Improving the lubricating properties of transmission oils by activating the processes of boundary films formation

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Abstract. The properties of the boundary lubricating films determine the performance of friction units, which is most important in the event of a loss of lubricant. It has been found that when sunflower oil is added to mineral transmission oil, strong boundary layers are formed during friction. These layers reduce wear and friction. Vegetable oils with the lowest iodine value have the best antiwear properties. The additional introduction of the product of the interaction of rosin with copper (II) hydroxide into the transmission oil makes it possible to form lubricating structured layers that improve the tribotechnical properties.

1. Introduction
One of the most important properties of oils is their ability to form lubricating films on friction surfaces. The ordered arrangement of molecules is one of the main reasons for the decrease in friction [1]. High lubricity is provided when shear is localized completely or in large part in the polymolecular boundary layer, in which the shear resistance is minimal and wear is practically absent [2-4].

Usually wear occurs when the thickness of the liquid film becomes less than the average height of the peaks of the sliding surface roughness, that is, under boundary lubrication conditions. The high viscosity of gear oils prevents the oil film from squeezing out of the engagement area of the gears, allowing metal parts to be divided. In case of loss of lubrication, the bearing capacity of the surface layer is set only by boundary films [5].

We have found that sunflower oil is capable of forming strong boundary films on the metal surface under friction [6]. The formation of such films significantly reduces the coefficient of friction and increases the maximum carrying capacity of the oil. This allows the use of lubricants based on sunflower oil in heavily loaded tribosystems [7].

In this work, we studied ways to improve the performance properties of SAE85W90 oil by modifying it with vegetable oils and an additive - the product of the interaction of rosin with copper (II) hydroxide. The aim of the work was to find the composition of the transmission oil that ensures the formation of strong boundary lubricating films.

2. Materials and methods
To determine the tribological characteristics of lubricants, a four-ball friction machine was used. The friction force was measured with a DEPZ-1D-0,1R-1 dynamometer with an accuracy of 0,01 N. The initial load on the lever was 98 N, then after 20 minutes it increased to 196 N, after another 20 minutes
to 294 N. After the experiment, the measurement was carried out the diameters of the wear scars of the balls using an optical microscope.

The kinetic patterns of changes in chemical bonds in the surface antifriction film were studied by IR ATR spectroscopy on a Nicolet 380 spectrometer.

The presence of the film on the friction surface was confirmed with a Zeiss EVO-18 MA scanning electron microscope (SEM) equipped with BSD and SE sensors. The accelerating voltage ranged from 5 to 15 kV. The film is an insulator, and therefore, its presence on the metal is clearly visible. For SEM study of the friction surfaces, excess lubricant was removed with a solvent (nefras).

The tribotechnical properties of SAE85W90 mineral oil, vegetable oils - sunflower, mustard, linseed, camelina, palm oils were studied.

3. Results and discussion

Tribograms of mineral and vegetable oils differ significantly from each other, Figure 1.

![Figure 1. Tribograms of SAE85W90 (1) and sunflower (2) oils](image)

On the tribogram of sunflower oil, at each step of increasing the load, a sharp increase in the friction coefficient is observed, and then its gradual decrease with subsequent stabilization (Figure 1). Gear oil is characterized by an increase in the friction coefficient over time at each load.

The dependence of the wear scar diameter on the concentration of sunflower oil in SAE85W90 is shown in Figure 2.
The data obtained can be explained by the fact that the addition of up to 30% sunflower oil makes it possible to activate the processes of formation of surface films. This results in a 35% reduction in wear. At high concentrations of vegetable oil, the viscosity of the transmission oil decreases, which negatively affects its tribotechnical properties.

Reducing the wear scar diameter during friction in a lubricant containing 70% of transmission oil and 30% of the sunflower oil medium is associated with the formation of boundary lubricating films, which are detected by instrumental methods, figure 3.

![Figure 3. SEM image of a boundary film formed in a lubricant containing 70% transmission oil and 30% sunflower oil](image)

Study of the friction surface by ATR IR spectroscopy, Figure 4, made it possible to identify the groups of atoms forming the boundary film.
Figure 4. IR spectrum of the surface formed by friction in a lubricant containing 70% transmission oil and 30% sunflower oil

The film contains absorption peaks 2953,8; 2927,1; 2852,1 cm\(^{-1}\) corresponding to stretching vibrations of CH bonds; 1747,1 cm\(^{-1}\) - stretching vibrations of C=O bonds; 1463,0; 1377,0; 1233,0 cm\(^{-1}\) - bending vibrations of CH\(_2\) and CH\(_3\) groups; 1166,4; 1104,5 cm\(^{-1}\) - stretching vibrations of C-O bonds of esters; 720,0 cm\(^{-1}\) - bending vibrations of CH\(_2\) groups. The form of the spectrum corresponds to the surface films formed by friction with sunflower oil [6].

It has been proven that the mechanism of action of vegetable oils as additives is associated with the formation of tribopolymer films that reduce the coefficient of friction and protect against wear.

The next step in our research was to study the effect of the chemical composition of vegetable oils on their tribotechnical properties. All vegetable oils, by their chemical nature, are esters of glycerol and higher carboxylic acids. The physicochemical and tribotechnical properties of vegetable oils depend on the structure of alkyl radicals of carboxylic acids, and, in particular, on the number and mutual arrangement of unsaturated C=C bonds in the hydrocarbon skeleton. The quantitative measure of the content of unsaturated bonds is the iodine value. A comparison of the tribological properties of oils with their iodine value is shown in Table 1.

| Lubricant         | Friction coefficient, at different load on the lever (N) | Wear scar diameter, mm | Iodine value |
|-------------------|----------------------------------------------------------|------------------------|--------------|
| SAE 85W90 mineral oil | 0,13 0,13 0,17                                          | 1,45                   | 0            |
| Sunflower oil     | 0,08 0,07 0,06                                          | 1,02                   | 132          |
| Mustard oil       | 0,15 0,14 0,16                                          | 1,24                   | 102          |
| Linseed oil       | 0,09 0,14 0,16                                          | 1,17                   | 181          |
| Camelina oil      | 0,13 0,14 0,13                                          | 1,37                   | 142          |
| Palm oil          | 0,08 0,07 0,05                                          | 0,7                    | 54           |
Analysis of the data obtained shows that with an increase in the iodine value, the diameter of the wear scar tends to increase. Palm oil exhibits the best antiwear properties with a minimum iodine value of 54.

High lubricity can be achieved when a liquid crystal structure of lubricating layers is formed in the friction zone [8-10]. In this regard, it is promising to study substances capable of forming epitropic structured layers. It has been shown [11-13] that the addition of liquid-crystal type cholesterol compounds to the lubricant leads to the formation of structured layers on the friction surfaces that significantly improve the antifriction properties of oils. The disadvantage of such additives is their high cost.

The product of the interaction of rosin with freshly precipitated copper (II) hydroxide (Additive) was studied as an additive that forms structured layers. The main component of rosin is resin acids, whose copper salts are structurally similar to cholesteryl esters. Due to the specific structural features of these compounds, it can be expected that they will create surfaces with a high orientation in the process of friction, which can provide an improvement in the lubricating properties and performance of the boundary layers. In addition, abietic acid, the main component of resin acids, contains a 1,3-butadiene fragment in its molecule, which is capable of participating in the formation of a three-dimensional network structure. This structure, like a sponge, can be filled with oil molecules and provide an additional decrease in the coefficient of friction [14]. The results of tribological tests of various compositions of transmission oils containing sunflower oil and an Additive are shown in Table 2.

| Lubricant | Friction coefficient, at different load on the lever (N) | Wear scar diameter, mm | Specific load, MPa |
|-----------|--------------------------------------------------------|------------------------|-------------------|
|           | 98  | 196 | 294 |                          |                      |                    |
| 70% SAE85W90 + 30% Sunflower oil | 0,09 | 0,10 | 0,07 | 1,23 | 21,05 |
| 70% SAE85W90 + 29,9% Sunflower oil +0,1% Additive | 0,08 | 0,08 | 0,07 | 1,10 | 26,32 |
| 70% SAE85W90 + 29,5% Sunflower oil +0,5% Additive | 0,07 | 0,08 | 0,07 | 0,78 | 52,45 |
| 70% SAE85W90 + 29% Sunflower oil +1,0% Additive | 0,07 | 0,07 | 0,07 | 0,77 | 53,72 |

Comparison of the data in Table 2 shows that the introduction of the Additive increases both the antiwear and loading properties of the oil. Thus, the Additive promotes the formation of boundary lubricating layers.

4. Conclusion
It is shown that when sunflower oil is added to mineral transmission oil, strong boundary lubricating films are formed during friction.

The addition of the product of the interaction of rosin with copper (II) hydroxide to the transmission oil allows the formation of structured boundary films that reduce friction.

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