INVESTIGATION OF THE PHYSICOCHEMICAL PROPERTIES OF A NEW SYNTHETIC LUBRICANT FOR PASSENGER CAR INTERNAL COMBUSTION ENGINES

BADANIE WŁAŚCIWOŚCI FIZYKOCHEMICZNYCH NOWEGO SYNTETYCZNEGO PREPARATU SMAROWEGO DO SILNIKÓW SPALINOWYCH SAMOCHODÓW OSOBOWYCH

Key words: engine oil, lubrication, organic friction modifier, HAB. Alkylbenzene, boundary lubrication, tribological tests, seizure load, diameter wear scar, limited seizure pressure, weld load, biodegradability.

Summary: The subject of the article is a synthetic lubricant for the latest generation internal combustion engines, used especially in passenger cars, equipped with both spark ignition engines and compression ignition engines, which is used in particular in passenger cars operating in urban conditions, overcoming relatively short distances, and therefore working usually below the recommended operating temperature of the engine. The developed 5W30 oil maintains excellent rheological properties (fluidity) also before reaching the correct operating temperature of the engine, especially at negative temperatures, which results in lower oil pump resistance and reduced friction of key engine components, which ensures better engine working conditions and affects its service life.

INTRODUCTION

There are many types of engine oils from various manufacturers on the market, with different viscosity classes, meeting different requirements imposed by individual car manufacturers. Motor oils can be broadly divided, among others, as mineral oils, semi-synthetic, and synthetic. One of the problems is the fact that oils offered as synthetic are often not fully synthetic, as the production process relies heavily on the use of mineral oil as the base oil [L. 1]. The mineral base oil meets the standards, but is not the solution for ensuring maximum engine protection, i.e. it does not allow to achieve optimal parameters, e.g., in conditions of low external temperatures, or when driving short distances, with the engine not warmed up. In addition, mineral oils, in the event of leakages or disasters during their transport, pose a very high threat to the natural environment.

The aim of the research was to develop a lubricant with a viscosity of 5W30 characterized by significantly better tribological properties and physicochemical parameters than oils with a viscosity of 5W30 available...
on the market, and then to verify the correctness of the developed recipe during the tests of the physicochemical and tribological properties [L. 2–15] of the new oil in comparison to the results obtained with commercial oils available on the market. The lubricant, according to the new formula, was developed for cars that cover short distances, and therefore usually operate below the recommended engine operating temperature. The developed 5W30 oil retains excellent rheological properties (fluidity) also before reaching the correct engine operating temperature, also in negative ambient temperatures, which results in lower resistance for the oil pump and reduced friction of key engine components, which ensures better engine operating conditions and influences its service life.

The new formula of 5W30 oil was also developed with the aim of achieving the best possible physicochemical properties, such as viscosity index and tribological properties [L. 2–15], such as seizing load compared to 5W30 oils currently available on the market. Achieving such properties of the 5W30 lubricant was possible, among others, through the use of a viscosator composed of a nucleus, around which are placed elastic arms of a polymer with a star structure. Thanks to them, the viscosator expands at high temperatures, which causes a significant increase in viscosity, which is desirable from the point of view of performance. In addition, the use of a synthetic base oil in the formulation, which is a mixture of heavy HAB alkylbenzene (96.8%) with linear LAB alkylbenzene (3.2%), provides the best spatial orientation of HAB molecules in relation to organic friction modifiers and thus allows achieving optimal properties of 5W30 lubricant.

**PREPARATION OF THE RECIPE**

The essence of the newly developed synthetic lubricant for use in the latest generation internal combustion engines, especially in passenger cars, constituting a mixture of components, which includes, among others, base oils, a viscosator, and additives in appropriately selected proportions consists in the fact that the base oil is a synthetic base oil consisting of a mixture of heavy HAB alkylbenzene with linear LAB alkylbenzene. The proportion of synthetic base oil in the formulation ranges from 10% to 40% (preferably 25%), while the remaining formulation components are organic friction modifiers, the proportion of which in the mixture ranges from 0.2% to 1% (preferably 0.6%), synthetic PAO oil, the content of which in the formulation ranges from 25% to 65% (preferably 45%), a package of additives in the form of inorganic friction modifiers, ranging from 10% to 18%, (preferably 13.4%) and a viscosator, the content of which in the formulation ranges from 12% to 20% (preferably 16%).

The basic physicochemical parameters of the components of the new lubricant are as follows:

- Base synthetic oil at 100°C, according to ASTM D-445, has a viscosity of approximately 3.53 cSt, while at 20°C, according to ASTM D-445, the viscosity ranges from 41.4 to 54.1 cSt, and its density at 20°C is preferably 0.8641 g/cm³, and ASTM D-93 flash point is at least 192°C, and ASTM D86 initial boiling point is not less than 349°C.
- Organic friction modifiers (containing only carbon atoms C, oxygen O and hydrogen H in their molecules, with a very high molecular weight ranging from 5,000 to 50,000 Dalton), at 100°C, has a viscosity of approximately 360 cSt (according to ASTM D445), whereas, at 40°C, the ASTM D445 Viscosity is approximately 6,400 cSt, and the ASTM D4052 density as measured at 20°C is preferably 980 kg/m³, and the ASTM D-93 flash point is at least 269°C.
- Synthetic PAO oil – the ASTM D445 viscosity at 100°C is approximately 4.1cSt, while the ASTM D445 viscosity at 40°C is approximately 19cSt, and the ASTM D97 pour point is preferably -66°C, while the ignition temperature according to ASTM D-93 is at least 220°C.
- A package of improvers containing inorganic friction modifiers, with low molecular weight particles ranging from 250 to 500 Dalton, are characterized by a viscosity at 100°C according to the level of 162 cSt (ASTM D445), while, at 40°C, according to ASTM D445, the viscosity is approximately 2642 cSt, and the density, as measured at 15°C by ASTM D4052, is approximately 946 kg/m³, the ignition temperature by ASTM D-93 is at least 110°C.
- A viscosator composed of a nucleus, around which are placed elastic arms of a polymer with a star structure, is characterized by a viscosity at 100°C according to the level of 259 (ASTM D445), while at 40°C, according to ASTM D445, the viscosity is approximately 2642 cSt, and the density, as measured at 15°C by ASTM D4052, is approximately 837.6 kg/m³, and the ignition temperature by ASTM D-93 is at least 216°C.

Thanks to the applied solutions, the following technical and operational benefits have been achieved:
- A reduction of friction associated with pumping excessively thick oil at low temperatures, which causes additional resistance to movement;
- A high value of the viscosity index was obtained in relation to engine oils available on the market;
- The lowest oil pour point was obtained from all tested engine oils available on the market; and,
- A reduction of the boundary friction at the contact of metals by the use of organic friction modifiers with particle sizes from 5,000 to 50,000 Daltons (the new oil achieved the highest result of seizing load in the conducted tribological tests).
The developed lubricant is a balanced mixture of appropriately selected components, which includes base oils, a viscosator, and additives in appropriately selected proportions. The composition of this mixture, determining the qualitative and quantitative composition, constitutes the formulation of the product. The individual elements of the formulation have been selected in such a way that they are characterized by synergy of action, thanks to which the previously mentioned technical and utility benefits were obtained. Importantly, the use of a synthetic base oil in the formulation, consisting of a mixture of heavy HAB alkylbenzene (96.8%) with linear LAB alkylbenzene (3.2%), described by the chemical formula below, provides the best three-dimensional orientation of HAB molecules in relation to organic friction modifiers.

Organic friction modifiers used in the recipe do not contain compounds of phosphorus P, sulphur S, calcium Ca, manganese Ma, zinc Zn, or Mo molybdenum, which have so far been commonly used in inorganic friction modifiers. In addition, the viscosator used is composed of a core around which resilient polymer arms with a star structure are placed. Thanks to them, the viscosator expands at high temperatures, which causes a significant increase in viscosity, which is desirable from the point of view of performance.

On the other hand, it shrinks at low temperatures, and the viscosity of the oil increases only slightly. This is a very advantageous phenomenon, as it ensures maintaining a sufficiently high viscosity at high temperatures under high engine loads, protecting the engine against seizure. At low temperatures, however, it does not thicken the oil, ensuring sufficient fluidity and enabling the engine to start even at extremely low temperatures. In addition, the viscosator used has a low value of the abrasion resistance index (SSI), which, in the case of other viscosators, may be in the range from 9 to even 60, while the lower the index, the longer the durability of the viscosator, which enables the extension of oil change intervals.

COMPARISON OF THE PHYSICOCHEMICAL PROPERTIES OF THE NEWLY DEVELOPED OIL AND COMMERCIAL OILS

Research methodology

Rheological properties

The rheological tests (CCS at -10°C, -15°C, -20°C, -25°C, -30°C) were performed on an automatic Cannon Instrument Company CCS-2100 (Cold Cranking Simulator) according to ASTM D5293 Standard Test Method for Determination of Yield Stress and Apparent Viscosity of Engine Oils at Low Temperature.

Kinematic viscosity at temperatures + 40°C and + 100°C, viscosity index (VI index)

Measurements were made in accordance with ASTM D7042 Standard Test Method for Dynamic Viscosity and Density of Liquids by Stabinger Viscometer (and the Calculation of Kinematic Viscosity) made on a Stabinger type SVM 3000.

Low temperature properties – Pour Point determination

The Pour Point value was measured using an Anton Paar Cloud & Pour Point Tester CAPP I. Automatic flow and cloud point testers were used according to ASTM D97 Standard Test Method for Pour Point.

Volatile product evaporation/Measurement of volatile substances content

The advanced chromatograph model TRACE 1200 by Thermo Scientific was used to test the content of volatile substances. The test was performed in accordance with ASTM D6417 (MOV) Standard Test Method Estimation of Engine Oil Volatility by Capillary Gas Chromatography.

Research results

Rheological properties – test results

This parameter shows the resistance of cooled oil. Viscosity measured with this method directly translates into whether the given oil will allow the engine to start at sub-zero temperatures. This parameter is the low temperature viscosity characteristic of the engine oil and is one of the most important indicators, since it is the basis for the classification of the product in accordance with the SAE J300 standard.
The graphs show the viscosity values at various temperatures of -10°C, -15°C, -20°C, -25°C, -30°C for five samples of commercial oils from well-known manufacturers and for a new engine oil formulation. The newly developed oil has the lowest viscosity values at each temperature, which is a very advantageous result, because lower viscosity means lower resistance to motion, which translates directly into lower fuel consumption and easier engine starting at lower temperatures. The measurements show that the newly developed 5W30 oil at -30°C has a viscosity like commercial oils at -25°C and similarly at -25°C as other oils at -20°C, etc. So it provides a certain safety buffer, even in the case of extremely negative ambient temperatures.

**Kinematic viscosity at temperatures of + 40°C and + 100°C, viscosity index (VI index) – test results**

The kinematic viscosity at temperatures of + 40°C and + 100°C and the viscosity index calculated on their basis (VI index) were also tested. Oil viscosity is of decisive importance for the operation and maintenance of the oil layer (film) between rubbing metal surfaces. It provides smooth friction and protects against wear. It affects the amount of energy lost to overcome frictional resistance (node efficiency). The speed and energy needed to start the engine depend on the viscosity, the efficiency of heat dissipation, the degree of the sealing of the piston-cylinder pair, the efficiency of the filters, and oil consumption. Viscosity measurement at 40°C and 100°C allows one to determine the viscosity index of the product, which allows one to assess whether the oil has the necessary viscosity stability, i.e. whether it maintains its properties both when the engine is started and when it is fully warmed up.

Oil viscosity at 40°C is not a standard value, but it is marked as the standard one, in order to determinate Viscosity Index (VI).

On the other hand, the measurement of the kinematic viscosity at 100°C is very important, because this parameter is used to classify the oil in accordance with the SAE J300 standard.

As you can see, the viscosity at 100°C of the new 5W30 oil is in the middle of the minimum and maximum values for this type of oil, and it is the closest to the W sample, while the M and K samples are practically at the lower limit, and the Q sample at the upper limit, so they are far from optimal.

The VI (Viscosity Index) determines how the viscosity of oil changes with a decrease in temperature and how its viscosity decreases with an increase in temperature. The higher the VI, the better is the lubricant, as it is less dense at lower temperatures and correspondingly highly viscous / thick at high temperatures. The index is calculated automatically, e.g., the previously made viscosity measurements at 40°C and 100°C made on the Stabinger SVM 3000.
Fig. 2. Kinematic viscosity test results at 40°C. Made on Stabinger type SVM 3000, in accordance with ASTM D7042 Standard method for testing dynamic viscosity and density of liquids using a Stabinger viscometer (and calculating the kinematic viscosity)

Rys. 2. Wyniki badania lepkości kinematycznej w temperaturze 40°C. Badanie wykonane na aparacie Stabinger typ SVM 3000 zgodnie z normą ASTM D7042 Standard Test Method for Dynamic Viscosity and Density of Liquids by Stabinger Viscometer (and the Calculation of Kinematic Viscosity)

Fig. 3. Kinematic viscosity test results at 100°C. Made on Stabinger type SVM 3000, in accordance with ASTM D7042 Standard method for testing dynamic viscosity and density of liquids using a Stabinger viscometer (and calculating the kinematic viscosity)

Rys. 3. Wyniki badania lepkości kinematycznej w temperaturze 100°C. Badanie wykonane na aparacie Stabinger typ SVM 3000 zgodnie z normą ASTM D7042 Standard Test Method for Dynamic Viscosity and Density of Liquids by Stabinger Viscometer (and the Calculation of Kinematic Viscosity)

Fig. 4. Viscosity index (VI index) for the tested oils, made on the Stabinger SVM 3000, in accordance with ASTM D7042 Standard Test Method for Dynamic Viscosity and Density of Liquids by Stabinger Viscometer (and the Calculation of Kinematic Viscosity)

Rys. 4. Wskaźnik lepkości (Wskaźnik VI) dla badanych olejów, pomiar na aparacie Stabinger typ SVM 3000 zgodnie z normą ASTM D7042 Standard Test Method for Dynamic Viscosity and Density of Liquids by Stabinger Viscometer (and the Calculation of Kinematic Viscosity)
As the Fig. 4 shows, the value of the viscosity index is the highest for the newly developed 5W30 oil, which means that it is the best compared to the comparable oils, because its viscosity does not increase excessively with the drop in temperature (it ensures optimal engine lubrication also during frost), and additionally does not decrease excessively with increasing temperature, so it maintains good engine operating conditions also at high temperatures.

Low temperature properties – Pour Point determination – test results

Another test performed is the determination of Pour Point. The pour point is the temperature at which the oil is on the verge of losing its fluidity but is still liquid and keeps the engine running properly. The oil with a lower pour point ensures the correct operation of the engine at a lower temperature, minimizing the friction of the mating surfaces also at low temperatures, when the engine has not yet reached its normal operating temperature.

The Fig. 5 shows the Pour Point values for five samples of commercial oils from well-known manufacturers and for the new 5W30 oil. The oil, developed according to the new recipe, has the lowest Pour Point values, which is a very favourable result, as it will allow the engine to start correctly even at extremely low ambient temperatures. Sample T has a Pour Point value of -39°C, which is as much as 12°C higher than that achieved by the newly developed 5W30 oil.

Volatile products evaporation / Measurement of volatile substances content – test results

The content of volatile substances according to ASTM D6417 in engine oils is a very important parameter due to the very high operating temperature of the engine. The evaporation of volatile substances from the oil at elevated temperatures changes the composition of the product, and thus increases the viscosity. As a result, the oil loses its lubricating properties which ultimately lead to a decrease in pumpability, especially at low temperatures, higher fuel and engine oil consumption, engine wear, and increased emissions. The lower amount of volatile substances in the oil improves the operational properties of the oil and translates directly into more energy-saving operation of the engine throughout its operation, up to the time of changing the oil to a new one.

The oil, according to the new formula, is only 6.7% behind the lowest result; however, it should be noted that the values of the volatile substances content of the remaining oils are much higher. The low level of volatile substances translates into minimizing the need to refill the engine oil, and also translates into more energy-efficient operation of the engine throughout its lifetime.

The temperatures at which a given percentage of the amount of the tested oil sample evaporated were also examined. Higher temperatures means less oil loss due to evaporation, which means that there is no need or the possibility of less frequent refilling of the oil level in the engine between oil changes. The measurement results for 10% and 20% are presented below.

Among the tested oils, the oil developed according to the new formula shows a very high resistance to evaporation, because only 10% of the oil volume is evaporated at the temperature of 408.5°C. The Q sample
Fig. 6. Measurement of volatile substances content in the tested oils according to ASTM D6417 (MOV) Standard Test Method Estimation of Engine Oil Volatility by Capillary Gas Chromatography, made on a chromatograph model TRACE 1200 by Thermo Scientific

Rys. 6. Pomiar zawartości substancji lotnych w badanych olejach zgodnie z ASTM D6417(MOV) Standard Test Method Estimation of Engine Oil Volatility by Capillary Gas Chromatography, na chromatografie model TRACE 1200 firmy Thermo scientific

Fig. 7. Measurement of the evaporation temperature 10% of the volume for the tested oils

Rys. 7. Pomiar temperatury odparowania 10% objętości próbki dla badanych olejów

Fig. 8. Measurement of the evaporation temperature 20% of the volume for the tested oils

Rys. 8. Pomiar temperatury odparowania 20% objętości próbki dla badanych olejów
reached a similar temperature, and the remaining oils are characterized by a significantly lower evaporation temperature. A high evaporating temperature is a very important parameter, because it translates directly into the need to refill the oil between oil changes, and thus reduces operating costs, and ensures stable engine operating conditions.

Among the tested oils, the oil developed according to the new formula shows a very high resistance to evaporation, because only 20% of the oil volume is evaporated at the temperature of 422.4°C. The Q sample reached a similar temperature, and the remaining oils are characterized by a significantly lower evaporation temperature. A high evaporating temperature is a very important parameter, because it translates directly into the need to refill the oil between oil changes, and thus reduces operating costs, and ensures stable engine operating conditions.

COMPARISON OF THE TRIBOLOGICAL PROPERTIES OF THE NEWLY DEVELOPED OIL AND COMMERCIAL OILS

Research methodology

Seizure load

The tests were carried out on a four-ball apparatus at the Institute of Sustainable Technologies – National Research Institute, Department of Pro-ecological Technologies in Radom by testing in accordance with the requirements of PN-76 / C-04147.

Diameter of the wear pattern $D_{100}$ [mm]

The tests were carried out on a four-ball apparatus at the Institute of Sustainable Technologies – National Research Institute, Department of Pro-ecological Technologies in Radom by testing in accordance with the requirements of the J_PB / LBT / 02.

Limit seizure pressure $P^m$ [N/mm$^2$]

The tests were carried out on a four-ball apparatus at the Institute of Sustainable Technologies – National Research Institute, Department of Pro-ecological Technologies in Radom by testing in accordance with the requirements of the J_PB / LBT / 02.

Weld load $P_z$ [N]

The tests were carried out on a four-ball apparatus at the Institute of Sustainable Technologies – National Research Institute, Department of Pro-ecological Technologies in Radom by testing in accordance with the requirements of PN-76 / C-04147.

Results of tests of tribological properties

Seizure load $P_t$ [N] according to PN-76 / C-04147 – test results

The newly developed oil achieved the highest seizure load result, which was at the same level as sample M. This means that the new 5W30 oil provides very good working conditions for the engine, protecting it from damage.

![Seizure load Pt](image_url)

Fig. 9. The results of the seizure load test for the tested oils. Test performed on a four-ball apparatus in accordance with ASTM D4172 Standard Test Method for Wear Preventive Characteristics of Lubricating Fluid Four-Ball Method.

Diameter of the wear scar $d_{wt} [\text{mm}]$ – test results

Fig. 10. Results of the wear scar diameter test for the tested oils. Test performed on a four-ball apparatus in accordance with ASTM D4172 Standard Test Method for Wear Preventive Characteristics of Lubricating Fluid Four-Ball Method

The new 5W30 oil showed the second lowest result in the wear scar diameter test, and the T sample showed the lowest result, while it achieved a very low result in the seizure load test, which also translates into the wear mark diameter achieved.

Limited seizure pressure $P_{oz} [\text{N/mm}^2]$ – test results

The loss of lubricating properties of the tested oils is evidenced by a large increase in the friction torque after exceeding the seizing load, with a simultaneous increase in the diameter of the wear marks of the balls constituting the elements of the friction junction.

The tested sample achieved the second highest result of limited seizure pressure.

Fig. 11. Results of the limited seizure pressure test for the tested oils. Test performed on a four-ball apparatus in accordance with ASTM D4172 Standard Test Method for Wear Preventive Characteristics of Lubricating Fluid Four-Ball Method


Weld load $P_z$ [N] – test results

![Graph of weld load $P_z$](image)

Four tested oils, including the newly developed oil, achieved the same weld load result at the level of 7848 N, which is also the highest result achieved in this study.

SUMMARY

The aim of the research was to develop a lubricant with a viscosity of 5W30 characterized by significantly better tribological properties and physicochemical parameters than oils with a viscosity of 5W30 available on the market, and then to verify the correctness of the developed recipe during the tests of the physicochemical and tribological properties [L. 2–15] of the new oil in compared to the results obtained with commercial oils available on the market.

The newly developed oil achieved the highest viscosity index among the tested oils, which is a very important parameter, because the higher the viscosity index (VI index), the better the lubricant is, as it is less thick at lower temperatures. At the same time, it is highly viscous / dense at high temperatures. The high viscosity index ensures optimal engine operation conditions both at low and high temperatures. The new 5W30 oil shows a very low evaporation rate (the second lowest among the tested oils), as well as the highest evaporation temperature of 10 and 20% of its volume. The new 5W30 oil also has the lowest Pour Point value, which guarantees correct engine starting even at extremely low temperatures.

During the tribological tests, the newly developed oil achieved a high value of the seizing load, with one of the lowest diameters of the wear mark, which proves its very good tribological properties and thus ensuring optimal engine operating conditions.

The lubricant according to the new formula was developed for cars that cover short distances and therefore usually operate below the recommended engine operating temperature. The performed tests confirmed its criteria, i.e. ensuring optimal engine operating conditions, also when the optimal operating temperature was not achieved, so it will be perfectly suitable for use in cars operating in urban conditions.

Thanks

I would like to thank Professor Elżbieta Rogoś and the entire team of the Department of Proecological Technologies from Łukasiewicz – Institute of Sustainable Technologies in Radom for participating in tribological tests of oil preparations.
REFERENCES