ISSN 0208-7774 TRIBOLOGIA 2/2022 p. 7–13
DOI: 10.5604/01.3001.0015.9716

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THE COMPLETE APPROACH TO THE IMPACT OF SELECTED LUBRICATING ADDITIVES ON THE TRIBOLOGICAL PROPERTIES OF ENGINE OILS BY MEANS OF A PARTIAL EXPERIMENTAL DESIGN

KOMPLEKSOWE UJĘCIE WPŁYWU WYBRANYCH DODATKÓW SMARNOŚCIOWYCH NA WŁAŚCIWOŚCI TRIBOLOGICZNE OLEJÓW SILNIKOWYCH ZA POMOCĄ CZĄSTKOWEGO PLANU EKSPERYMENTU

Key words: lubricating additives, engine oil, wear.

Abstract: This paper presents the effect of lubricating additives used in engine oils on wear processes characteristic of rolling contact in the presence of a lubricating medium. A comprehensive approach to the problem was proposed by applying a D-optimal poliselective experimental design incorporating the influence of the most significant operational factors (load, temperature and lubricating additives). The study aimed to compare the effect of lubricants on surface wear at elevated temperatures using oils typical of engines used in passenger vehicles as a base enriched with additives. Using graphite, molybdenum disulphide, and ultra-dispersible copper particles can bring advantages and disadvantages that will increase the wear of engine components instead of prolonging their operation. Tribological tests were carried out on a T-03 tribotester (four-ball apparatus) under operating conditions taking into account the influence of temperature, load, type of additive or engine oil of different viscosity. The tribological tests carried out made it possible to determine the values of friction coefficients and the durability of the tested combination, while metallographic tests made it possible to determine the wear trace and, thus, the intensity of wear.

Słowa kluczowe: dodatki smarnościowe, olej silnikowy, zużycie.

Streszczenie: W artykule przedstawiono wpływ użytych w olejach silnikowych dodatków smarnościowych na procesy zużywania charakterystyczne w skojarzeniu tocznym w obecności medium smarnego. Zaproponowano kompleksowe podejście do zagadnienia poprzez zastosowanie D-optymalnego poliselekcyjnego planu eksperymentu ujmującego wpływ najbardziej istotnych czynników eksploatacyjnych (obciążenia, temperatury i dodatków smarnościowych), którego celem było porównanie wpływu środków smarnościowych na powierzchniowe zużycie w podwyższonej temperaturze z zastosowaniem olejów typowych dla silników stosowanych w pojazdach osobowych jako bazy wzbogaconej dodatkami. Zastosowanie grafitu, dwusiarczku molibdenu i ultradyspersyjnych cząstek miedzi może przynieść zarówno korzyści, jak i negatywne aspekty, które spowodują wzrost zużycia podzespołów silnika zamiast wydłużyć jego działanie. Badania tribologiczne przeprowadzono na tribotesterze T-03 (aparat czterokulowy) w warunkach eksploatacji uwzględniających wpływ temperatury, obciążenia, rodzaju dodatku czy oleju silnikowego o różnej lepkości. Przeprowadzone badania tribologiczne pozwoliły na określenie wartości współczynników tarcia oraz trwałości badanego skojarzenia, a badania metalograficzne na określenie śladu zużycia, a tym samym intensywności zużywania.

INTRODUCTION

Modern engine oils consist of a base oil and an additive package. Almost 20% of the volume of currently manufactured engine oils consists of additives; the remaining 80% is a mixture of base oils. Additives improve the overall quality of the oil, including tribological properties. Even the best oil base is not able to protect engine components against high temperatures and shear forces, against

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chemicals contained in fuels and against water, causing corrosion **[L. 1]**.

After analysing the available literature **[L. 2, 3, 4, 5]** and adopting the criterion of application time, the lubricating additives used in oils may be divided, on the basis of popularity and availability, into the following groups:

(a) graphite (used as a first and simple additive for lubricating greases),
(b) molybdenum disulphide,
(c) metallic additives with low shear strength (e.g., Cu nanoparticles).

The authors of the paper **[L. 3]** used graphite-based additives and concluded that additional tests should be carried out to confirm the beneficial effect of lubricating additives of this type on tribological properties. On the other hand, the authors of the paper **[L. 6]** used a nano-additive with the structure of molybdenum and carbon disulphide. The study showed that the use of the additive increases viscosity, which is beneficial during cold engine start-up. The shear strength of copper changes as a function of temperature from 110 MPa at ambient temperature to 5 MPa at 900°C, which makes it possible to use friction-deposited Cu coatings to reduce friction and wear of associations, e.g., piston rings/cylinder liner of an internal combustion engine or piston compressor **[L. 7]**. Adding 0.1% Cu nanoparticles to Lotos Semisyntehtic engine oil and to Mixol 0.1% oil allowed the friction coefficient to be maintained in the range of 0.01––0.02 under limited lubrication simulating cold engine conditions start-up conditions at pressures of 2 MPa and speeds of 0–1 m/s. The paper **[L. 8]** presents the results of tribological tests carried out on a four-ball apparatus to determine the effect of base oil modification with copper nanoparticles and copper oxides of granulation 40 and 100 nm. It was found that modification of base oil with the discussed copper nanoparticles, added in the amounts of 0.02% and 0.25% wt. % does not significantly improve tribological properties of steel friction nodes, i.e., reduces their wear and increases their resistance to seizure. Due to its structure, Molybdenum disulphide is characterised by a high molecular bond energy within the layer and lower bond energy between atoms from neighbouring layers. Consequently, it has low shear strength and works as a solid lubricant. In a tribological paper **[L. 2]**, the authors tested a rolling bearing material made of EN31 alloys under lubrication conditions with conventional oil of viscosity SAE 20W40 with the addition (0.5 wt% and 1 wt%) of MoS_2 particles. They found that as the diameter of the MoS_2 particles decreased, the value of the friction coefficient decreased, and wear decreased from about 30% to 60% compared to the lubricant without the additive.

This study aims to determine the effect of lubricity additives used in engine oils of different viscosities at ambient and high temperatures. The application of the D-optimal poliselective experimental design, taking into account the influence of factors (load – Q, oil viscosity – η, additive density – δ), made it possible to determine the operation function, i.e., the dependence of friction forces (F) and the area of the wear trace (P) depending on selected ambient conditions. Graphical interpretation of the results will make it possible to determine the positive/negative effects of introducing lubricating additives to engine oils.

MATERIALS AND METHODS

Tribological tests were carried out using a T-03 tribotester (modified four-ball surface testing apparatus) under variable load (**Fig. 1b**). The tests aimed at determining the friction coefficient

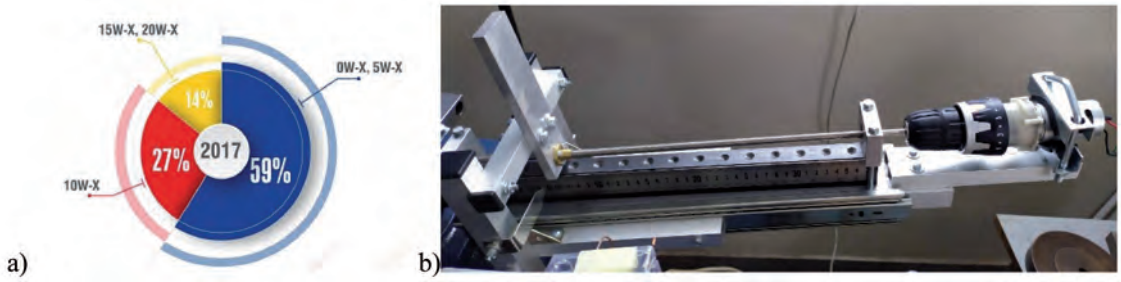


Fig. 1. Sale of oils for passenger vehicles, including viscosity classes (a) and tester for lubricant film durability with modified arm (tribotester T-03)

Rys. 1. Sprzedaż olejów dla pojazdów osobowych z uwzględnieniem klas lepkości (a) oraz zmodyfikowane ramię do badania trwałości filmu smarnego (tester T-03) and the dominant wear mechanism. The surfaces of wear traces obtained after tribological testing were subjected to metallographic tests, and then a quantitative metallographic analysis made it possible to determine the surface area of the wear trace. In this way, it was possible to determine the wear intensity.

The following engine oils with strongly different rheological properties were selected for testing, i.e., mineral oil 15W-40, semi-synthetic oil 10W-40 and synthetic oil 5W-30, while the quality class was the same, i.e., ACEA: A3/B3 due to wide application by manufacturers of internal combustion engines (**Fig. 1a**) **[L. 9]**.

Based on recommendations from manufacturers for selected oils and analysis of the available literature **[L. 1, 8]**, the following lubricating additives were selected:

- MoS_2 (2%),
- graphite (5%),
- Cu nanoparticles (Cu suspension stabilised with oleic acid, min. content 10%).

Extreme values of the contents of additives were selected based on manufacturers' recommendations and analysis of the effects of these additives on tribological properties of oils, as well as based on own experiences **[L. 2, 6, 8]**. The following were selected as controlled factors (affecting the friction force and size of wear surface area):

- additive content approx. 2–10%;
- additive density approx. 2–9 kg/m^3;
- oil viscosity approx. 70103 mm^2/s.

Engine oils of diametrically different viscosities were selected for the tests due to the differences in the wear mechanism and friction resistance and based on commercial data **[L. 9]**. Lubricating additives were chosen because of their availability and ease of preparation of suitable mixtures. The mass proportion was selected empirically, taking into account literature studies **[L. 2, 3, 5, 6, 7]** and our own preliminary studies related to sedimentation and taking into account the sedimentation and taking into account oil channels in the engine block and head. The density of the additive was taken as one of the controlled factors due to longer engine standstills and the possibility of sedimentation, which would reduce the content of the component.

TEST PROCEDURE

The tests were carried out using a four-ball apparatus (T-03) with a sliding mechanism that allows a fluent load change. The study was designed to determine the effect of lubricating additives contained in popular engine oils on selected tribological properties. The surface area of the wear path (P) and friction force (F) was adopted as measures of tribological properties, and friction force (F) was used as measures of tribological properties. The test was performed for about 12 s, depending on the load-displacement time on the tribotester arm. The load was selected so as not to cause scuffing and seizing of the cooperating balls in the friction node, as it would not be possible to carry out stereological tests of the surface layer.

Moreover, the load values were selected so as to obtain the surface pressures (3.03–51.50 MPa) adequate to those occurring in the contact area of the journal and bearing cup **[L. 10]**. The spindle rotational speed was 1450+50 rpm. The research was conducted based on a partial poliselective, D-optimal experimental plan **[L. 11]**. This plan assumes three levels of the controlling factor, i.e., minimum indicated by “-1”, central “0”, and maximum “+1”. The frictional forces and the surface areas of the wear path were taken as output quantities (dependent variables) (**Tables 3** and **4**). The plan makes it possible to determine the dependence based on only 11 measurement points and their appropriate combination in the considered parameter range from minimum to maximum. This makes it possible to shorten the overall testing time. Measurements were taken three times. The tests were performed with a four-ball apparatus ranging from ambient temperature to 90°C. The experiment was carried out under different operating conditions, and details are given in **Table 1**. A single test lasted twelve seconds, during which there was a smooth load change. Four new bearing balls made of 102Cr6 steel for each test were placed in the grips, and 0.01 dm^3 of the test lubricant with the specified lubrication additive was applied.

The quantity of additives was measured using a laboratory balance with an accuracy of 0.1 mg (**Table 2**). The mass fraction was selected based on the literature analysis presented in the introduction and own experience conducted during tribological tests on the T-03 test stand. An increase in the proportion of additives above the values presented in **Table 2** does not cause a significant improvement in tribological properties and a visible decrease in the intensity of wear (the 3-sigma rule – standard deviations).

Table 1. Overview of controlled factors
Tabela 1. Zestawienie czynników sterowanych

Value factor	X_1 Load Q [N]	X_2 Oil (viscosity in 40°C η [mm²/s])	X_3 Lubrication additive ρ [g/cm³])
-1	41.2	5W-30 (69.2 mm²/s)	Powdered graphite (2.23 g/cm³)
0	50.9	10W-40 (88.5 mm²/s)	MoS_2 (5.06 g/cm³)
+1	60.8	15W-40 (103.2 mm²/s)	Nanoparticles Cu (8.96 g/cm³)

In this way, a container with a mechanical mixer was used to obtain a homogeneous and consistent consistency of the oil and the lubricating additive, and the components were heated while being mixed together. This procedure guaranteed the dispersion of the lubricating additives into the oil matrix and made it possible to obtain a homogeneous mixture.

Table 2. Percentage content of additives in the prepared test oils
Tabela 2. Procentowy udział dodatków w przygotowanych olejach testowych

Lubricant additive type	Mass fraction
MoS_2	5%
Graphite powder	2%
Nanoparticles Cu	10%

Image analysis with the Metilo graphic software was used to calculate the wear surface area. Macrophotographs (8x) were taken of the ball surface after the tests, on which the dimensions of the wear trace were determined. The photographs were processed by filling the wear path with a contrasting colour. A quantitative metallographic analysis made it possible to determine the size of the actual wear path and to calculate the surface area using the software mentioned above (**Fig. 2**). If the programme does not automatically detect the surface of the wear trace, it is possible to change the sensitivity or, as a final option, to correct the analysed image (**Fig. 4f**) manually.

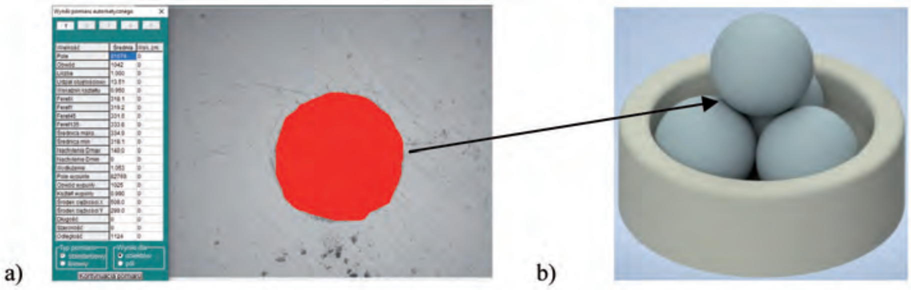


Fig. 2. Surface detection of the wear path (a) and the friction node under test (b)
Rys. 2. Detekcja powierzchni śladu zużycia (a) oraz rozpatrywany węzeł tarcia (b)

TEST RESULTS AND DISCUSSION

Tables 3 and **4** lists the results of surface area (S) measurements of wear traces from balls mounted in the base of the friction node and the averaged values of friction forces (F) acting during individual tests. The surface areas of the wear patches were determined based on quantitative metallographic analysis using the Met-Ilo program, and the number of repetitions of tribological tests guaranteed adequate statistics of the obtained results (standard deviation σ_S or the surface area and standard deviation σ_F for the friction force).

The analysis of the measurement results carried out based on the experimental plan was performed by determining the coefficients of the polynomial of the second degree, verifying their significance and the adequacy of the polynomial (by Fisher's test). The obtained polynomial of the second degree, as a result of applying the poliselective D-optimal experimental plan (results in **Tables 3, 4**), obtained the following equation in the normalised scale with its constant coefficients (k_{ij}):

$$z = k_0 + k_{11}x_1^2 + k_{22}x_2^2 + k_{33}x_3^2 + k_{13}x_1x_3 + k_{12}x_1x_2 + k_{23}x_2x_3$$

By calculating the operational function based on the above equation, it is possible to determine the direction of the curves of the surface area of the wear path and the maximum friction force depending on selected controlled factors (Q, η, ρ).

As a result of the calculations, operating functions were determined (**Fig. 3**) that define the influence of input factors (load, type of oil, type of lubricant additive) on tribological properties (friction forces and surface area of the wear path).

Table 3. Statement of results of tribological tests at 20°C
Tabela 3. Zestawienie wyników badań tribologicznych przy 20°C

No.	X_1	X_2	X_3	Average wear area S [μm^2]	Standard deviation σ_S [μm^2]	Max. friction force F [mN]	Standard deviation σ_F [mN]
01	-1	-1	+1				
02	+1	-1	-1	121609.67	34.27	2060	18
03	-1	+1	-1	37741.00	49.93	1940	11
04	+1	+1	+1	375831.33	62.67	7650	62
05	-1	0	0	74486.33	27.68	2170	34
06	+1	0	0	92455.00	34.00	2630	29
07	0	-1	0	89314.67	36.47	2300	19
08	0	+1	0	91214.00	19.29	1790	31
09	0	0	-1	91374.67	13.20	1610	28
10	0	0	+1	97184.67	17.56	3370	37
11	0	0	0	84506.67	32.52	3230	44

Table 4. Statement of results of tribological tests at 90°C
Table 4. Zestawienie wyników badań tribologicznych przy 90°C

No.	X_1	X_2	X_3	Average wear area S [μm^2]	Standard deviation σ_S [μm^2]	Max. friction force F [mN]	Standard deviation σ_F [mN]
01	-1	-1	+1				
02	+1	-1	-1	147513.82	69.20	725	29
03	-1	+1	-1	54619.61	15.68	579	13
04	+1	+1	+1	61985435.74	129.54	23571	112
05	-1	0	0	81674.98	19.35	880	32
06	+1	0	0	5496563.36	96.87	11650	78
07	0	-1	0	106566.49	37.29	8780	61
08	0	+1	0	117266.57	41.28	5561	47
09	0	0	-1	120169.62	31.41	1638	26
10	0	0	+1	181526.14	52.76	4285	39
11	0	0	0	121562.21	26.74	1490	29

It can be observed from **Figure 3** that the surface area of the wear path at the central load is larger (P = 1.8x107 μm^2) at a higher temperature. The lowest values were observed during friction with the highest viscosity engine oil with added graphite and the lowest viscosity oil with added copper particles. The addition of graphite causes the contact to be able to carry high loads even

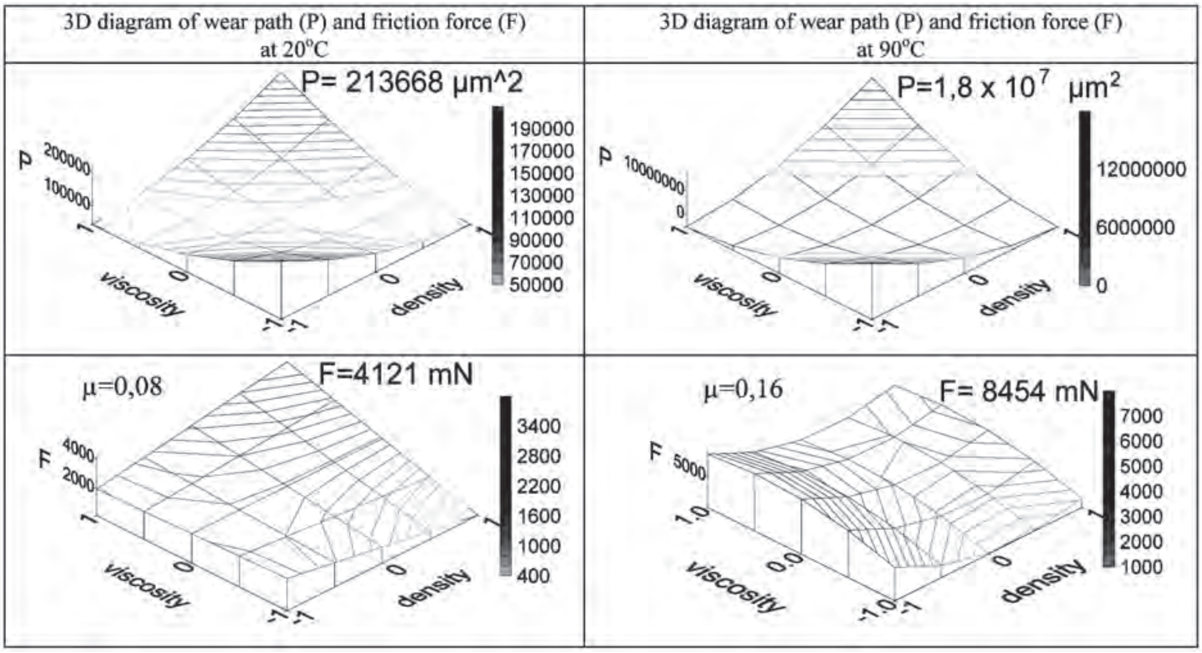
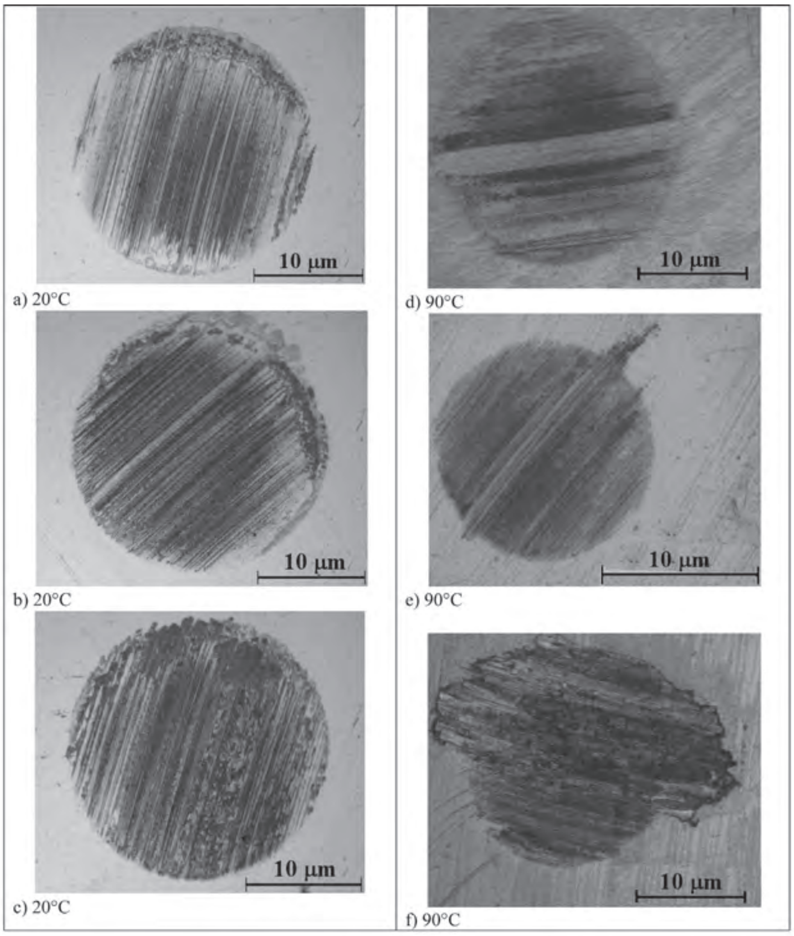


Fig. 3. Dependence of wear area (P) and friction force (F) on engine oil viscosity (η), the density of modifying additive (ρ) for load at central level (Q = 0)

Rys. 3. Zależność pola powierzchni zużycia (P) oraz siły tarcia (F) od lepkości oleju silnikowego (η), gęstości dodatku modyfikującego (ρ) dla obciążenia na poziomie centralnym (Q = 0)


a) 20°C

b) 20°C

c) 20°C

d) 90°C

e) 90°C

f) 90°C

Fig. 4. Surface of friction wear path with MoS_2 (a, d) and graphite (b, e) additives and Cu nanoparticles (c, f)

Rys. 4. Powierzchnia śladu zużycia po tarciu z dodatkami MoS_2 (a, d) i grafitu (b, e) oraz nanocząstek Cu (c, f) when oil with worse lubricating properties is used. The addition of copper particles to oil with high penetrating properties leads to a faster separation of the contact surfaces and a lower friction force). Adding molybdenum disulphide to oil operating at elevated temperatures is the best solution because the coefficient of friction is the lowest.

Adding MoS_2 is the optimum solution, resulting in low friction force and surface area values for all oil types under various loadings.

The metallographic tests carried out confirmed the results of the tribological tests. **Figure 4** shows the surface of the abrasion trace, taking into account the influence of one selected factor, i.e., the lubrication additive, while the other factors (load and oil type) were at the same level. It was determined that abrasive wear dominated the ball's surface examined in all cases, with micro-cutting and adhesive wear initiated with both graphite and copper particles. The smallest wear path was observed with the use of oil with the addition of MoS_2.

CONCLUSIONS

Based on the conducted research, it was concluded that:

- selection of the type of lubricating additives for engine oil and their suitable % content in the oil base makes it possible to achieve suitably beneficial changes in tribological properties,
- the lubricating additive in the form of molybdenum disulphide showed the lowest wear intensity and the lowest friction resistance in all engine oils used,
- the percentage of lubricating additives was selected correctly to find important differences in the wear process of the tested combination,
- optimum wear, the smallest surface area of the friction path and friction force is found in combination with MoS_2 additive,
- the abrasive wear mechanism dominates in the rolling contact, whereas adhesion wear occurs in motor oils with graphite and copper particle additives.

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