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TRIBOLOGICAL INTERACTION STUDIES OF ENGINE OIL ADDITIVES AND THEIR COMBINATIONS

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ABSTRACT

Modern engine oil formulations usually contain many kinds of additives, such as detergents, dispersants, antioxidants, VI improvers, anti-wear and friction modifiers at different dosages so that the oil to have the desired physico-chemical and performance characteristics. These additives makes the oil to perform in the oil and give benefits like increased durability to components by reducing wear, reducing overall energy consumption by minimizing the Coefficient of Friction (COF) between the surfaces, increasing the ODI (Oil drain interval), etc. The combinations of different additives result in interactions with each other and exhibit antagonistic or synergistic effects compared to the performance of the individual additives in lubricating oil in tribological performance (friction and wear). In this work, tribological performance of and interactions between two key additives viz., anti-wear and Dispersant in engine oil under boundary lubrication is studied. The test samples comprise combinations of base oil (Group I and Group II), primary and secondary zinc dialkyl dithiophosphate (ZDDP), and N-based polymeric dispersant additive. Tribological testing was carried out employing ball-on-disc test rig (SRV) and four-ball tester. This study provided a better understanding of the frictional properties of primary and secondary ZDDP and the polymeric dispersant and their combinations in Group I and Group II base oils.

KEYWORDS: Additive interaction, Wear, Engine oil additives, Tribology

1.0 INTRODUCTION

Over the past several decades, Zinc dialkyldithiophosphate (ZDDP) has been widely used as an anti-wear additive in engine oil formulations alongside other additives such as dispersants and detergents. Extensive research has been conducted to investigate the anti-wear properties of ZDDP, both individually and in combination with dispersants. Studies have shown that the addition of dispersants to ZDDP can influence its anti-wear performance in both antagonistic and synergistic ways. However, limited information is available regarding the interaction between these two additives in terms of their anti-friction properties. This study aims to examine the impact of dispersants on the anti-wear and anti-friction properties on ZDDP when combined in varying dosages.

2.0 LITERATURE SURVEY

Engine oils play a critical role in ensuring the smooth operation and longevity of internal combustion engines. They reduce friction, prevent wear, dissipate heat, and protect engine components from corrosion and contaminants. The performance of engine oils largely depends on their formulation, which includes various additives designed to optimize specific properties. These additives such as anti-wear (AW) agents, friction modifiers, detergents, dispersants, antioxidants, viscosity index (VI) improvers etc., are selected to ensure the oil's effectiveness under different operating conditions (Moser et al., 2012). Among these, anti-wear agents, particularly zinc dialkyl dithiophosphate (ZDDP), play an essential role in reducing friction and minimizing metal-to-metal contact, which is critical for enhancing engine efficiency and extending component life (Liu et al., 2020).

There may be interactions between different additives in the oil and the performance of engine oils is also influenced by these interactions. Dispersants, for example, maintain engine cleanliness by preventing the formation of sludge and deposits. These additives achieve this by keeping contaminants suspended in the oil. On the other hand, anti-wear agents like ZDDP form protective tribo-films on metal surfaces, which prevent excessive wear during boundary lubrication, a condition where the oil film is too thin to completely separate the contacting surfaces. However, the interaction between ZDDP and dispersants can either enhance or reduce the oil's overall lubrication performance, depending on factors such as additive concentration and the oil's composition (Kasprzyk et al., 2019). Therefore, understanding these interactions is crucial for designing more effective engine oils. The coefficient of friction (COF) is a key parameter in evaluating lubricant effectiveness over time. Previous studies have shown that base oil properties significantly influence frictional stability and lubrication efficiency (Smith et al., 2020; Lee and Kim, 2018).

The base oil in engine oil formulations is also a significant factor influencing lubrication properties. Base oils are classified into different groups, viz., Group I, Group II, Group III (mineral base oils), Group IV and Group V based on their types and refining processes. Group II oils have fewer impurities and better oxidative stability than Group I oils, making them more suitable for modern high-performance lubricants (Liu et al., 2020). The base oil affects not only the solubility and stability of the additives but also the oil's overall friction and wear reduction characteristics. The base oil properties and its compatibility with additives are also responsible for the overall efficiency of the lubricant in various operating conditions, especially under high stress or extreme temperatures.

The three lubrication regimes under which engine oil operates determine engine oils's design and performance. In hydrodynamic lubrication, a thick oil film separates the contacting surfaces, reducing friction and wear. However, in boundary lubrication, where the oil film is too thin to separate the surfaces, metal-to-metal contact occurs, which can lead to increased wear and friction. During boundary lubrication, the oil's ability to form protective tribo-films is crucial for minimizing wear. ZDDP is commonly used for this purpose, as it reacts with metal surfaces to form phosphate-based films that act as a protective barrier, reducing friction and wear (Wang et al., 2020). However, the presence of other additives, such as dispersants, can impact the formation and effectiveness of these tribo-films, highlighting the complexity of additive interactions.

Additive interactions in engine oils are complex and can have significant effects on their tribological properties. Dispersants, although vital for maintaining engine cleanliness, can interfere with the performance of anti-wear agents like ZDDP. For instance, some studies have shown that dispersants can hinder the formation of ZDDP tribo-films, reducing the oil's ability to protect against wear. Conversely, other studies have suggested that when combined in appropriate proportions, dispersants and ZDDP can work synergistically to improve lubrication performance by enhancing the formation of protective films while also maintaining engine cleanliness (Zhang et al., 2021). These varying interactions underline the importance of careful formulation and optimization of additives in engine oils. Zhang et al. (2021) investigated the effect of ZDDP and polymeric dispersants on friction and wear. Their results demonstrated that the interaction between these additives could be either synergistic or antagonistic wear protection depending on their concentrations and the base oil used. Similarly, Wang et al. (2020) studied primary and secondary ZDDP in combination with dispersants and observed that the presence of dispersants significantly influenced friction and wear behavior, further emphasizing the need to understand additive interactions in oil formulations.

This study aims to investigate the tribological performance of ZDDPs (both primary and secondary types) and dispersants and also effects of interactions between ZDDP and dispersants in engine oils under boundary lubrication conditions. By focusing on tribological performance and additive interactions and it's influence tribo-film formation and the oil's friction and wear performance, the research seeks to provide insights into how different additives and base oils interact to optimize lubrication under challenging conditions. The testing will be conducted using blends of primary and secondary ZDDP and nitrogen-based polymeric dispersants in Group I and Group II base oils, with tribological testing performed using a ball-on-disc test rig (SRV) and four-ball tester (Huh et al., 2019).

Through this research, a deeper understanding of the tribological properties of additive combinations will be gained, which could help in formulating engine oils that offer improved wear protection, enhanced fuel economy, and longer service life for engine components. The automotive industry faces increasing pressure to develop more efficient and sustainable technologies, and optimizing engine oils is a crucial step in meeting these challenges. The results of this study will contribute to the development of high-performance lubricants that reduce friction and wear, improving engine performance while supporting sustainability goals.

3.0 MATERIALS & METHOD

3.1 Tribological Experimental Setup

In this study two tribological experimental techniques were used viz., Four Ball Test and SRV Test.

3.1.1 Four-Ball Wear Test Machine

The anti-wear properties of lubricants under modest loads are assessed using four-ball wear test equipment. The test consists of three balls firmly fixed in an oil cup called ball pot and the fourth ball is held in a rotating spindle. An electric motor is used to rotate the spindle. The rotating ball is loaded against the three stationary balls either using dead weights or a pneumatic loading device. Tests are run under pre-decided test conditions, such as load speed, duration, and temperature. After the test, three bottom balls are taken out and their wear scar diameters are measured using a 0.01 mm accuracy microscope. Two measurements are taken on each ball as sometimes they are elliptical. Mean Wear Scar Diameter (MWSD) is the average of six scars. A good oil will give a lower MWSD. Following are the test conditions for this test.

Table 1. Test Conditions for evaluation on four-ball wear test, as per ASTM D4172

Parameter	**Test Conditions**
Load, kg	40
Temperature, ˚C	75
Spindle speed, RPM	1200
Duration, h	1

3.1.2 SRV Tester

The SRV Tester is a reciprocating device used to evaluate the EP and anti-wear properties of greases and lubricants. The Optimol SRV®5 oscillation system was selected for the measurement of COF. It is a linear reciprocating type friction and wear test. A steel ball reciprocates on a flat disc. The load is applied through a spring, and the reciprocating motion is created by an electro-mechanical drive. The oil is heated by heaters placed under the disc. A Linear Variable Differential Transformer (LVDT) measures and controls the amplitude, while a Programmable Logic Controller (PLC) controls the temperature. Load cells measure the load applied to the specimen and the COF. A Data Acquisition System collects the output data. The ASTM D6425 test method has been used for evaluating the COF for the oil. During the test, a continuous graph of the Coefficient of Friction COF is available throughout the test. From the COF graph, specialised software calculates minimum COF (fmin), maximum COF (fmax), and mean COF (fmean). At the end of the test duration, the wear scar diameter is measured along the X-axis and Y-axis, and the Mean Wear Scar Diameter is reported.

Table 2. Test Conditions for evaluation on SRV, as per ASTM D6425

Parameter	**Test Conditions**
Temperature, °C	50
Duration, h	2
Load, N	300
Frequency, Hz	50
Amplitude, mm	1
Precision for Coefficient of Friction	
Repeatability	0.01
Reproducibility	0.03
Precision for Wear Scar Diameter	
Repeatability, mm	0.07
Reproducibility, mm	0.20

Repeatability

To establish the repeatability of the two test methods, data has been generated on two reference oils to draw error bars as per details given below

1. Wear scar diameter (WSD) data generated on Four-Ball wear test machine on a laboratory-prepared reference oil containing ZDDP in a mineral base oil. Five repeat tests were conducted in accordance with ASTM D4172. The results obtained were 0.66 mm, 0.64 mm, 0.60 mm, 0.61 mm, and 0.63 mm respectively. The average WSD of the five tests was 0.63 mm, and the stand deviation was 0.02 mm

2. Similarly, Coefficient of friction (COF) data were generated on SRV on a reference oil supplied by Optimol Instruments, Germany, the supplier of the machine. Here again five repeat tests were conducted as per standard test method supplied by the manufacturer. The results obtained were 0.130, 0.128, 0.124, 0.121, and 0.121 mm respectively. The average COF of the five tests was 0.125, and the stand deviation was 0.004

Data of both WSD and COF fall within ± 2 times the standard deviation with 95% confidence level.

3.1.3 Samples (Blends) Evaluated

Table 3gives the details of the active component (chemistry) of each additive. Tables 4-8 shows the details of the samples studied i.e., the blends of individual additives and combinations of additives in the two base oils used for the study.

Table 3. Details of active components of additives studied

Code	Components
A	Primary ZDDP
B	Secondary ZDDP
C	N-based Polymeric Dispersant
N	Group I Base Oil
J	Group II Base Oil

Table 4. Details of the Base oil used for the study

Candidate	Composition (%Wt.)
N0	100% (Group I Base Oil)
J0	100% (Group II Base Oil)

Table 5. Blends of only Primary ZDDP

Candidates	N0 /J0 (Base Oil) (%Wt.)	NA1 /JA1 (%Wt.)	NA2 / JA2 (%Wt.)	NA3 / JA3 (%Wt.)
A	-	0.75	1.00	1.25
N/J	100.00	99.25	99.00	98.75
Total	100.00	100.00	100.00	100.00

Table 6. Blends of only Secondary ZDDP

Candidates	NB1 / JB1 (%Wt.)	NB2 / JB2 (%Wt.)	NB3 / JB3 (%Wt.)
B	0.71	0.95	1.19
N/J	99.29	99.05	98.81
Total	100.00	100.00	100.00

Table 7. Blends of only Dispersant

Candidates	NC1 / JC1 (%Wt.)	NC2 / JC2 (%Wt.)	NC3 / JC3 (%Wt.)
C	5.25	7.00	8.75
N/J	94.75	93.00	91.25
Total	100.00	100.00	100.00

Table 8. Blends of Dispersant and Primary ZDDP combinations

Candidates	NCA1 / JCA1 (%Wt.)	NCA2 /JCA2 (%Wt.)	NCA3 / JCA3 (%Wt.)	NCA4 / JCA4 (%Wt.)	NCA5 / JCA5 (%Wt.)
A	1.00	1.00	1.00	0.75	1.25
C	5.25	8.75	7.00	7.00	7.00
N/J	93.75	90.25	92.00	92.25	91.75
Total	100.00	100.00	100.00	100.00	100.00

Table 9. Blends of Dispersant and Secondary ZDDP combinations

Candidates	NCB1 / JCB1 (%Wt.)	NCB2 /JCB2 (%Wt.)	NCB3 / JCB3 (%Wt.)	NCB4 / JCB4 (%Wt.)	NCB5 / JCB5 (%Wt.)
B	0.95	0.95	0.95	0.71	1.19
C	5.25	8.75	7.00	7.00	7.00
N/J	93.80	90.30	92.05	92.29	91.81
Total	100.00	100.00	100.00	100.00	100.00

4.0 RESULTS AND DISCUSSION

4.1 Base Oil

4.1.1 Anti-Frictional Property

The Fig.1 shows that initially, both Group I and II (N0 and J0) oils exhibited low COF, but N0 experienced a sharp spike at around 1000 seconds, indicating possible boundary lubrication failure or surface interaction issues, whereas J0 maintained stability. Over time, N0 stabilized but maintained a higher COF, while J0 showed a gradual and more controlled increase. The COF was observed lower for Group I during the initial stage than Group II base oil. However, after 2000 seconds their behavior are same.

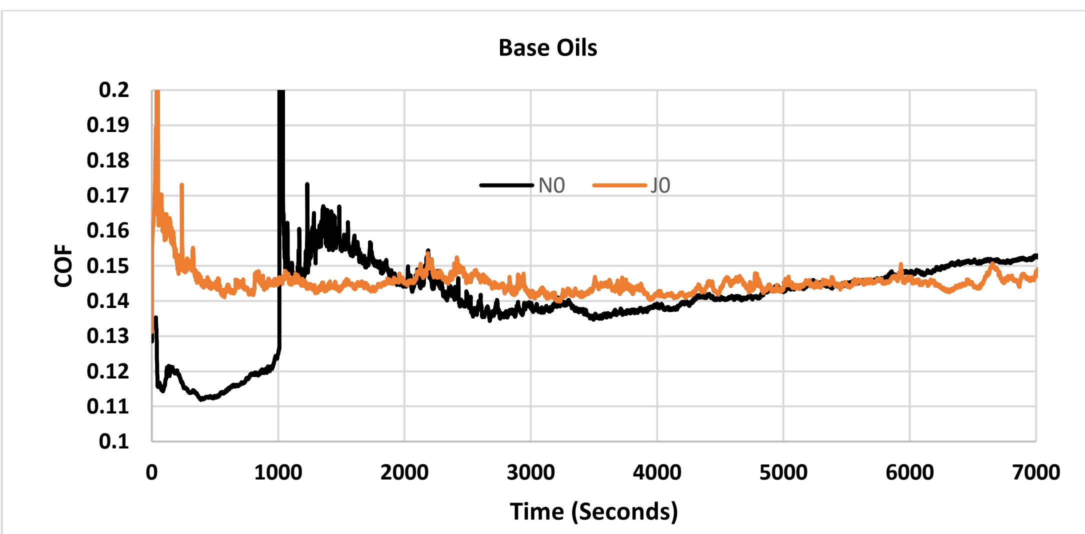

Fig.1 Base Oils: Coefficient of Friction (COF)

4.1.2 Anti-Wear Property

The Wear Scar Diameter values in Table 10 reveal that J0 gives significantly less wear compared to N0, slightly.

Table 10. Wear Scar diameter values of base oils

Code	Base oil	Wear Scar Diameter Value, mm
N0	Group I Base Oil	0.85
J0	Group II Base Oil	0.88

4.2 Primary ZDDP

4.2.1 Anti-Frictional Property

As mentioned above, between the two base oils, Group II oil exhibits lower and more stable coefficients of friction (COF) than Group I oil, indicating superior lubrication properties. However, for both base oils (Fig.2and3) there is an initial spike before stabilizing, but Group II oils maintains a more consistent COF with less fluctuation. The addition of Primary ZDDP, promotes stable tribo-chemical film by preventing film breakage compared with the base oil alone. In Group II base oil the lower (JA1) and higher (JA3) dosages gave lower COF than the middle (JA2) dosage. There is no significant difference in COF at the three dosages in Group I base oil.

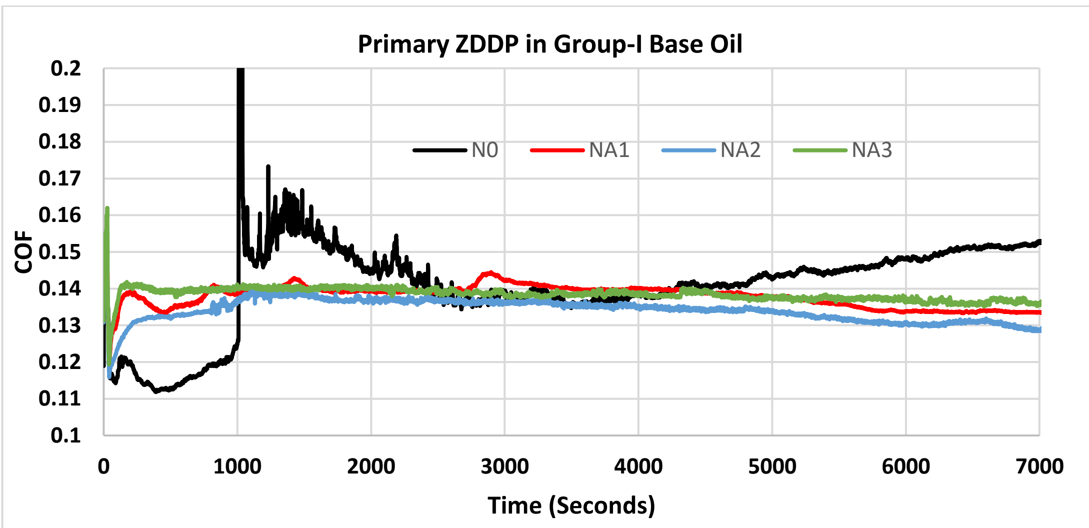

Fig.2 Primary ZDDP: Coefficient of Friction (COF)

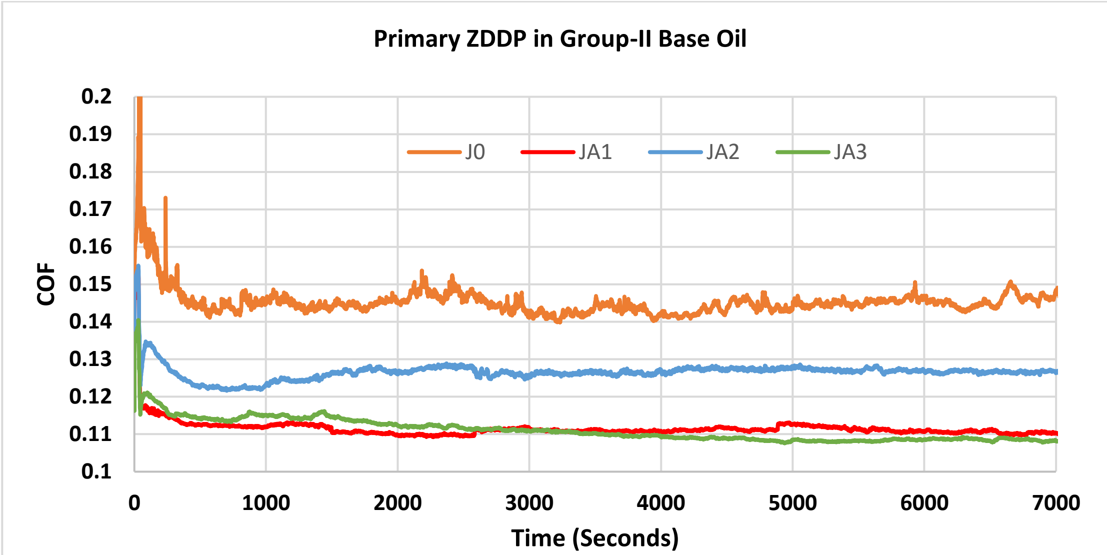

Fig.3 Primary ZDDP: Coefficient of Friction (COF)

4.2.2 Anti-Wear Property

The wear scar diameter (WSD) results indicate (Fig.4) that base oils alone gives higher wear, while the addition of ZDDP significantly reduces wear. Among the tested oils, those with ZDDP in Group I exhibit slightly better wear protection than those in Group II. Overall, Group I Base Oil: ≈50% reduction in wear scar diameter. Group II Base Oil: No significant change in wear scar diameter.

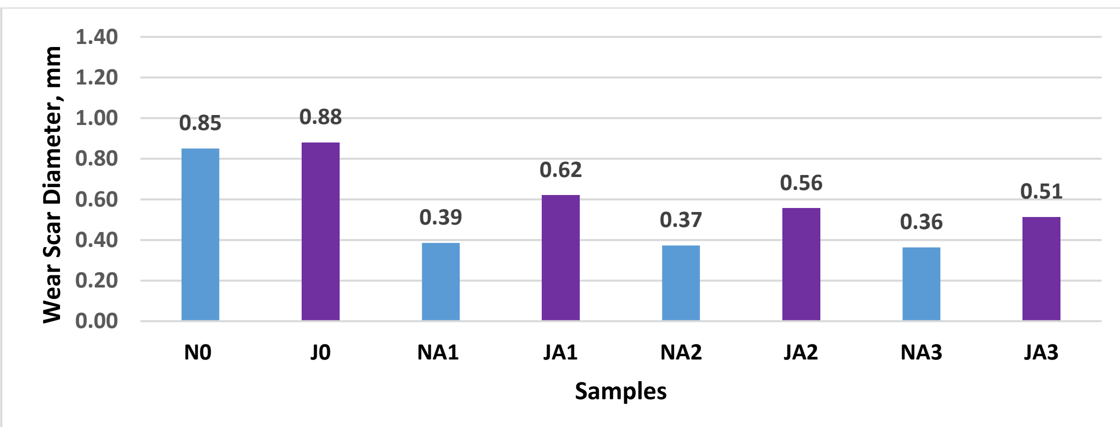

Fig.4 Primary ZDDP: Wear Scar Diameter

4.3 Secondary ZDDP effect in Base Oils

4.3.1 Anti-Frictional Property

As shown in Fig.5, in Group I base oil, the higher dosage of ZDDP (NB3) gives lower COF during the test duration compared to others. There is no significant difference in COF at the three dosages in Group II base oil (Fig.6). Performance of both Primary and Secondary ZDDP in Group II base oil is better than in Group I base oil. This suggests that Group II oil responds more effectively to Anti Wear additive than Group I oils.

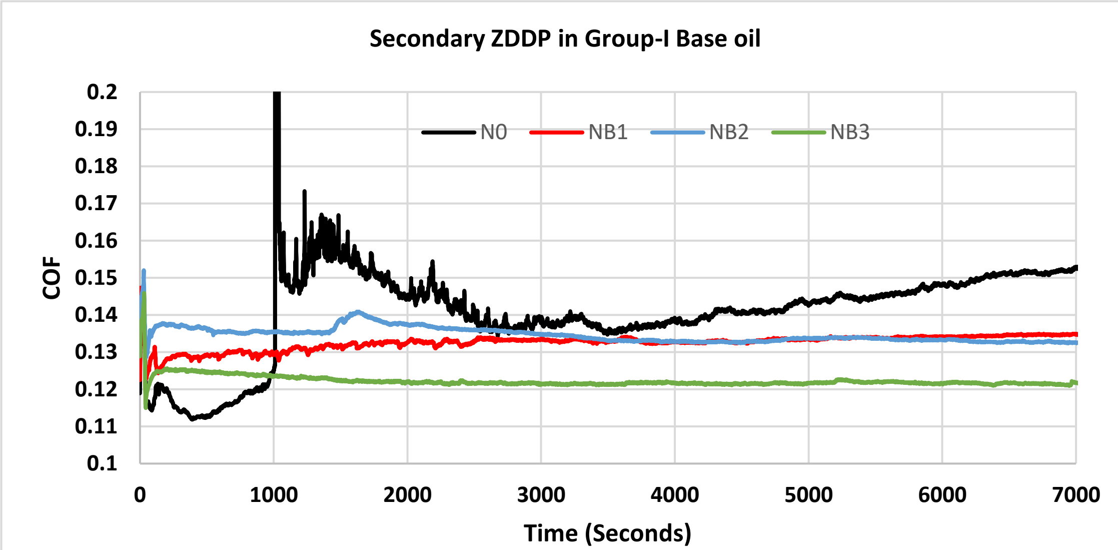

Fig.5 Secondary ZDDP: Coefficient of Friction (COF)

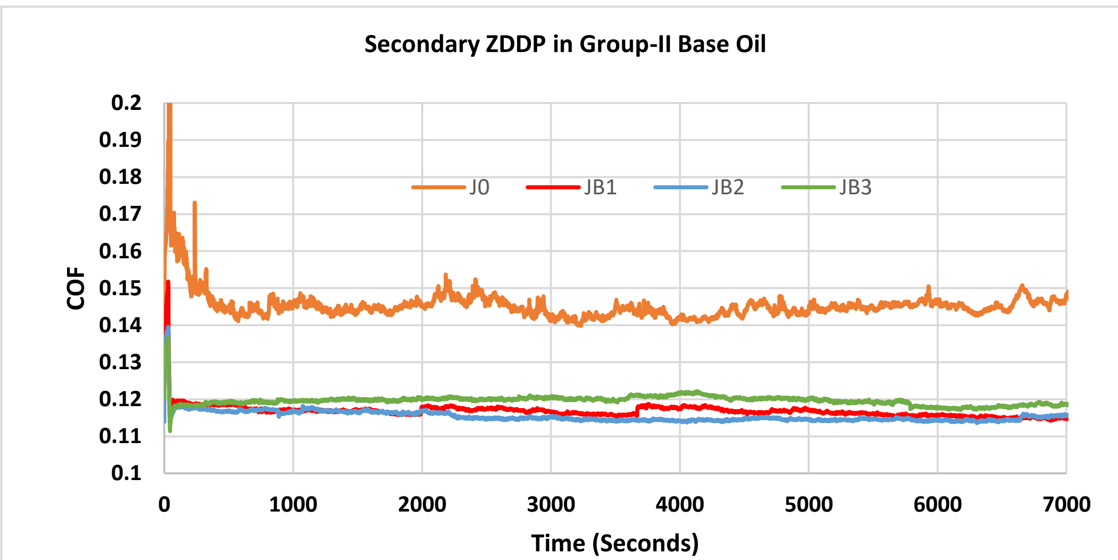

Fig.6 Secondary ZDDP: Coefficient of Friction (COF)

4.3.2 Anti-Wear Property

In both base oils (Fig 7), as the additive dosage increases, the WSD progressively decreases or wear protection enhances. At the highest additive dosages (NB3 and JB3) the lowest WSD is achieved. However, at each dosage level, Group I oil blends (NB series) exhibit lower WSD compared to Group II oils (JB series), suggesting that secondary ZDDP performs more effectively in Group I oils. This could be due to differences in base oil composition, which influence ZDDP's ability to form protective anti-wear films. Overall Group I Base Oil: ≈50% reduction in wear scar diameter. Group II Base Oil: No significant change in wear scar diameter.

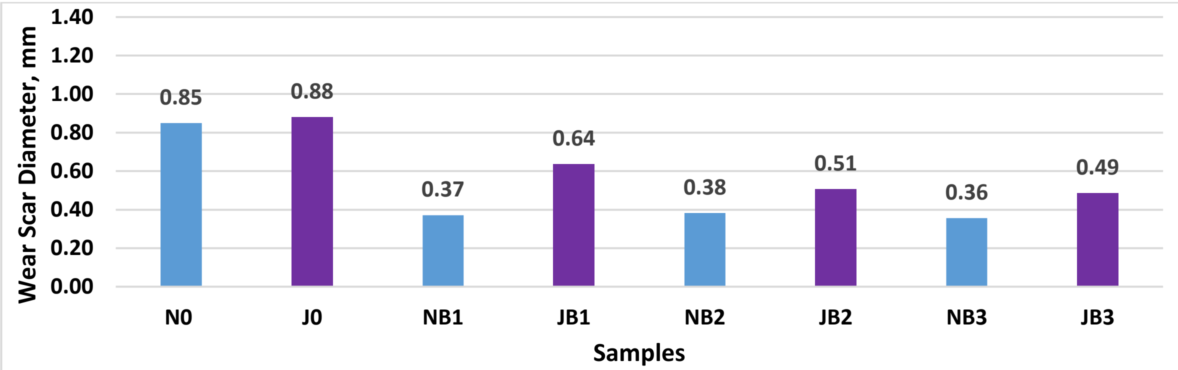

Fig.7 Secondary ZDDP: Wear Scar Diameter (COF)

4.4 Dispersants effect in Base Oils

4.4.1 Anti-Frictional Property

The graphs (Fig. 8 and 9) presents the coefficient of friction (COF) curves for dispersant blends and compare with the respective base oil. Initially, for all samples there is a spike or high COF, which quickly stabilizes. JC1 shows a slightly higher COF than J0 plain base oil, followed by JC2 (optimal dispersant dosage), while JC3 (higher dispersant dosage) exhibits the highest COF. Over a period, all samples display a gradual increase in COF, suggesting progressive deterioration in performance or oil degradation. These trends indicate that there is an increase in COF when dispersants are added in the base oil either it is Group I or Group II, no variations when the dosages are changed in both base oils.

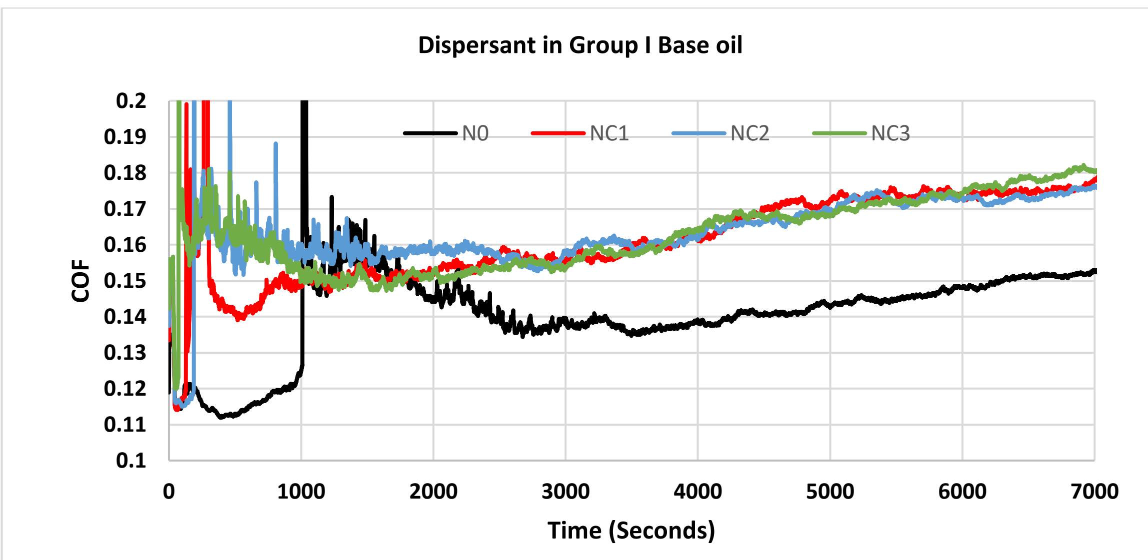

Fig.8 Dispersant: Coefficient of Friction (COF)

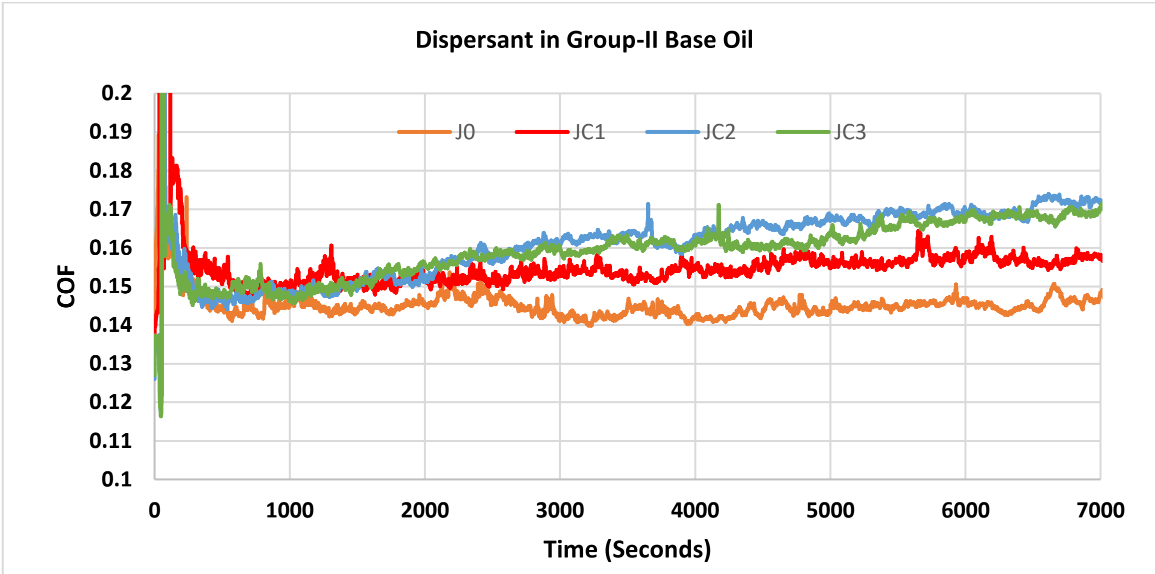

Fig.9 Dispersant: Coefficient of Friction (COF)

4.4.2 Anti-Wear Property

The data (Fig.10) indicates that adding dispersants to base oils significantly improves the anti-wear performance, as evidenced by the lower Wear Scar Diameter (WSD) values in dispersant-containing samples compared to the base oils.

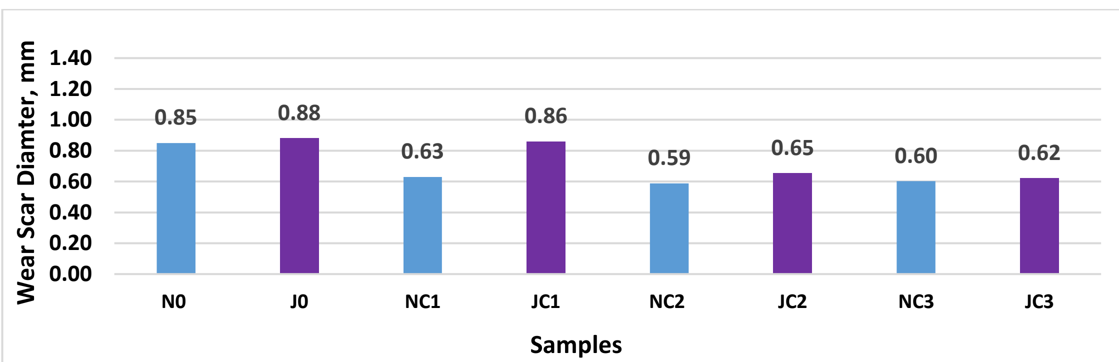

Fig.10 Dispersant: Wear Scar Diameter

Among the tested samples, some blends exhibited better wear reduction than others, suggesting that the effectiveness of dispersants varies depending on the composition: as the proportion of the additive increases, the WSD values decrease.

Overall, Group I Base Oil: ≈30% reduction in wear scar diameter. Group II Base Oil: Slight increase in wear scar diameter.

4.5 Dispersant with Primary ZDDP

4.5.1 Anti-Frictional Property

In Group I: The trend of coefficient of friction of combination of primary ZDDP and dispersant in Group I base oil is given in the graph (Fig.11). It is seen that adding the dispersant with primary ZDDP reduces the COF values compared to individual values of ZDDP alone (Fig.2), indicating a synergistic effect with dispersant. The minimum COF was achieved with the medium dosage of primary ZDDP and higher dispersant dosage combination. The maximum COF occurred with the higher ZDDP dosage and the medium dispersant dosage combination.

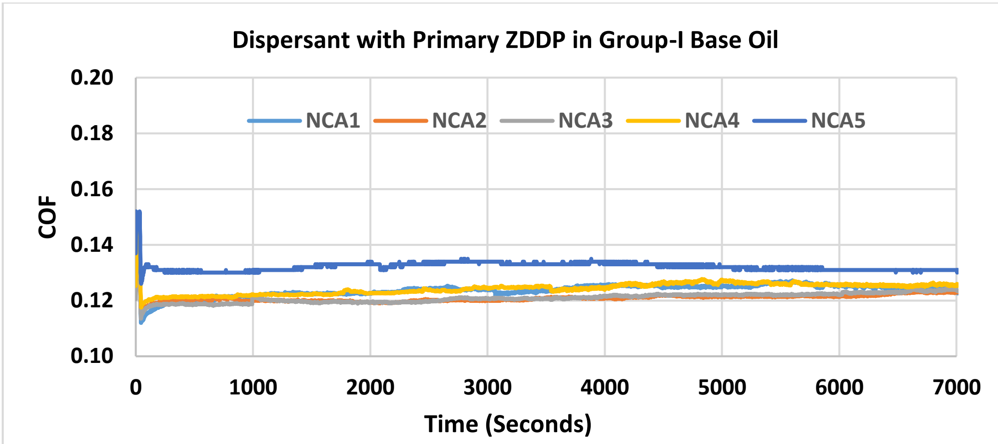

Fig.11 Dispersant with Primary ZDDP: Coefficient of Friction (COF)

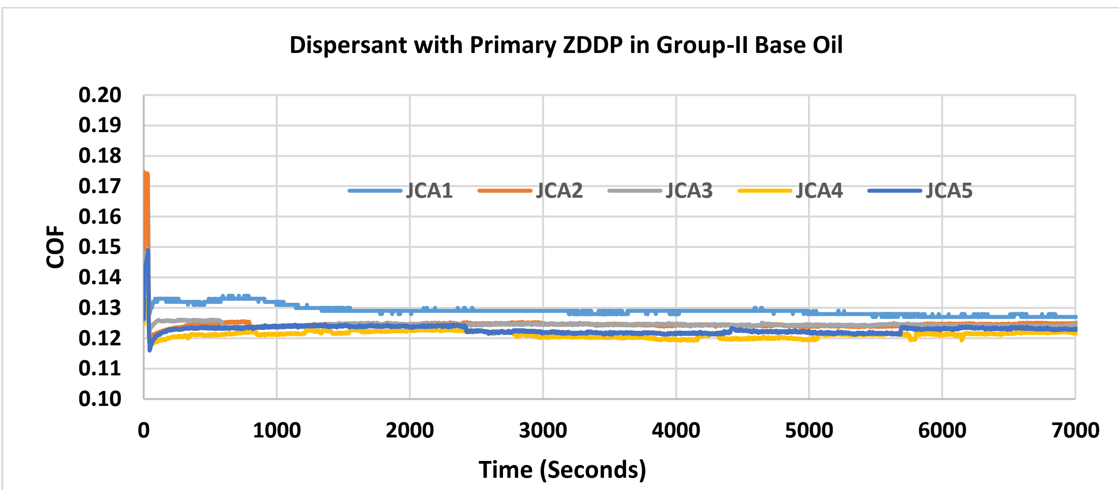

Fig.12 Dispersant with Primary ZDDP: Coefficient of Friction (COF)

In Group II: The corresponding COF plots are given in the Fig. 12. On comparing the values of COF of these combinations with the individual values of ZDDP (Fig.3), it is seen that the COF values of the combinations are more or less same as that of ZDDP alone but in all samples there is stable state after slight initial increase. After stabilization, all samples show consistent COF, ensuring reliable performance over time. Adding the medium dispersant dosage with either lower or higher ZDDP dosage increase COF values more compared to individual values, indicating an antagonistic effect. The differences in COF trends between Group I and Group II base oils suggest that base oil type affects ZDDP performance.

4.5.2 Anti-Wear Property

The data of wear for the blends of combination of primary ZDDP with dispersant in Group I and II base oils is given in Fig.13 and 14 respectively.

For Group I base oil: The blends of mixture of additives (NCA series) is shown in Fig.13. The data shows that there is an increase of wear for primary ZDDP and dispersants blends compared to the primary ZDDP alone. Therefore, there is an antagonistic effect on wear when primary ZDDP is mixed with dispersant in Group I base oil. Among the blends of mixture of additives, the lowest WSD values are observed for medium dispersant dosage with medium/lower ZDDP dosage, indicating that a balanced combination of dispersant and ZDDP provides better wear protection. However, an excess ZDDP dosage does not necessarily improve wear resistance and, it is seen in some cases that it may lead to increased wear or more antagonistic effect.

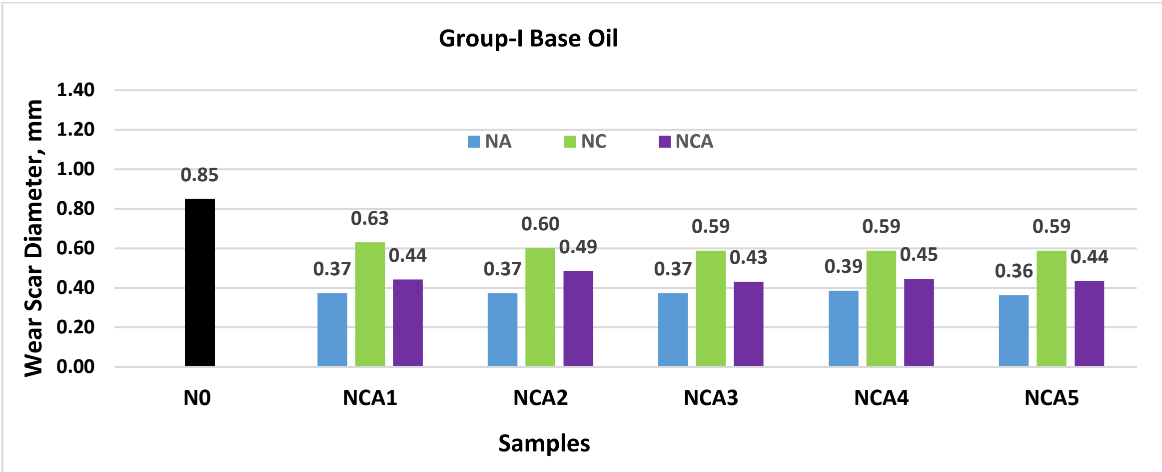

Fig.13 Dispersant with Primary ZDDP: Wear Scar Diameter

For Group II base oil: As observed in Fig.14, in mixture of additives in Group II oil (JCA series), the blends exhibit superior wear reduction compared to individual additive blends (JA and JC series) showing a synergistic effect clearly. The lower and optimal dosages of ZDDP with optimal dose of dispersant blends demonstrate the best wear protection, reinforcing the idea that an optimized dispersant-ZDDP combination is crucial for achieving better wear.

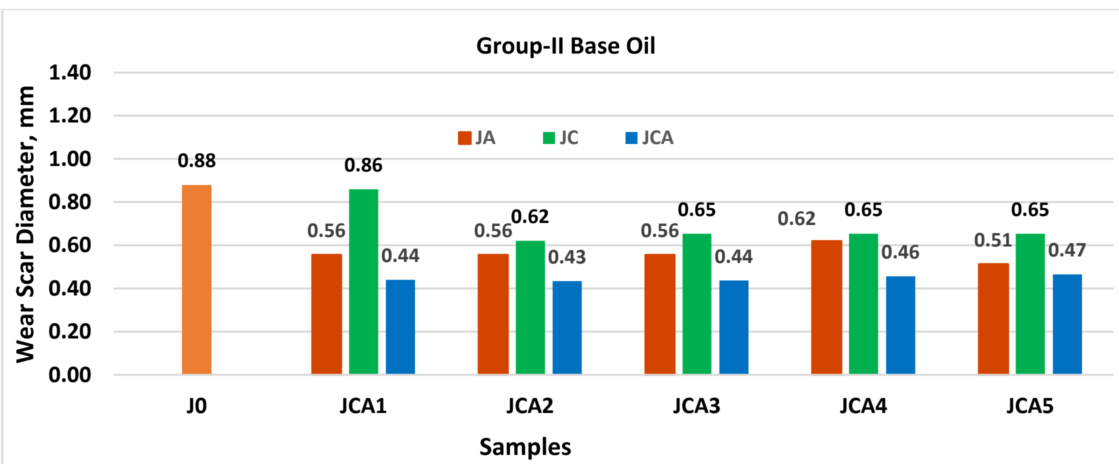

Fig.14 Dispersant with Primary ZDDP: Wear Scar Diameter

Overall, the wear trend analysis indicates that a well-balanced ratio of dispersant and ZDDP leads to the lower wear, while an excessive or suboptimal additive combination may result in higher WSD values due to possible antagonistic effects. The results emphasize the need for precise additive formulation in lubricant development to enhance anti-wear performance effectively.

4.6 Dispersant with Secondary ZDDP

4.6.1 Anti-Frictional Property

The antifriction performance of mixtures of the secondary ZDDP with dispersant is shown in Fig. 15 and 16.

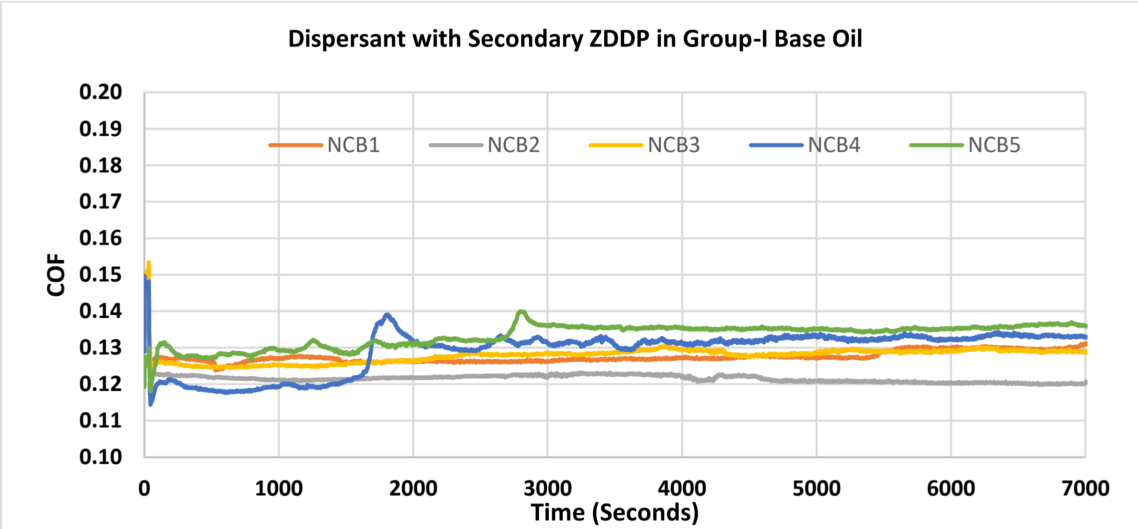

Fig.15 Dispersant with Secondary ZDDP: Coefficient of Friction (COF)

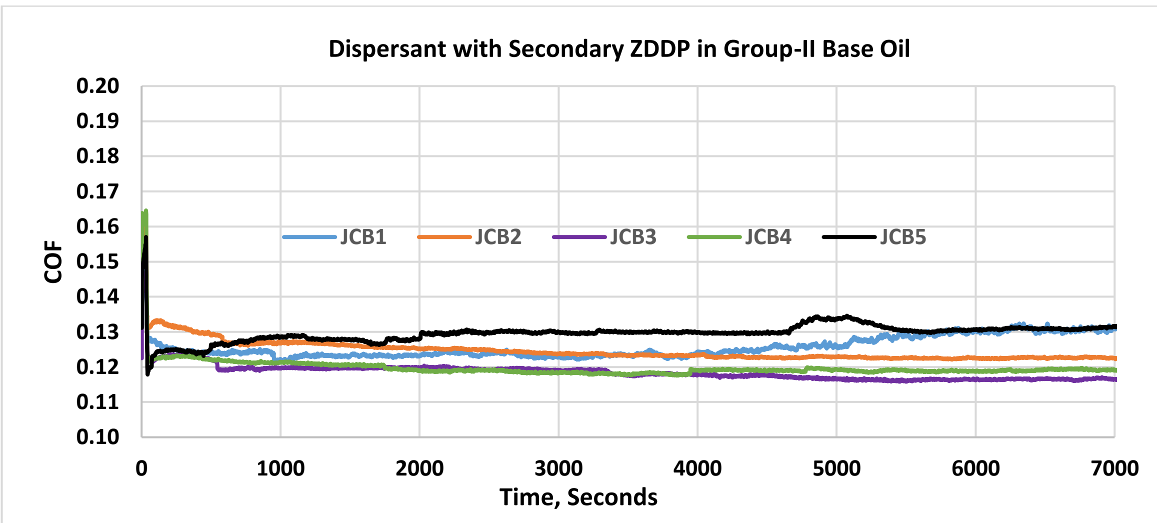

Fig.16 Dispersant with Secondary ZDDP: Coefficient of Friction (COF)

In Group I: When comparing the values of COF values of the additive blends (Fig.15) with the curves of secondary ZDDP alone (Fig.5), it is seen that on combining the dispersant with secondary ZDDP, overall, a minor lowering of COF values is observed indicating synergistic effect at optimum dosage. Among the different blends, medium dose of ZDDP and lower dispersant dosage has the lowest COF, making it the best at reducing friction. Some blends (NCB2–NCB5) have slightly higher COF values with minor variations, possibly due to surface interactions or lubrication inconsistencies. However, all samples stay within the 0.12–0.14 COF range, proving Group I Base Oil ensures friction stability. Overall, adding dispersant with secondary ZDDP lowers COF values compared to their individual values, indicating synergistic effect at the medium dosage.

In Group II: On comparing the graphs in Fig.16 with the plots of the individual additives in Fig. 6 shows that, overall, the combination of dispersant and secondary ZDDP at the medium dosage shows no change in COF. Adding lower dispersant dosage with medium dose of secondary ZDDP increases COF compared to individual values resulting into an antagonistic effect.

4.6.2 Anti-Wear Property

The data of anti-wear characteristics of blends of mixtures of secondary ZDDP with dispersant in Group I and II base oils (NCB and JCB series) is presented in Fig. 17and18.

Group I oil: Due to the addition of dispersant along with secondary ZDDP, there is an increase in wear scar diameter on all the dosages for Group I base oil: Antagonistic Effect

Group II Oil: Due to the addition of dispersant along with secondary ZDDP, there is a marginal reduction in wear scar diameter on all the dosages for Group II base oil: Synergistic Effect.

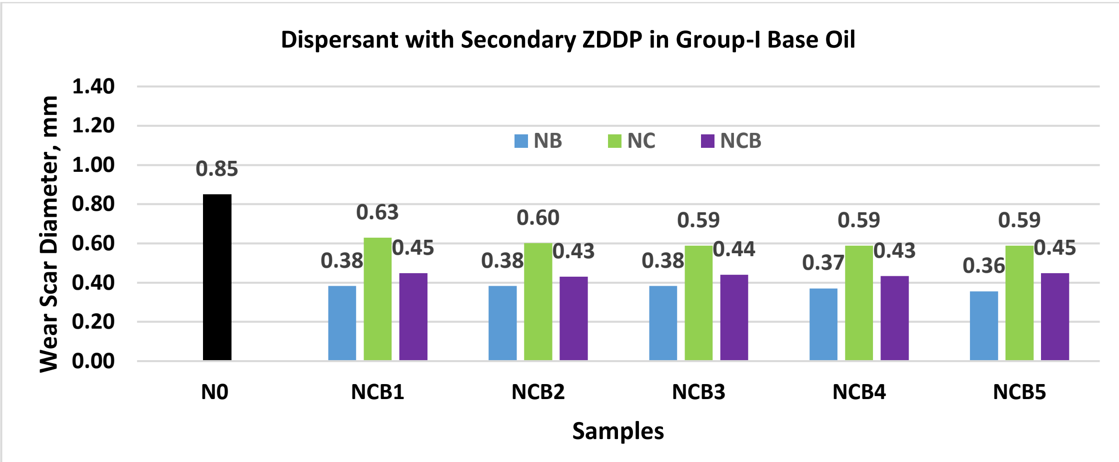

Fig.17 Dispersant with Secondary ZDDP: Wear Scar Diameter

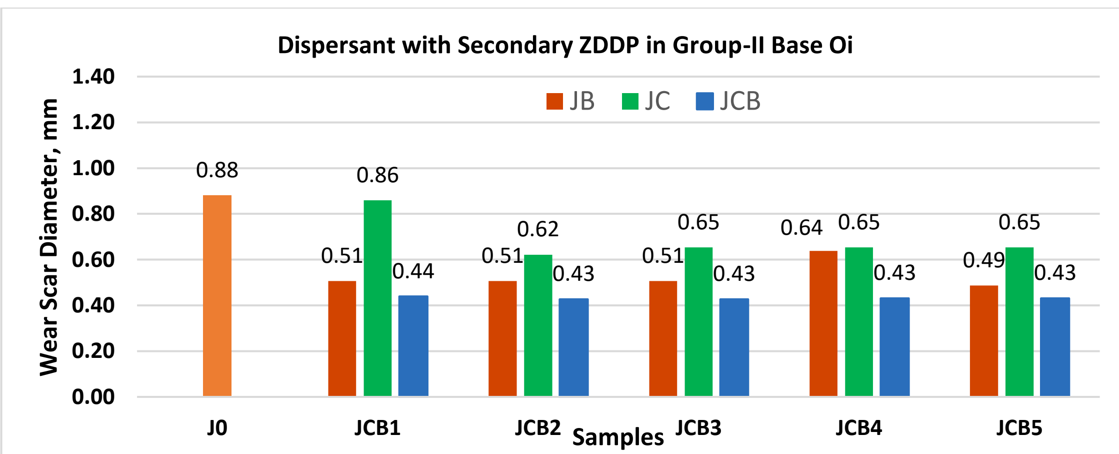

Fig.18 Dispersant with Secondary ZDDP: Wear Scar Diameter

5.0 Conclusion

A study was conducted to determine individual performance in antifriction and anti-wear properties of primary and secondary ZDDPs, dispersant additive in different base oils and also the influence of dispersants on the anti-wear and anti-friction properties of ZDDPs at different dosages. The individual performance of these additives vary among themselves and also differ according to the base oils in which it is used. It was also found that adding dispersants to a blend containing anti-wear additives alters friction and wear properties in both antagonistic and synergistic ways. The effect varies based on the base oil type and the dosage of anti-wear additives and dispersants. Dispersants alone deteriorate the anti-wear properties of Group II base oil but enhance them in Group I base oil. In Group I base oil, an overall improvement in anti-friction properties is observed with the addition of dispersants in formulations containing Primary/Secondary ZDDP. Meanwhile, in Group II base oil, dispersants improve overall anti-wear properties in formulations containing Primary/Secondary ZDDP. The data can be used for formulating energy-efficient engine oils.

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