Anti-wear additive content in fully synthetic PAO and PAG base oils and its effect on electrostatic and tribological phenomena in a rotating shaft–oil–lip seal system

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Abstract. The paper presents the results of experiments on electrostatic and tribological aspects of different anti-wear additive’s contents when an additive is blended with different fully synthetic (poly-α-olefin) and PAG (polyalkylene glycol) base oils in a rotating shaft–oil and oil–lip seal interfacial system. The experimental results are the relationships of electric potential induced in a lip seal’s stiffening ring to angular velocity of a rotating metal shaft and to temperature of the oils tested. The braking torque of a shaft is measured with a torquemeter sensor connected directly with a microprocessor-based system for controlling the rotational speed and for measuring the shaft’s braking torque and oil temperature. The beneficial and promising results are obtained for PAG when an external DC electric field is applied to the system and the braking torque is then reduced for a certain combination of the base oil and additive’s contents. On the basis of the former and present research results an analysis is made to permit one to show how the type of the oils and additives tested can affect both interfaces: rotating shaft–oil and oil–lip of the lip seal and especially the braking torque.

1. Introduction
Fully formulated engine oils consist of pure base oils and some part of different additives that improve the tribological properties of a base stock or blend of base stock as used in engine oil. As the base stock, mineral, semisynthetic and synthetic oils, and just recently research is carried out upon the introduction of new engine oils into the market that are based on PAGs (polyalkylene glycols) [1–4]. These base oils have unique properties and among them especially important are low toxicity and improved biodegradability which results in environmental friendliness [5, 6].

Synthetic oils (poly-α-olefins), known as PAOs, are obtained through the polymerization of olefins and next the hydrogenation of products so obtained is carried out to get saturated compounds. These oils are characterized by the high viscosity index, polarity and low toxicity. PAOs are mainly applied to formulate automotive engine oils where the low solidification temperature of oil, low volatility and good thermal-oxidative stability are required.

Polyalkylene glycols (PAGs) are the result of the chemical reaction of substrates that contain hydroxyl groups (alcohols, diols, polyols, carboxylic acids) with olefin oxides. PAGs have high polarity

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which results in their surface activity. In addition they have such properties as: good thermal and shear stabilities, good viscosity index (VI), high flash point and auto-ignition temperature, low toxicity and flammability. Lubricants produced on the basis of PAGs have practical applications to braking systems, compressors and hydraulic systems where the low flammability is required.

One of the important additives in engine oils are those of anti-wear (AW) type whose role is the protection of metal surfaces against the effects of boundary friction. The widely used an anti-wear additive is zinc dialkyldithiophosphate (ZDDP). Apart from the anti-wear properties it is also an antioxidant and protects from extreme pressures (EP additive) [7].

Another often used additive to oils is a friction modifier (FM). These agents reduce or increase the coefficient of friction according to a purpose. In engine and gear oils its main task to do is the reduction of friction and at the same time the protection of a metal surface against the friction wear. It use can reduce the fuel consumption and energy losses in friction junctions.

Rizvi in his book [8] says that “Anti-wear and extreme pressure agents have structures that are similar to those of the friction modifiers, with the difference that their hydrocarbon chains are much shorter and are thermally labile. In other words, their polar to non-polar ratio is fairly high, which makes them more surface active. Anti-wear and EP additives both provide protection by a similar mechanism, except that EP additives typically require higher activation temperatures and load than anti-wear additives. Simply stated, anti-wear additives perform under mild conditions and EP additives perform under severe conditions.” Also: “In addition to reducing friction, the friction modifiers also reduce wear, especially at low temperatures where the anti-wear agents are inactive, and they improve fuel efficiency.” The above statements show the properties of both additives that are interesting and important from the point of view of the research undertaken by the authors.

ZDDP and FM protect metal parts of machinery through the formation of an adherent film on metal surfaces. The film reacts with a ferric oxide layer which adheres to the surface and protects it from wear during metal–metal rubbing. During the relative movement of a metal surface and oil the outermost layer of the film is constantly sheared and replenished after it has been disrupted by the mechanical contact [9]. This layer is a transfer one that reduces friction.

While the metal shaft rotates friction occurs and the outermost ZDDP (AW) or FM layers are disrupted. Each contact and friction generates electric charges during the process of tribocharging. Tribocharging occurs not only at this surface but also in the oil film, as well as at the surface of a lip of a lip seal. It can produce long-range electrostatic effects which affect friction and braking torque in the interfacial system: rotating shaft–oil–lip seal (a friction junction). The charges generated in the system can play an important role in the adhesion at the surfaces in both interfaces: rotating shaft–oil and oil–lip of the lip seal [10]. Tribocharging always takes place in the similar interfacial systems and affects the operation of rotating or moving parts in different types of machinery [11, 12].

Here some experimental results of research upon tribocharging of the synthetic PAO and PAG base oils without and with the AW (ZDDP) and FM agents added to form their blends of different concentrations. The important factors that affect tribocharging are the temperature of pure base oil or the AW/FM–oil blend and the angular velocity of a shaft.

The effect of an external DC electric field applied between the rotating shaft and the stiffening ring of a lip seal on the braking torque of the shaft is also examined. The electric field is used to compensate for the natural electric field generated by net charge of mobile ions and molecules in the zone between both interfaces.

The motivation for doing such research is the introduction of new PAG-based engine oils into the market and the PAG’s quite good biodegradability [2, 5, 6, 13] with relatively low kinematic viscosity. Also its relatively low resistivity suggests it be charged during tribocharging less intense than other base oils [14–16]. This in turn should result in the lower friction and reduced braking torque. As a result and as is supposed the effect of a DC electric field on the reduction of the shaft’s braking torque should also be more visible, beneficial and even stronger. It can be predictable on the basis of the theory and the authors’ many years’ experience in the research upon tribocharging of different pure base oils and their blends with different additives under different dynamic and temperature conditions.
2. Test stands, materials tested, and measurements

2.1. Experimental set-ups and measurement procedure

The test stand, as shown in figure 1, permits one to conduct experiments on tribocharging of different fully formulated engine oils, pure engine base oils as well as their blends with additives imparting or improving certain properties of petroleum products and especially engine oils.

The experimental set-up is made up of: the housing of a sump with the seating of a rotary lip seal (1) and base oil or the AW/FM–base oil blend (2); a rotary lip seal (3); a stiffening ring (a metal ring) of a seal (4); a dielectric ring (5); an earthed steel shaft (6) rotating and driven by an electric motor (7) with a regulated angular velocity; an electric oil heater (8) controlled by a microprocessor-based PID controller; a thermocouple (9); a standard capacitor (10); an electrometer Keithley 6517A (11), and a computer (12).

The potential \( U_e \) of a stiffening ring is induced by electric charges in the oil film and is a certain measure of the process of tribocharging that occurs in the gap between both surfaces of the shaft and of the lip seal – its lip. The ring is directly connected with the electrometer the input of which is in parallel to the standard capacitor \( C_s \) of relatively high capacitance to attenuate fluctuations of the ring’s potential and to assure accurate measurements of the potential with respect to the earth with the use of an electrometer Keithley 6517A.

To determine the effect of a DC electric field on the braking torque of the rotating shaft another test stand is used, which is shown in figure 2. It consists of: the housing of an oil chamber (1); a seal’s stiffening metal ring (2); the lip seal tested (3); an insulator (4); the oil tested (5); an air bearing (6); the sensor of a torquemeter (7); an electric engine (8); a steel shaft (9) earthed through carbon brushes; a microprocessor-based system for controlling the angular velocity and for measuring the braking torque of the shaft and the temperature of oil (10); a DC power supply (11); an oil heater (12), and a thermocouple (13). The chamber is filled with the oil tested up to a geometrical axis of the rotating shaft. The whole chamber is a simplified model of the part (oil sump or crankcase) of a real car engine.

The braking torque \( M \) is measured with a torquemeter which is connected with its sensor mounted on an earthed rotating metal shaft. The torque sensor is a non-contact and inductive one and is based upon the phenomenon of electromagnetic induction. The DC voltage \( U_{DC} \) is applied between the seal’s stiffening ring and the earth to produce a DC electric field; here the rotating shaft is precisely earthed as
is the housing of an oil chamber. The chamber is filled with the oils and their blends up to the shaft’s geometrical axis as are original crankcases of cars.

Both measurement systems, as presented in figures 1 and 2, are microcomputer-based ones to enable the measurement data processing, analysis, acquisition, display, and storage.

2.2. Materials tested and experimental procedure

The experiments are carried out for the following pure synthetic base oils: PAO 6 produced by NESTE OIL N.V., Beringen, Belgium and ROKOLUB68® (PAG) produced by PCC ROKITA, Brzeg Dolny, Poland. A specification of the oils tested is shown in table 1. ZDDP Lubrizol 1395 (AW) produced in Austria by LUBRIZOL and IRGALUBE F10A (FM) produced in France by CIBA are additives widely used in engine and gear oils. In the experiments on tribocharging the synthetic PAO and PAG base oils are used without and with the AW and FM agents added to the oils. The agent’s contents in the blends are 0.1 and 0.5% by weight.

| Quantity and unit | ROKOLUB68 | PAO 6 |
|-------------------|-----------|-------|
| Kinematic viscosity |           |       |
| at 40°C            | 56.4      | 30.2  |
| at 100°C           | 10.5      | 5.8   |
| Viscosity index, [–] | 176      | 138   |
| Density at 15°C, [kg⋅m⁻³] | 990 at 20°C | 825 |
| Resistivity |           |       |
| at 40°C            | 1.3⋅10⁷   | 2.6⋅10¹¹ |
| at 100°C           | 3.5⋅10⁶   | 6.4⋅10¹⁰ |
| Relative permittivity |           |       |
| at 40°C            | 5.8       | 1.9   |
| at 100°C           | 5.1       | 1.9   |

The steel shaft roughness is 0.32 μm. An 88 mm diameter fluorocarbon lip seal is used in all the tests performed.

The pure base oils and their blends with the AW and FM agents tested at the experimental set-up, as shown in figure 1, are heated from 60 to 110°C every 10°C in an oil chamber and are controlled by a microprocessor-based PID controller. For each temperature within the range the measurements of the potential are performed for given angular velocities of 500, 750, and 1000 rpm. It permits one to obtain many
various relationships for the stiffening ring’s potential as a function of both the temperature and the angular velocity of the shaft.

When the same base oils and the AW/FM–oil blends are tested at the test stand (figure 2), the range of temperatures is 70 to 120°C while the shaft’s angular velocity is changed from 500 to 3000 rpm and here the braking torque is a function of DC voltage for the temperature and angular velocity as parameters. All the experiments upon the effect of a DC electric field on the braking torque are carried out according to the design of experiments (DOE).

3. Results and discussion
Some selected experimental results are presented in the form of different characteristics (relationships) which are obtained at both experimental set-ups (figures 1 and 2).

3.1. Measurement of the potential
Figures 3 to 8 show the plots of the stiffening ring’s potential $U_e$ as a function of the temperature $T$ for shaft’s angular velocities of 500, 750, and 1000 rpm, and for the pure PAO 6 and PAG base oils, and their blends for 0.1 and 0.5 wt% contents of the AW or FM agents, correspondingly.

**Figure 3.** PAO 6. Potential as a function of the temperature for 500 rpm and the different FM contents: ○ – pure, △ – 0.1 wt%, and □ – 0.5 wt%.

**Figure 4.** PAO 6. Potential as a function of the temperature for 500 rpm and the different AW contents: ○ – pure, △ – 0.1 wt%, and □ – 0.5 wt%.

**Figure 5.** PAO 6 – pure. Potential as a function of the temperature for the different angular velocities: ● – 500 rpm, ▲ – 750 rpm, and ■ – 1000 rpm.
In general the potential of the seal’s stiffening ring always increases with increasing temperature and is positive regardless of base oil and its blend with the different additives and their contents in the blends. PAO 6 only exhibits a stronger increase in the potential compared to PAG which results in the broader range of potential changes within the same range of temperatures. It means that in the case of PAO 6 tribocharging is more intense in layers in the gap between the surfaces of the rotating shaft and the lip of the lip seal. It must be attributed to the distinct difference in resistivity of both oils (table 1). It is interesting and strange that for PAO 6 the potential and thus tribocharging is stronger only for 0.1 wt% and moreover the AW agent causes the range of changes in the potential to be greater than for the FM agent. In the case of PAG oil the averaged dependence of the potential on temperature is somewhat stronger for pure base oil than for the AW/FM–oil blends. Here the chemistry of the oil and its blends should play an important role in the process of tribocharging that yields such surprising results.

The effect of the shaft’s angular velocity on the potential and tribocharging is also surprising all the more so because one can expect that the process should always be more intense and give the stronger electric field for higher velocities. Here in the case of PAG this prediction confounds and contradicts the generally recognized knowledge and theory of static electrification. Chemistry again?

3.2. Measurement of the braking torque
The braking torque \( M \) measured is presented here as a relative one \( M_r \) (a dimensionless value) to enable the comparison of the torques for different oils and their blends with additives of different viscosities. The relative torque \( M_r \) means the ratio of the braking torque \( M_{DC} \) measured under the action
of the DC electric field of both polarities (+/−) to the braking torque $M_{NDC}$ without any external DC electric field applied: $M_{r} = M_{DC}/M_{NDC}$. The trends of the relative dimensionless value of the braking torque $M_{r}$ as a function of the DC voltage of both polarities are shown in figures 9–12. The graphic symbols used for the data points mean: ● – pure base oil, ▲ – base oil and 0.1 wt% additive, ■ – base oil and 0.5 wt% additive for negative DC voltage; and ○ – pure base oil, △ – base oil and 0.1 wt% additive, □ – base oil and 0.5 wt% additive for positive DC voltage. The research results shown here are selected out of many other obtained during a long series of experiments and are preliminary and most representative ones.

![Figure 9](image9.png) ![Figure 10](image10.png)

Figure 9. The sample plot of the relative braking torque as a function of DC voltage for PAO 6 and its blend with the FM agent – 70°C and 3000 rpm.

Figure 10. The sample plot of the relative braking torque as a function of DC voltage for PAO 6 and its blend with the AW agent – 70°C and 3000 rpm.

The results obtained for the PAO 6 and PAG base oils as well as for their blends with the FM and AW agents suggest that their chemical structure play a significant role in the process analysed and has an effect on the shaft’s braking torque under external DC electric field. The relative braking torque $M_{r}$ as a function of the DC voltage applied of the negative and positive polarities is shown in figures 9 and 10 for PAO 6 and its blend with the FM and AW agents under steady state conditions for a constant angular shaft velocity of 3000 rpm and a temperature of 70 °C. The positive polarity of the DC voltage applied to the system causes the relative braking torque to decrease only for the AW agent (figure 10). For the FM agent and for the DC voltage of both polarities the braking torque tends to increase in some range of DC voltages (figure 9).

A 33% increase in the relative braking torque of the rotating shaft is observed for PAO 6 blended with the FM and AW (figures 9 and 10) when the DC voltage of both polarities is applied.

The PAG base oil and its blends with the FM and AW agents with the same concentrations are also examined. The results yielded are quite different from those presented for PAO 6. The relative braking torque always decreases both with the negative and positive DC voltage applied.

Maximum reductions of about 7% and 5% in the relative braking torque occur for PAG blended with the same agents, respectively, as shown in figures 11 and 12. These results are obtained under steady state conditions for a constant oil temperature of 70°C and the negative DC voltage.

The chemical constitution of the oils tested results in their polarity, and especially, the polarity of their bonds, as supposed. PAO is non-polar while PAG is polar. It can explain the difference in their behaviour under external DC electric field and effect on the reduction of the braking torque. The external DC electric field affects polar chemical constitutions more strongly than those non-polar, as observed here.
4. Concluding remarks

The results of preliminary experiments presented here demonstrate that the PAG’s chemical and physical properties cause the braking torque of the rotating shaft to be reduced under the action of an external DC electric field and especially when the polarity of the DC voltage applied to the interfacial system is negative. It is observed both when it is tested both as pure base oil and in the blend with both additives used. This outcome is similar to the results obtained by the authors earlier [17, 18]. The chemical and physical properties of the oil and additives exert a significant and beneficial effect on the reduction of the braking torque under external DC electric field. This in turn suggests the possibility of such reduction in the braking torque in real engines, in fuel consumption and energy losses.

Figure 11. The sample plot of the relative braking torque as a function of DC voltage for PAG and its blend with the FM agent – 70°C and 3000 rpm.

Figure 12. The sample plot of the relative braking torque as a function of DC voltage for PAG and its blend with the AW agent – 70°C and 3000 rpm.

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