Study of impact of tribotechnical composition on rubber technical products to assess its applicability in wheeled transport engine

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Abstract. Tribotechnical coating helps to reduce the friction factor and improves the performance of the internal-combustion engine, but in the process, the generic components of the engine oil and other additives interfuse together. Besides, the coating mixture excretes acids and can destroy general mechanical rubber goods and metals. For this research the oil-gasoline-resistant rubber was used which is half-disk shaped with the dimensions of 27x7x2 mm. These samples of rubber have been heated to 110°C and exposed to generic components of engine oil, tribotechnical coating «ACTIVE PLUS» and strong acid H₂SO₄. In the total, the volume of the tribotechnical coating and engine oil was approximately 1 % of strong acid H₂SO₄. The article describes most common properties of aged rubbers such as rubber hardness, resilience, elasticity after exposure to generic components of engine oil and its additives. Results were obtained in the laboratory where samples of rubber were exposed to heat, engine oil, tribotechnical coating in conditions of absence of mechanical load. This study has identified an important issue according to which sulfuric acid destroys the system of oil-ultrafine particles in the absence of swelling of rubber.

1. Introduction
The tribotechnical composition used for the gasoline engine has not only a detergency effect (removes carbon deposits and deposits from the surfaces of power unit parts), but also forms a wear-resistant layer on the metal surface with a low friction index. This ability of the tribotechnical composition (TC) is connected with the layered silicates present in it (the active component is ultrafine particles of serpentines, chlorites and other minerals), which are chemically neutral to all substances included in the lubricant stuff additive package as it is pointed out in the literature.

In the process of engine operation, the base additives presented in the engine oil “wear off”; engine oil compositions change [1-4]. Organic acids are formed from the components of the lubricant. These acids reacting upon metals and rubber technical products can destroy these materials. For example, water running into the crankcase has the same effect on metals. However, there is no information about the effect of organic acids and water on the tribotechnical composition, the motor oil does not mix with TC. There are no data on the impact of the tribotechnical composition on rubber technical products; that is why it is necessary to analyze the mentioned influence and impact. This will allow assessing the
tribotechnical composition applicability for wheeled transport engines (commercial transport) operating under heavy loads imposed on the cylinder-piston group, crank gear, valve train and lubrication system.

2. Experimental
The tribological composition «ACTIVE PLUS», multigrade synthetic engine oil «GENESIS CLARITECH» 5W-30, engine oil, sealant (oil seals) of 2108-170342-01 (16x30x7 [mm]) type were the subject of the study. Sealant is made of oil and petrol resistant rubber, which can not be heated above 110°C according to rated values. The samples of rubber in the shape of a semicircle with the size of 27x7x2 [mm] were studied. One of the samples was aged burning off the rubber product during 91 hours at ~ 150°C in the stream of air pumped forcibly through a reactor with rubber placed into it. The aged sample did not have such features as elasticity and resiliency typical of any other rubber.

The kinematic viscosity of studied products was determined (in the temperature range from 20°C to 100°C) with VPJ-4 viscometers, the density (ρ) of the liquids was measured with the oleometer.

The calculation of viscosity (ν, cCt) was carried out according to the equation:

\[ ν = C \cdot τ, \]

where C is a constant viscometer, cCt · c⁻¹; τ is the arithmetic mean time of fluid sample outflow, (in seconds).

The calculation of the viscosity index (VI) of the initial engine oil (EO), functioned engine oil (FO) and TC was performed using an online calculator.

The concentrated sulfuric acid was used to determine the presence of unsaturated (alkenes, olefin) and aromatic hydrocarbon in the initial engine oil (EO) and tribotechnical composition (TC). 0.2 ml of concentrated H2SO4 was added to 20 ml of the liquid. The percentage of acid (by volume) did not exceed ~ 1%.

The process of impact of oil, tribotechnical composition and liquid containing sulfuric acid on rubber is in heating (during 15 hours, temperature - 80°C) and mixing (magnetic stirrer) of the sample (volume 20-20.2 ml) with rubber placed in it. The swelling of rubber is estimated by measuring (VLTE-150 portion scales) the mass of the samples before and after the experiment. The maximum permissible error of the weights is ± 0.003 g; the standard deviation is 0.0015 g.

The viscous flow activation energy (Ea) is determined using the methods of mathematic statistics, Microsoft Office Excel software (Analysis Package – Analysis Data – Regression) or STATISTICA [5, 6]. The dependence of the viscosity of the steady-state flow process on temperature is described by Frenkel-Andrade equation [7, 8]:

\[ ν = A \exp\left(\frac{E_a}{RT}\right), \]

where A – constant, Ea – activation energy, R – absolute gas constant, T – absolute temperature.

To determine Ea the viscosity indexes measured at 20, 40, 70 and 100°C temperatures were used. The dependency was analyzed:

\[ y = a + bx, \]

where y – logarithmic viscosity number lnν; a – absolute term, b – coefficient of regression which is equal to Ea to R; x – inverse absolute temperature 1/T.

The evaluation of detergent-dispersing properties of the operated engine oil was carried out using the spot test analysis («oil stain»).

3. Result and Discussion
From a comparison of the data (table 1), it follows that viscosity characteristic, as well as an engine oil viscosity index, is greater than ν and VI of tribotechnical composition. The density of TC is greater than ρ of an engine oil.
Table 1. The values of viscosity, density, viscosity index (VI), activation energy of viscous flow of the original engine oil (EO), tribotechnical composition (TC) and liquids containing sulfuric acid (TCC, IOC).

| Parameter   | TC   | TCC  | EOC  | EO^a |
|-------------|------|------|------|------|
| \( \nu \) at 40°C, cCt | 62.2 | 64.3 | 66.7 | 68.65\(^b\) |
| \( \nu \) at 100°C, cCt | 7.7  | 8.3  | 11.4 | 11.23 |
| VI          | 84   | 97   | 166  | 169  |
| \( \rho \) (15°C), kg \( \cdot \) m\(^{-3}\) | 890.4 | ---- | ---- | 847.2 |
| \( E_a \), kJ \( \cdot \) mol\(^{-1}\) | 35.8 | 35.3 | 30.9 | ---- |

\(^a\)standard values of density (at 15°C), viscosity and viscosity index of engine oil GENESIS CLARITECH 5W-30; \(^b\)laboratory results [Oil-club.ru]

Viscosity index, \( \nu \) of TCC liquid containing TC and sulfuric acid exceed the values of VI, the viscosity of the composition without \( \text{H}_2\text{SO}_4\)\(^{\text{concentrated}}\). In comparison with tribotechnical composition, sulfuric acid has a small effect on \( \nu \) characteristics, VI of engine oil. These differences in VI, \( \nu \) values for samples with and without \( \text{H}_2\text{SO}_4\)\(^{\text{concentrated}}\) are reflected in changes of TCC liquid color and the formation of black precipitation in it. The TCC liquid is getting color, which is as a rule observed in reaction between \( \text{H}_2\text{SO}_4\)\(^{\text{concentrated}}\) and aromatic (unsaturated) hydrocarbon [9, 10]. As a result, the tribotechnical composition can contain aromatic (unsaturated) hydrocarbon in it. Sulfuric acid destroys the system of oil-ultrafine particles (dispersion medium-dispersed phase).

The percentage of precipitated out aggregates forms because of ultrafine particles adhesion is equal to 2% of liquid mass. The engine oil gets cloudy after reacting with sulfuric acid. In contrast to TC, there are no distinctive changes in engine oil indicating the reaction of sulfuric acid with hydrocarbons. The turbidity of liquid containing sulfuric oil and engine oil is associated with emulsion formation.

The value of viscous flow activation energy of TC and TCC are not so different (table 1). This small difference may be due to the fact of absence of ultrafine particles in TCC liquid. During the process of viscosity measurement in tribotechnical composition there was a phenomenon of sedimentation - particle deposition of dispersed phase. That is why the obtained value of activation energy of the tribotechnical composition can not be considered as correct.

The parameter \( E_a \) of the emulsion containing engine oil and sulfuric acid is lower than the activation energy of TC and TCC by 13-14%. It should be expected that in mixtures of EO with TC the number of molecules of tribotechnical composition available to transit from one layer to another will be lower than the number of engine oil molecules in this process.

The rubber mass (including an aged sample) both before and after reacting with tribotechnical composition, engine oil, liquids containing sulfuric acid, does not change within the measurements error. Consequently, the rubber does not swell when affected by tribotechnical composition, engine oil, liquids containing sulfuric acid. The same result was obtained for working engine oil, which did not lose its detergent-dispersant properties. Dispersing ability of working engine oil was 0.4 conditional unit (c.u.) which is higher than the critical unit of 0.3 c.u.

4. Conclusion
Thus, the rubber test (used for vehicle seal production) shows that swelling processes of the material reacting with tribotechnical composition do not proceed when effected by heat and there are no mechanical loads. The sulfuric acid destroys the system of oil-ultrafine particles. Particles while sticking together form aggregates whose dimensions far exceed the size of ultrafine particles. The use of the tribotechnical composition in the wheeled transport engine should be considered possible. However,
such applicability can restrain the destructive effect on the system of oil-ultrafine particles of sulfuric acid, which is formed in the crankcase while water reacts with sulfur oxide (fuel with high sulfur content) which penetrates from the combustion chamber through the leakage of piston rings. No doubts, to confirm the conclusion made about the applicability of the tribotechnical composition, additional research should be carried out. For example, the research, studying the effect on the stability of the indicated composition of organic acids, analyzes not the composition itself but its mixtures with engine oil.

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