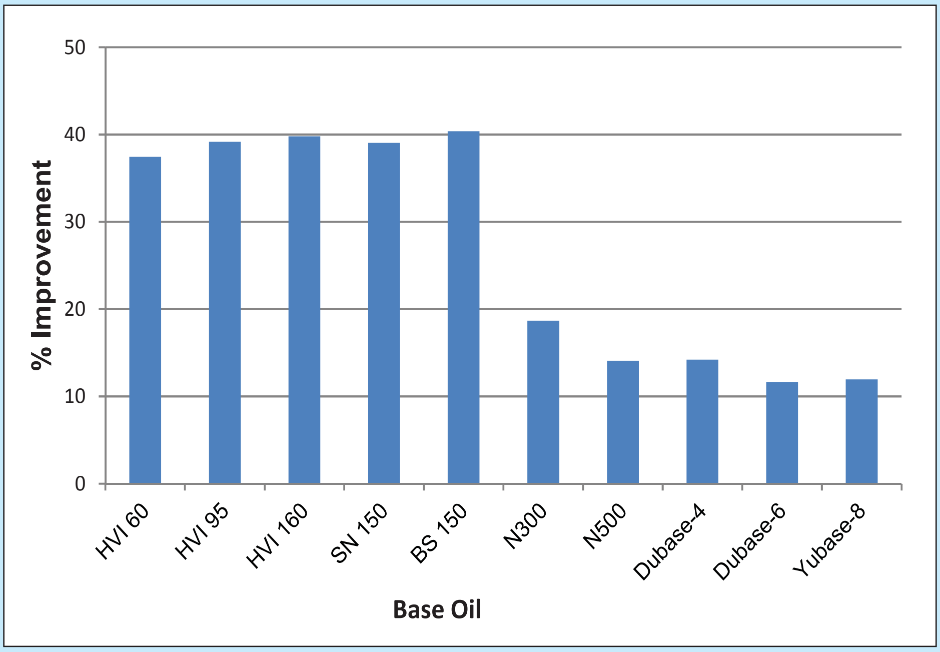
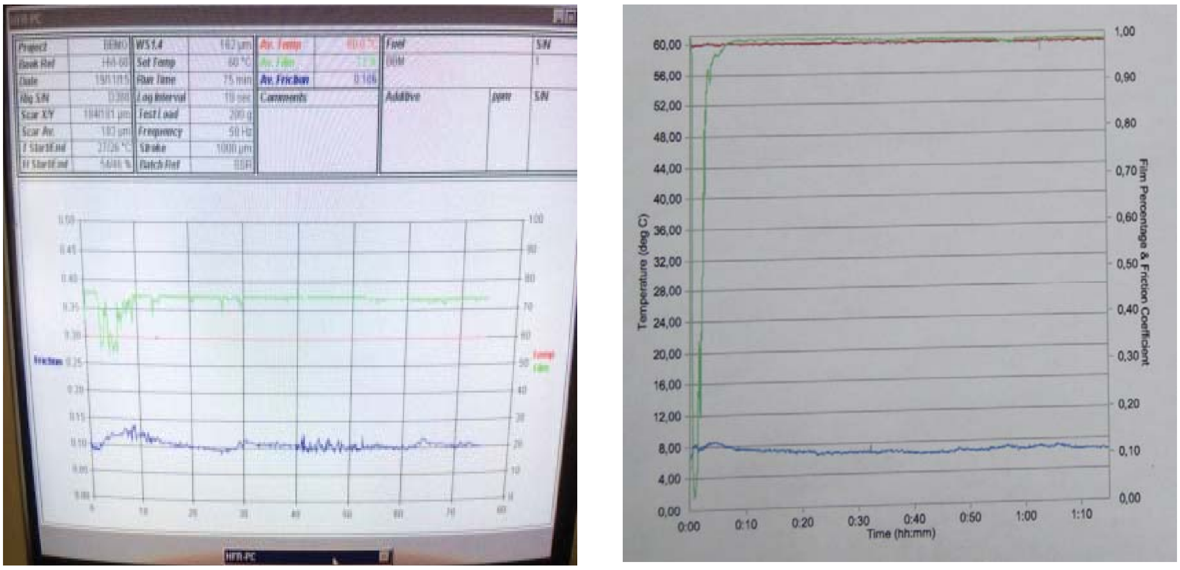


Figure 3
Anti-Wear properties of samples by the addition of 0.5%-wt of WS_2.

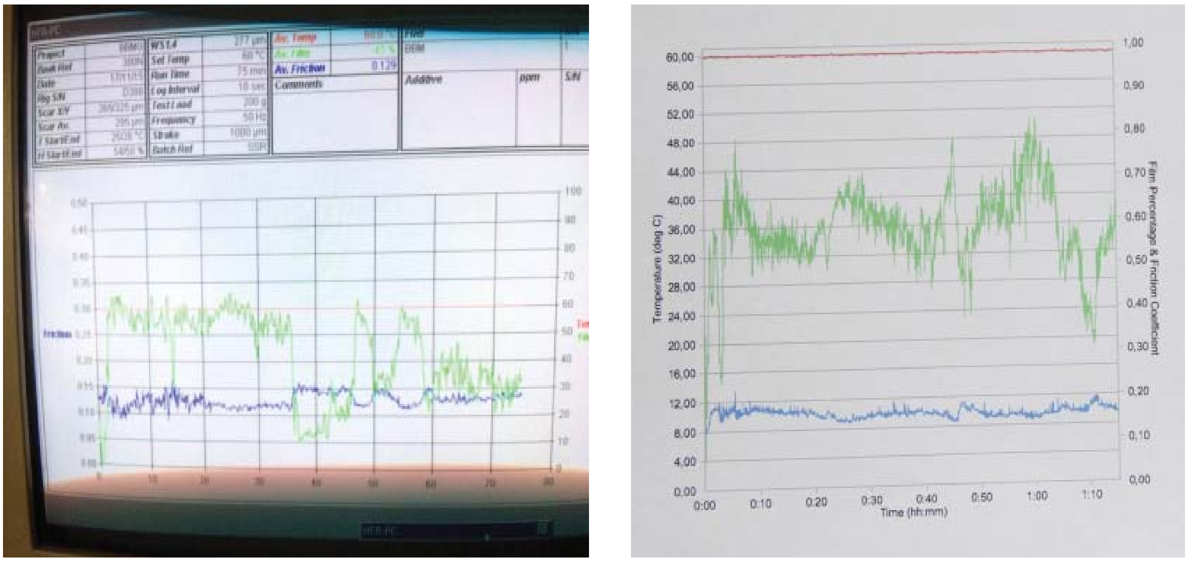
the beginning of the test, which gets lower at the end of the test, resulting in an average friction coefficient of 0.106. The addition of 0.1% WS_2 friction modifiers to base oil increased its friction coefficient by around 7.5% to 0.114 as seen at Figure 4.b. A similar result occurred when 0.1% of WS_2 friction modifiers were mixed with base oil N300 and Yubase 8. The addition of 0.1% of WS_2 resulted in an increasing friction coefficient of N300 of about 26% from 0.129 to 0.163 as shown in figure 5, while addition to Yubase 8 was about 35% from 0.106 to 0.144 as shown in Figure 6.

Theoretically, friction coefficient of synthetics base oil are lower than those from mineral base oil



(a) (b)

Figure 4
Friction coefficient of HVI 60 (a) and with addition 0.1% WS_2(b).



(a) (b)

Figure 5
Friction coefficient of N300(a) and with addition 0.1% WS_2(b).

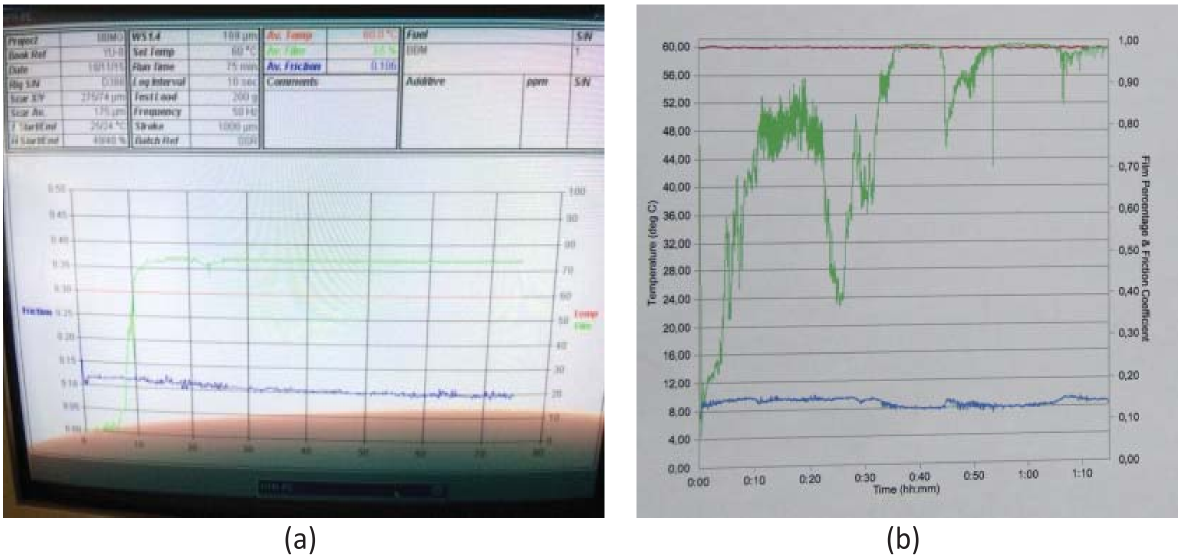


Figure 6
Friction coefficient of Yubase 8(a) and with addition 0.1% WS_2(b).

because of the uniform arrangement of molecules resulting in a better load distribution on the surfaces area, as shown schematically in Figure 7 and the addition of friction modifiers to base oils will reduce their friction coefficient.

However, the opposite results were demonstrated from the test. This happened because of the slow formation of the lubricant layer on the surface of the test specimen, resulting in the high friction coefficient at the beginning of the test which became lower at the end of the test. Green lines from figure 4 to figure 6 represent average film formation. The lines indicate that the film layer formed were inhomogeneous. The commercial additive was used for comparison of WS_2 nanoparticles and resulted in a fluctuated curve as illustrated in Figure 8. The addition of additive to HVI 60 base oil increased the average friction coefficient value from 0.106 to 0.150.

Evaluation of the overall test results illustrate that the Group III as a high-grade base oil has a better homogenous arrangement of molecules, consequently, it has better load carrying distribution. This impacts on wear protection characteristics where the scar diameter of the samples have the lowest value (Table 3). The homogeneity of base oils also affects the percentage improvement from the addition of WS_2. Contrary to the theory, the addition of WS_2 nanoparticles to base oils results in a higher coefficient of friction. Preparation of additives are the main factors suspected to cause the deviations because the particles of additives tend to settle and resist the shear-force applied onto surfaces (Rudnick &Leslie 2003).

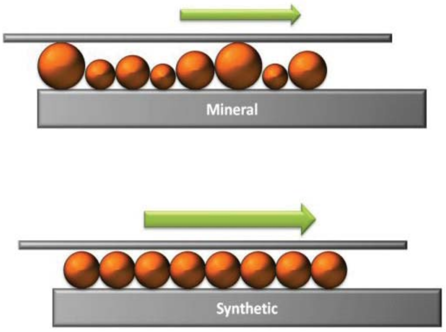
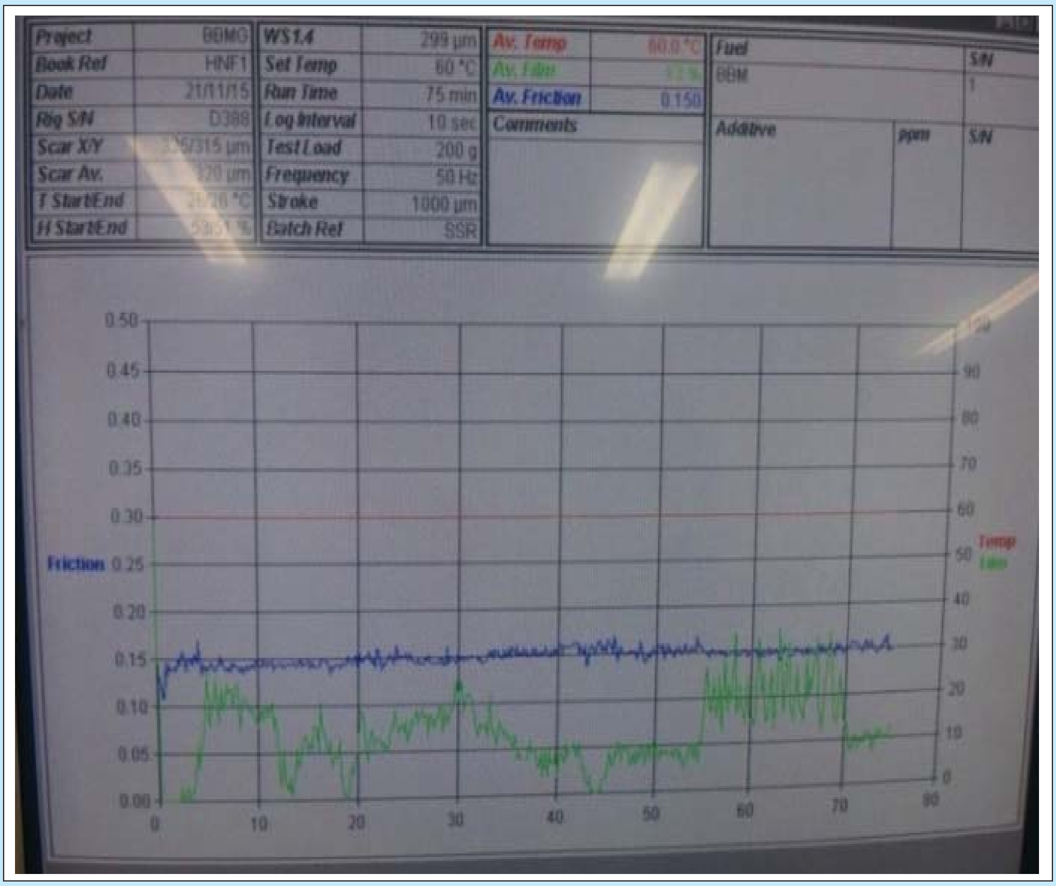


Figure 7
Schematic movement of plate onto mineral and synthetic base oil.

The friction coefficient testing for N300 base oil was relatively high and significantly increased after the addition of 0.1% wt of WS_2 nanoparticles. This is due to the nature of boundary lubrication, in which chemical interactions between the lubricant and the surface take place. The reaction plays a significant role in the effectiveness of the lubrication process, whereas the lubricant viscosity has a limited effect on friction and wear (Hsu & Gates 2005). The important aspect to improve the lubrication of mineral base oil



Project	BBMG	WS1.4	299 µm	Av. Temp	60.0 °C	Fuel	S/N
Book Ref	HNF1	Set Temp	60 °C	Av. Film	[illegible]	BBM	1
Date	21/11/15	Run Time	75 min	Av. Friction	0.150		
Rig S/N	D388	Log Interval	10 sec	Comments		Additive / ppm	S/N
Scar X/Y	[illegible]/315 µm	Test Load	200 g				
Scar Av.	[illegible] µm	Frequency	50 Hz				
T Start/End	[illegible] °C	Stroke	1000 µm				
H Start/End	[illegible] %	Batch Ref	SSR				

Figure 8
Friction coefficient of HVI 60 mixed with commercial friction modifier.

is nanoparticles interaction with the metal surface. The addition of nanoparticles to base oil will present the behavior of third body, in changing the friction coefficient. According to Chinas and Spikes, nanoparticles penetrate the contact area and then deposit on it because they are smaller or similar in size to lubricant film thicknesses (Chinas-Castillo & Spikes 2000).

The formation of electrically insulating films was measured during the HFRR test using the ECR. The surface coverage caused by generation and removal of surface film layers was measured under boundary lubrication between a steel-sliding ball and a steel disk. The electrical resistance between the two contacting surfaces gives an idea of the amount of direct metal to metal contact (Viesca et al. 2010). The films covering the rubbing surfaces affect the surface roughness and structure. Thus, the friction behavior shows a corresponding response to the film formation between surfaces under boundary lubrication conditions. Figures 4, 5, 6, and 8 show the film formation behavior of the samples that presented as a green color curve. The film formation is strongly influenced by base oil and EP additive. Figure 4 describes that the film formation is developed in 60 seconds, and in this period the friction coefficient curve of base oil HVI 60 is similar to its curve after being mixed with an additive. Base oil N300 has different behaviors in comparison with HVI 60 and Yubase 8. Fluctuations during the test that occurred were due to the adhesion of lubricant layers not being strong and were easily removed by the motion of the ball-test. The samples with low friction coefficient show a good percentage of the film. Since the average film percentage of HVI 60 decreased from 73% to 60%, consequently the damage occurred. This decrease might be caused by the presence of WS_2 nanoparticles in boundary film formation. The decrease in friction coefficient was observed when achieving the end period of testing as the nanoparticles became a rolling medium between the contact surfaces.

IV. CONCLUSION

This current study shows that the addition of both 0.1% and 0.5%wt of WS_2 increased the anti-wear characteristic of base oil group I by around 40% and 12% for other groups. Preparation of additives are the main factors suspected of causing the deviations in the friction coefficient values. The nanoparticle additives tend to settle and to resist the shear-force applied onto surfaces. This phenomenon results in friction coefficient values which are contrary to the theory, where the addition of WS_2 nanoparticles to base oils resulted in higher coefficient values of friction. The increase in the friction coefficients was in a range of between 7.5% to 35% higher as a result of the addition of additives. Homogenizing the samples containing WS_2 additives using physical or chemical treatment are needed so that the additives form a homogenous layer and decrease the friction coefficient of surfaces.

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