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Study of degradation phenomenon for transmission lubricants

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Lubricants degradation process is quantified by the changes in physical characteristics and chemical composition of oils, which are caused by internal and external factors and the severity of operating conditions. Experimental methods for determining the degree of lubricants wear and their durability led to the development of a methodology for the assessment and the quantification of lubricants life cycle.

The degradation phenomenon of two transmission lubricants was investigated using physico-chemical, rheological and microscopic methods. For comparison, the lubricants were tested in fresh state and used state.

The rheological measurements were performed on a Brookfield viscometer CAP2000+ equipped with cone-and-plate geometry, for a temperature range between 20 … 70°C, using the viscometer Peltier system. For the microscopic tests a transmission electron microscope JEOL Japan - JEM - 200 CX was used, in order to obtain information on the wear particles shape and concentration.

The experiments have shown that the wear degree of the lubricant influences the rheological behavior of the tested samples over the whole range of temperatures and determines the presence of specific wear particles in used lubricants.

Keywords: Lubricant, Degradation, Rheology, Microscopy

INTRODUCTION

The lubricants degradation is a quantified process, by using physical characteristics and changes in chemical composition of oils; these are caused by internal and external factors and by the severity of operating conditions. The degradation of lubricants during time is due to the mechanical loads, to the operating temperature and contamination; the result is the lubrication deterioration and the worsening of other functions (providing cooling parts, their corrosion protection, etc.). The degradation process is progressive and it is more intense if the service conditions are more severe. There is a variety of external factors involved in determining of the lubricants degradation and their disuse [1–3]:

- the contamination with different impurities or chemical agents during the usage, transport or storage;
- the mechanics of thermal overstressing;
- the possibility of increased aeration and water penetration into the oil in bigger quantity.

The consequence of reported changes is the shortened lubricant use, which is associated, in some cases, with endangering the safety of the equipment. The problem of a long use of industrial lubricants is transposed over the existence of a life cycle, which is economically satisfactory. The lubricants choice affects the longer use of the production equipment and life cycle costs [4].

The basic physical and chemical characteristics of the lubricant quality do not always reach the limit values at the oil drain interval and the transmission oil is still suitable for future use. Knowing the chemical characteristics and intensity of the wear products on lubricant, it is possible to evaluate the transmission performance parameters to determine the optimized oil change intervals [5, 6].

One of the most important factors for lubricant degradation is the modification of the rheological properties at different temperatures [7]. Rheological modeling of lubricants has always been a subject of great importance when working with oil from different fields of interest. The need for predicting the rheological behavior of lubricants when experiencing conditions outside the available measuring range for the equipment designed in accordance with API specifications has always been present [8, 9]. Another indicator for the deterioration of operational characteristics of the transmission oils is the occurrence of the oxidation phenomenon, which takes place through the formation of oxidized aliphatics. The increase in acidity changes the structure and lubricating properties of the oil, even in the presence of commercial additives [10, 11].

During the operation of the mechanical transmission, the wear particles of organic (hydrocarbon) and inorganic (wear debris) products represent one of the main types of oil contamination [12, 13]. In order to monitor the presence of such particles in the lubricant, the transmission electron microscopy (TEM) and selected area electron diffraction (SAED) methods can be used [14–16].

The purpose of this paper is to investigate the rheological properties of two transmission

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lubricants for motorcycle gearboxes (75W90 and 75W140), in fresh and used state, correlated with the oxidation phenomenon and the presence of the contaminated particles in the oils.

THEORY

The rheological model proposed for the prediction of the lubricant behaviour is based on Cross equation [17–20], which can be found on virtually every research rheometer software package and it can be used to extract some meaningful numbers from the "full" viscosity *versus* shear rate profile:

$$\eta = \eta_{\infty} + \frac{\eta_0 - \eta_{\infty}}{1 + (\lambda\dot{\gamma})^m} \quad (1),$$

where:

- $\dot{\gamma}$ – shear rate;
- η – viscosity at any given shear rate $\dot{\gamma}$;
- η_0 – zero shear viscosity representing the magnitude of the viscosity at the lower Newtonian plateau;
- η_{∞} – infinite shear viscosity;
- λ – Cross time constant which has dimensions of time;
- m – dimensionless rate constant indicating the degree of dependence of the viscosity on shear rate in the shear-thinning region.

Concerning the thermal model assumed for the variation of the rheological parameters of the studied lubricants, three possibilities have been considered [21]:

Jarchov and Theissen model:

$$\eta = \eta_{50} e^{B \cdot \frac{50-t}{95+t}} \quad (2),$$

where:

- η – lubricant apparent viscosity;
- η_{50} – lubricant apparent viscosity at 50 ^{0}C;
- B – non-dimensional parameter;
- t – temperature.

Cameron model:

$$\eta = K e^{\frac{b}{95+t}} \quad (3),$$

where:

- η – lubricant apparent viscosity;
- K – viscosity parameter;
- b – temperature parameter;
- t – temperature.

Reynolds model:

$$\eta = \eta_{50} e^{m(t-50)} \quad (4),$$

where:

- η – lubricant apparent viscosity;
- η_{50} – lubricant apparent viscosity at 50 ^{0}C;
- m – temperature parameter;
- t – temperature.

In order to obtain the main values of the characteristic parameters specific for Cross model (Eqn. 1) and for all three thermal models (Eqns. 2, 3 and 4), the experimental data were numerically treated using the regression analysis method [22–25].

EXPERIMENTAL

The rheological measurements were performed on a Brookfield viscometer CAP2000+ equipped with cone-plate geometry and using a Peltier system for controlling the temperature. The CAP 2000+ Series viscometers are medium to high shear rate instruments with integrated temperature control of the test sample material. Concerning the technical parameters of the viscometer, rotational speed selection ranges from 5 to 1000 rpm. Temperature control of sample is possible between either 5°C (or 15°C below ambient, whichever is higher) and 75°C. The viscometer uses a Capcalc32 software for complete control and data analysis. A "velocity imposed gradient" test was used at the room temparature of 20^{0}C. The experimental test consists of a load from the 10 s^{-1} to 13333 s^{-1} shear rate gradient, followed by an unload in order to highlight the thixotropy of the lubricant - "shear memory".

For the microscopic tests a transmission electron microscope JEOL Japan - JEM - 200 CX was used, in order to obtain information on the wear particles shape and concentration. The main characteristic parameters of the microscope are:

- lattice resolution [Å]: 1.4;
- point-to-point resolution [Å]: 2.6;
- acceleration voltage [kV]: 80, 100, 120, 160, 200;
- magnification: ×1000 to ×300000.

Oil samples were allowed to decant by sampling the densest part. The extracted sample was dropped in a small size crucible and washed several times with heptane to remove the fatty portion. The heptane treatment (washing) was done until the traces of oil had completely disappeared, so that the useful sample could be inserted into the electron microscope without danger for the high vacuum in the column. Remaining part: additions, impurities, deposits from wear representing the sample of interest was prepared for electronic microscopy.

The main steps to sample preparation for TEM + SAED were:

- the non-fat part was mixed with ethyl alcohol and deposited on special microscope grids, 3 mm in diameter, of Cu or Ni covered with C;
- some of the grids were covered/overshadowed with a very thin layer of C in a JEOL vacuum evaporation installation for fastening in the beam and for increasing the contrast.

The method is used for particle systems less than 10 μm. Particle studies also involve the determination of the existing phase, which can be highlighted by electron diffraction on a selected area (SAED). The advantage, compared to X-ray diffraction, is the possibility of showing particles found in the sample in extremely small quantities (<<0.1% or even a single group of particles).

Table 1. Physicochemical properties of fresh lubricants

Parameter \ Lubricant	75W 90	75W 140
Density at 15°C (59°F) ASTM D1298	900 kg/m^3	906 kg/m^3
Kinematic viscosity at 40°C (104°F) ASTM D445	72.6 mm²/s	170 mm²/s
Kinematic viscosity at 100°C (212°F) ASTM D445	15.2 mm²/s	24.7 mm²/s
Viscosity index VIE ASTM D2270	222	178
Flash point ASTM D92	200°C	212°C
Pour point ASTM D97	-60°C	-36°C

The lubricants used for testing are two transmission lubricants (75W90 and 75W140), in fresh and used state (2000 km). These are 100% synthetic extreme pressure lubricants, characterised by an efficient antiwear protection, with a better resistance at high temperature and a longer life time. The lubricants are specially designed for racing vehicle gearboxes, synchronised or not synchronised gearboxes, gearbox/differential, transfer gearboxes and hypoïd differentials. The physical and chemical properties of the lubricants in fresh state, offered by the manufacturer, are presented in Table 1.

RESULTS AND DISCUSSION

The first stage of the experiment was focused on the influence of the wear degree of the lubricant on its rheological properties. The rheograms (Figure 1) are obtained by plotting viscosity as a function of the shear rate, as an average of three points, using the Capcalc32 software specific for the viscometer. Analysing the rheograms from Figure 1, it can be seen that all the lubricants, in fresh or used state, do not exhibit any thixotropic behaviour. For lubricant 75W90, there is almost no difference between fresh state and used state, both of them having the same viscosity for the whole range of the investigated shear rates. Regarding the lubricant 75W140, there is a significant difference between the two states, observing that the viscosity of used lubricant is always smaller than of the fresh one, for any shear rate in the considered field.

The corresponding rheological parameters for both the lubricants in fresh and used state, according to the Cross model (Eqn. 1), are presented in Table 2.

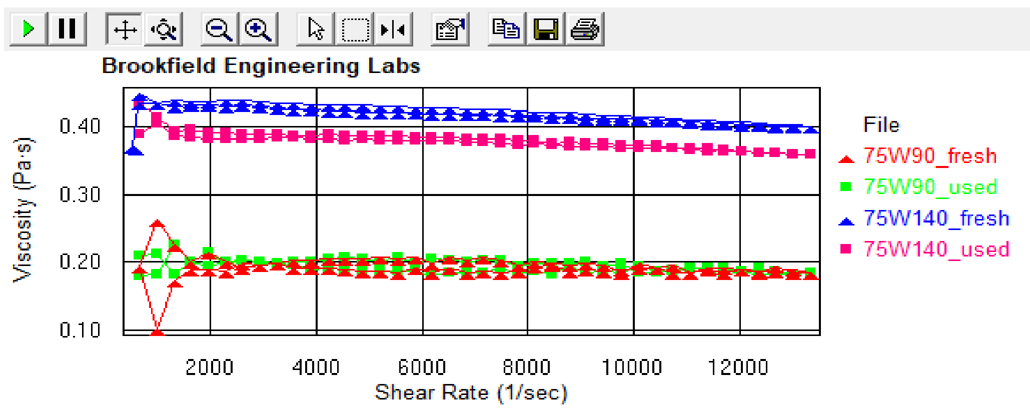


Figure 1. Rheograms for 75W90 and 75W140 oils in fresh and used state

Table 2. Parameters of the Cross model for the transmission lubricants in fresh and used state

Type of oil	Wear degree	Cross model			
		η_∞, Pa·s	η_0, Pa·s	λ, s	*m*
75W90	fresh	0.153	0.229	$7.595\cdot10^{-4}$	0.065
	used	0.118	0.307	$3.057\cdot10^{-3}$	0.175
75W140	fresh	0.257	0.628	$1.725\cdot10^{-3}$	0.104
	used	0.220	0.574	$1.753\cdot10^{-3}$	0.095

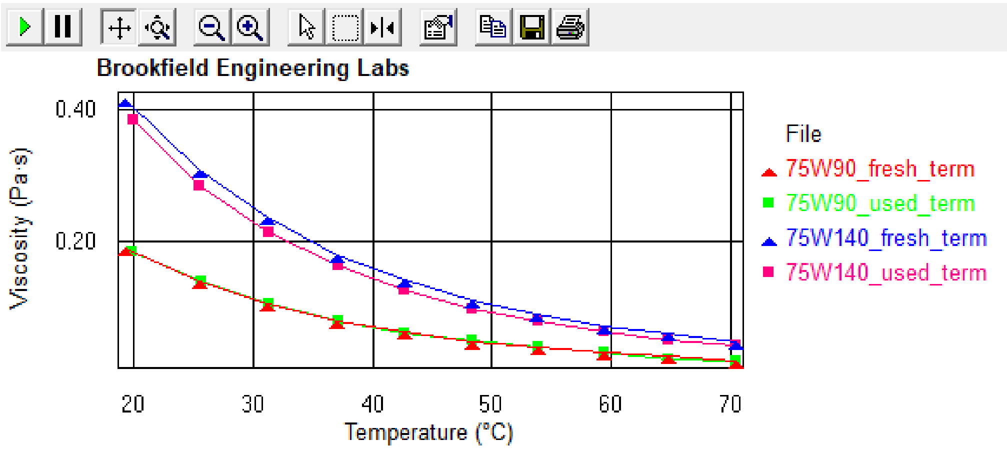


Figure 2. Variation of the apparent viscosity with temperature for 75W90 and 75W140 oils, in fresh and used state

Table 3. Variation of the rheological parameters of lubricants with temperature

Lubricant \ Parameter		Jarchov and Theissen model			Cameron model			Reynolds model		
		η_{50}, Pa·s	*B*	Corr. coeff.	*K*, Pa·s	*b*, ^{0}C	Corr. coeff.	η_{50}, Pa·s	m, $^0C^{-1}$	Corr. coeff.
75W90	Fresh	0.0446	5.419	0.998	$1.979\cdot10^{-4}$	785.75	0.998	0.0435	-0.0473	0.999
	Used	0.0446	5.517	0.997	$1.776\cdot10^{-4}$	799.97	0.997	0.0432	-0.0478	0.999
75W140	Fresh	0.1043	5.232	0.998	$5.572\cdot10^{-4}$	758.58	0.998	0.1021	-0.0454	0.999
	Used	0.0919	5.520	0.999	$3.678\cdot10^{-4}$	800.46	0.999	0.0899	-0.0477	0.998

Table 4. Chemical properties of tested oils

Type of oil	Wear degree	Acidity value, mg KOH/g	Total Base Number, mg KOH/g
75W90	fresh	1.62	11.30
	used	1.64	11.38
75W140	fresh	1.71	11.54
	used	1.79	12.01

In order to investigate the influence of the lubricant wear degree on the apparent viscosity, a supplementary thermal test was performed. Figure 2 presents the variation of the apparent viscosity with the temperature, for both lubricants in fresh and used state, at a constant shear rate of 13333 s^{-1}. It can be seen that for 75W90 oil, there are almost no differences between fresh and used lubricant, while the oil 75W140 presents significant changes in used state comparative to fresh state.

Table 3 shows the values of the thermal rheological parameters of the studied lubricants, according to Jarchov and Theissen, Cameron and Reynolds models (Eqns. 2, 3 and 4). Analysis of the data from this table reveals that all three proposed models are appropriate to approximate the variation of the apparent viscosity with temperature, having values of the correlation coefficient almost equal to 1.

The explanation for the changes of the rheological properties of 75W90 and 75W140 oils during the working period can be found by analyzing two of the most important chemical properties of the oils (see Table 4): Acidity value (ASTM D664) and Total Base Number (ASTM D2896).

It can be seen that for the oil 75W90 there is almost no change in acidity number and total base number during the entire operating period. This observation is directly correlated with the rheological and thermal behavior of the oil, in fresh and used state, for the whole range of shear rates and temperatures investigated.

For the oil 75W140, which clearly showed differences for thermal and rheological properties between fresh and used state, this presents an increasing trend in acidity and alkalinity (total base number).

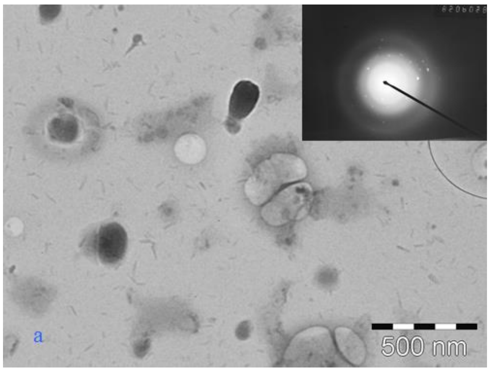
Regarding the wear particles' shape and concentration identified in fresh and used oil, electronic microscopy was used. For both oils, 75W90 and 75W140, in fresh and used state, the same type of particles was identified:

- type of solid particles identified in fresh lubricant: ZnO hexagonal (ASTM 80-0075), δ - CaP_2O_6 (X) (ASTM 15-0185) and amorphous phase (Table 5);
- type of solid particles identified in used lubricant: FeC orthorombic (ASTM 03-0400), V_2O_3 rhombohedral (ASTM 15-0185), $Fe_{0.11}V_2O_{5.15}$ orthorhombic (ASTM 82-1871), SiO_2 hexagonal (ASTM 83-2187) and amorphous phase (Fig. 3).

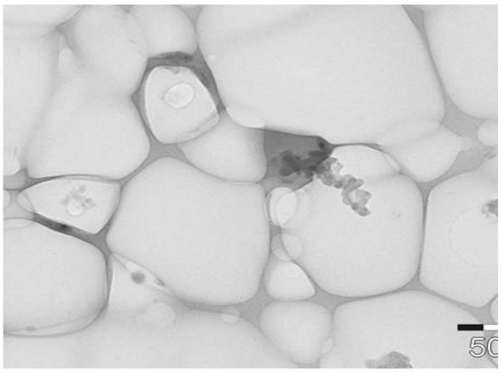
Based on this microscopic analysis, it can be concluded that the presence of the solid particles in lubricants does not affect their rheological properties.

Fresh oil

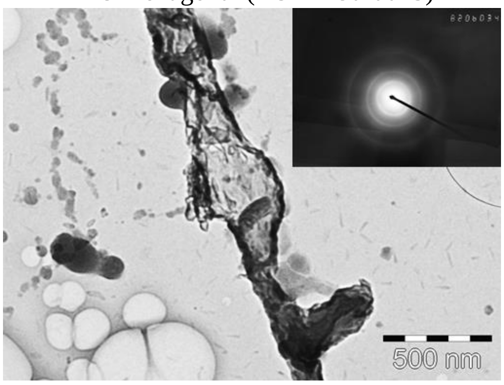
Used oil



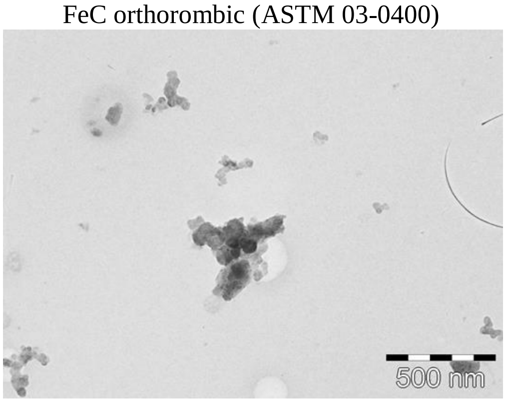
ZnO hexagonal (ASTM 80-0075)



FeC orthorombic (ASTM 03-0400)



δ - CaP_2O_6 (X) (ASTM 15-0185)



V_2O_3 rhombohedral (ASTM 15- 0185)

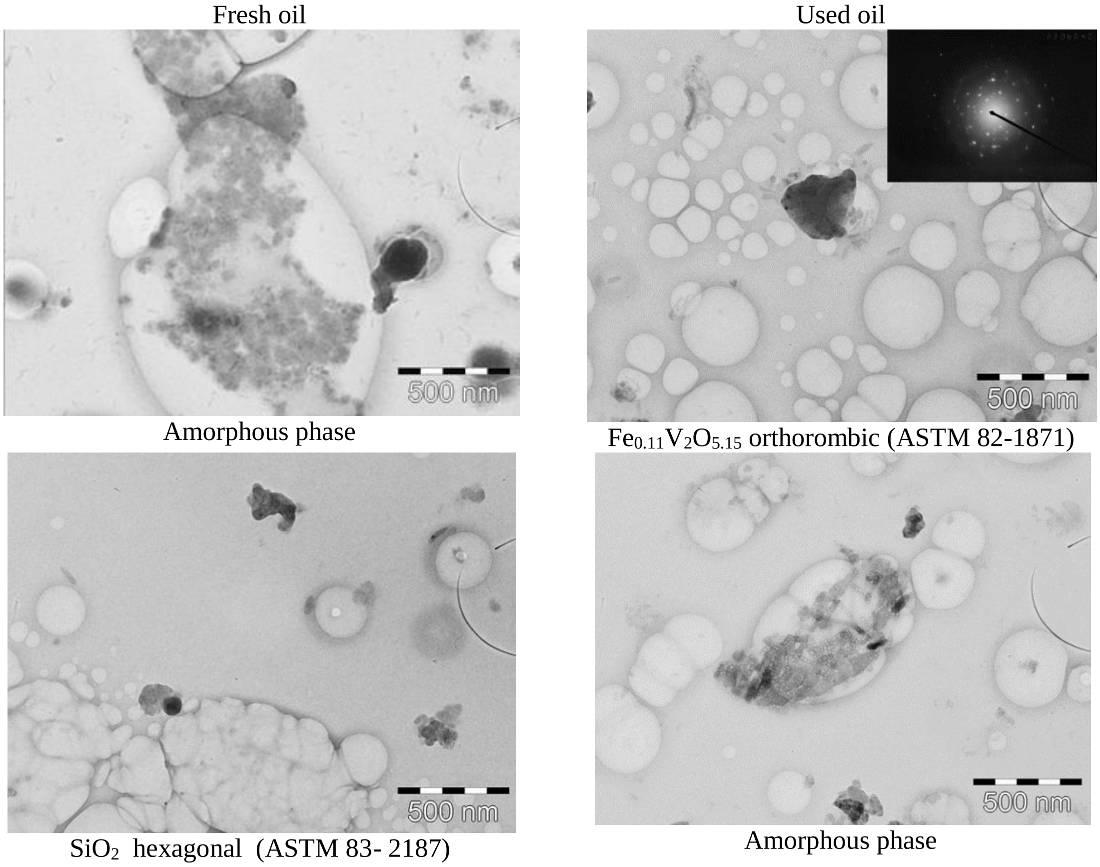


Fig. 3. Structural composition of fresh and used transmission oils.

CONCLUSIONS

The present paper investigated the rheological and chemical properties of two transmission lubricants for motorcycle gearboxes (75W90 and 75W140), in fresh and used state, correlated with the identification of the contaminated particles in the oils.

It was found that the lubricants do not exhibit a yield stress and thixotropy and that, above a critical shear rate, they exhibit shear-thinning behaviour, well described by the Cross model.

For lubricant 75W90, there is almost no difference between fresh state and used state, both of them having the same viscosity for the whole range of the investigated shear rates and the same thermal rheological parameters.

Regarding the lubricant 75W140, there is a significant difference between the two states, observing that the viscosity of the used lubricant is always lower than for the fresh one, for any shear rate in the considered field. The same conclusion is valid also for its thermal rheological parameters.

All three proposed models, which approximate the variation of the apparent viscosity with temperature (Jarchov and Theissen, Cameron and Reynolds), are appropriate for both lubricants, in fresh and used state.

The determination of the parameters for the rheological Cross model and also their variation with temperature is very usefull to model the functioning of different friction couples, using the thermo-hydrodynamic theory of lubrication based on Reynolds equations.

There is a direct connection between the modification of the rheological properties of the lubricants in fresh and used state and the changes of their chemical properties (Acidity value and Total Base Number).

The presence of the solid particles in lubricants does not affect their rheological properties, but they are a clear indicator of the wear degree of lubricants. It is necessary to perform supplementary investigations in this direction, in order to connect the existence of the wear particles with the tribological properties of lubricants.

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