Results of Research Replacement of Graphite by Petroleum Coke in Lubricated Compositions

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***Abstract*— The article presents the results of studies to reduce the wear of rails and wheels by creating new lubricant compositions for the lubrication of rails based on the replacement of graphite with petroleum coke. Cheap components of the composition, easily accessible products or waste products are presented. During the tests, it was determined that the composition is easily applied to the rail, does not flow from the side surface of the rail head, has a high protective effect. When the rolling stock moves, the grease is spread by the wheels, ensuring uniform distribution on the side surface of the rail head. Including in the composition of hydrocarbons can be biodegradable. This confirms the environmental safety and harmlessness of this composition. The viscosity of the composition is regulated by the content of spent diesel oil. The components of the composition are easily mixed to form a stable consistency during storage. The composition to prevent wear in the wheel-rail friction pair, in which graphite is replaced by a cheaper component – petroleum coke, has high efficiency and minimal impact on humans and the environment.**

Keywords—lubricant composition; modeling; petroleum coke; properties of compositions; wear

I. INTRODUCTION

Graphite is part of many lubricants that are used not only in rail transport [1]. Figure 1 shows a graphite crystalline lattice diagram [1], clearly showing its antifriction properties. The coefficient of friction of graphite for steel is 0.04÷0.08. The widespread use of graphite is also determined by its high adhesion to metal and high electrical conductivity, which contributes to the removal of electrostatic charges and preserving the strength of the lubricating layer.

However, graphite and other solid antifriction materials (MoS_2, $MoSe_2$ etc.) are the most expensive components of lubricant compositions based on them. To obtain graphite from natural materials requires laborious methods of enrichment. Synthetic graphite with the best technical performance compared to natural graphite is produced by graphitizing petroleum or metallurgical coke, which requires high energy and labor costs. At the same time, coke is mixed with pitch and pressed under a pressure of 250 MPa, then fired at 1200 °C and graphitized at 2600°÷3000 °C. The resulting intermediate product is again impregnated with liquid pitch, subjected to firing and graphitization. These operations must be repeated up to 5 times [2].

However, most of the carbon varieties (charcoal, soot, coke, and others) occurring in nature or artificially obtained and called “amorphous” carbon, according to X-ray structural analysis, consist of the smallest differently oriented graphite crystals [2]. Obviously, for this reason, some of these carbon modifications have found use in lubricating compositions. For example, soot condensate is used to thicken plastic lubricants [3], and coal coke is used as a component to create an anti-friction self-lubricating material (10÷20 % wt., along with MoS_2, epoxy resin and graphite) [4].

Petroleum coke is a solid porous product with an ash content of less than 0.5%, which compares favorably with other carbon modifications. It is a complex dispersed system, which is based on crystallites, which are packages of several parallel layers. The sizes of crystallites: length is 2.4÷3.3 nm, thickness is 1.5÷2.0 nm, interplanar distance is 0.345 nm [5] (for graphite, the interplanar distance is 0.34 nm [1, 5]).

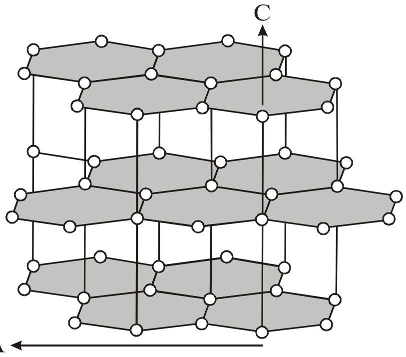

Fig. 1. Graphite crystalline lattice. A and C are crystallographic axes

Fig. 2 shows schematically the structure of petroleum coke in the form of a set of disordered crystallites. At the ends of the crystallites are carbon atoms that carry residual hydrogen and oxygen-containing functional groups.

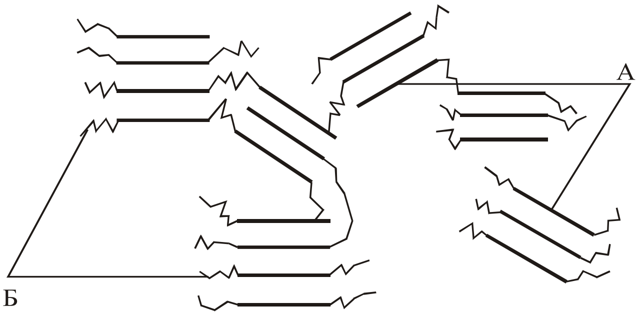

Fig. 2. The structure of petroleum coke. A – crystallites with an ordered graphite-like structure; B – disordered carbon.

The disordered arrangement of individual crystallites of a graphite-like structure in petroleum coke makes it highly porous, which determines the capacity for adsorption — the absorbing of various substances. While the density of graphite reaches 2.27 g/cm^3, the true density of petroleum coke does not exceed 2.13 g/cm^3, and its porosity reaches 56 % [5].

Comparison of Fig. 1 and 2 shows that petroleum coke cannot have antifriction properties, since the shift of crystallites relative to each other is difficult. However, under the action of high loads occurring in the friction zone, coke crystallites in the presence of hydrophobic hydrocarbon molecules are easily rearranged in such a way that the graphite planes become parallel to the friction plane and, thereby, provide an anti-friction effect (Fig. 3). Petroleum coke must contain a minimum amount of non-carbon impurities. Delayed coking petroleum coke meets these requirements. For dispersion it is advisable to use a coke mix with a particle size of <6 mm, which cannot be sold in most cases.

The external pressure exerted by the wheel on the lubricant in the contact zone, and a sharp increase in temperature at the same time lead to plastic deformation of the lubricant. In this case, mutual rearrangement of crystallites and filling of voids occurring in it, as a result of which the density of the material increases (Fig. 2, 3).

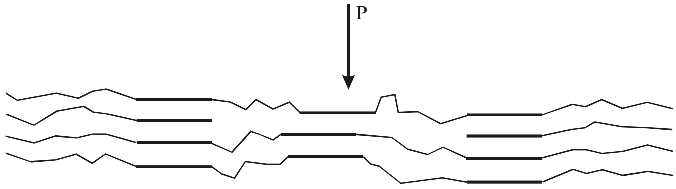

Fig. 3. The restructuring of the petroleum coke during the hydrocarbon material impregnation and the application of external load

Considering the behavior of the lubricant composition as a Bingham environment, the Murray equation [6] can be applied to the process of crystal rearrangement, which is used, in particular, to determine the compaction rate of refractory oxides during hot pressing.

$$\left(\frac{d\rho}{d\tau}\right)_p = \frac{d\rho}{d\tau} + \frac{3}{4}\frac{p}{\eta}(1-\rho) \tag{1}$$

where $\frac{d\rho}{d\tau}$ – the compaction speed without external pressure (only because of temperature); p – the external pressure (as already mentioned, reaching 3000 MPa); ρ – the density of the material after the restructuring; η – the coefficient of viscosity of the liquid phase, in the presence of which the rearrangement occurs.

Purely qualitatively, this equation shows that the rate of rearrangement of graphite-like crystallites substantially depends on the external pressure and viscosity characteristics of the medium.

The presence in the composition of waste diesel oil and low molecular polyethylene reduces the viscosity of the system (compared to solid material), which also increases the rate of restructuring of crystallites.

Naturally, other factors, in particular, the dispersiveness of the powder, affect the rate of transformation of the crystalline structure of petroleum coke. Its increase results in improvement in the tribotechnical characteristics of the lubricant. It should be noted that the finely dispersed petroleum coke with a particle size of less than 10 microns, which we obtained specially using a colloid mill, completely resembles the lubricating effect of graphite. However, the achievement of such a degree of grinding in real production conditions is associated with high-energy costs and technological difficulties.

Therefore, we carried out all further tests with compositions containing petroleum coke with a particle size of 0.1 mm (100 μm). Such grinding is easily achieved in standard ball mills.

II. Mathematical processing of experimental data on the effect of the petroleum coke grinding degree on wear.

Preliminary processing of the results of measurements or observations is necessary in order to use statistical methods to build empirical dependencies with the greatest efficiency, and most importantly – correctly.

The essence of preliminary processing mainly consists in eliminating gross measurement errors or errors that inevitably occur when rewriting digital material or loading information into a PC.

Rough measurement errors (anomalous, or very prominent, values) are very difficult to determine, although it is intuitively clear what it is.

There is an indication [7] that the anomalous values of the measured quantity are obtained as a result of a change in the experimental conditions, but this is not always the case.

Perhaps, the following example [8] explains the essence of gross errors better: assuming that 10% of measurements, representing anomalous values, are more than $3l$ from the average (l is a segment on the Ox axis), and the remaining observations are located within l, then when evaluating variance through S^2, these 10% of observations at least double the estimate.

Another important point in data preprocessing is to verify that the distribution of the measurement results corresponds to the law of normal distribution. If this hypothesis is unacceptable, then it is necessary to determine which distribution law obeys the experimental data, and, if possible, convert this distribution to normal. Only after performing the above operations we can proceed to final data processing, for example, building empirical formulas, using, for example, the least squares method.

The dependence of wear (in grams) on the degree of grinding (in millimeters) of petrochemical coke is given in Table I and Table II. Table I shows the results of experiments for movable rollers, and Table III shows the results for fixed rollers. The distribution range is shown in Fig. 4 and Fig. 5, respectively. An important step in preprocessing is the elimination of gross errors.

TABLE I. MOVABLE ROLLER

Wear	0,058	0,059	0,180	0,260	0,340	0,428	0,580	0,742	1,650
Grinding degree	0,05	0,1	0,15	0,2	0,25	0,3	0,35	0,4	0,45

TABLE II. FIXED ROLLER

Wear	0,126	0,205	0,283	0,364	0,442	0,508	0,630	0,812	1,903
Grinding degree	0,05	0,1	0,15	0,2	0,25	0,3	0,35	0,4	0,45

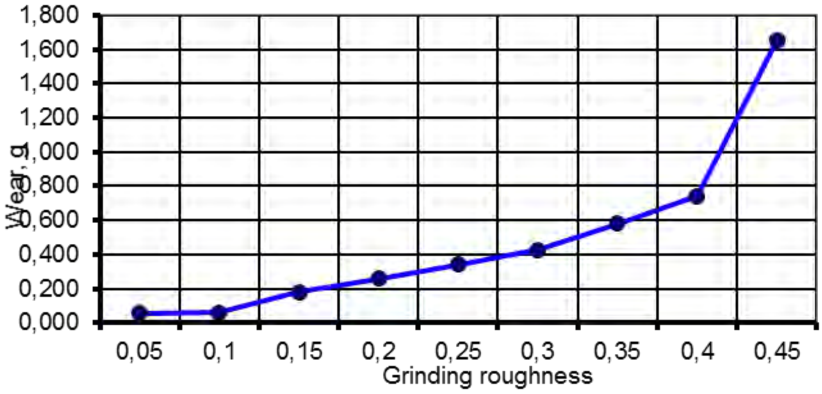

Fig. 4. Polygon distribution (movable roller)

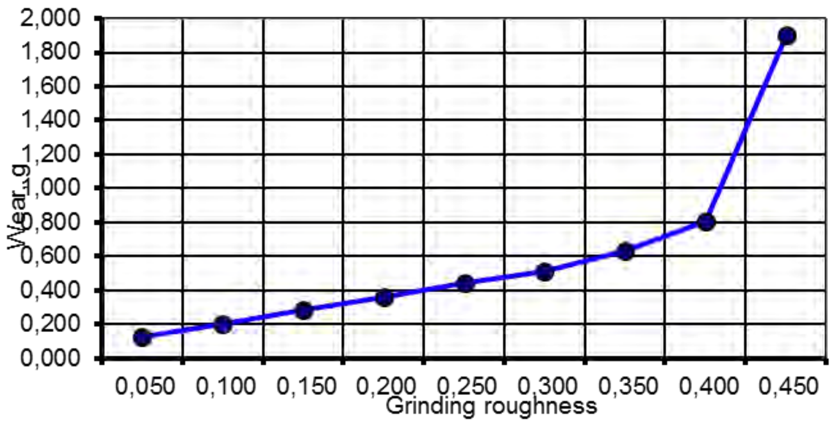

Fig. 5. Polygon distribution (fixed roller)

Empirical (selective) average:

$$\bar{x} = \frac{1}{n}\sum_{i=1}^{n} x_i \ . \quad (2)$$

The deviation d_i of each observation from the average:

$$d_i = x_i - \bar{x} \ . \quad (3)$$

Variance or second central moment $S^2=m_2$ of empirical distribution:

$$S^2 = \frac{1}{n}\sum_{i=1}^{n}(x_i - \bar{x})^2 \ . \quad (4)$$

Unbiased estimate for variance:

$$\bar{S}^2 = \frac{1}{n-1}\sum_{i=1}^{n}(x_i - \bar{x})^2 \ . \quad (5)$$

Selected standard deviations can be found by the formulas:

$$S = \sqrt{S^2} \ ; \quad (6)$$

$$\bar{S} = \sqrt{\bar{S}^2} \ . \quad (7)$$

Moments of the third and fourth order:

$$m_3 = \frac{1}{n}\sum_{i=1}^{n}(x_i - \bar{x})^3 \ ; \quad (8)$$

$$m_4 = \frac{1}{n}\sum_{i=1}^{n}(x_i - \bar{x})^4 \ . \quad (9)$$

The selective value of the coefficient of variation v, which is a measure of the relative variability of the observed value, can be calculated by the formula (in percent):

$$v = \frac{\bar{S}}{\bar{x}} \times 100 \ . \quad (10)$$

Calculated estimates are consistent, unbiased, and effective [9]. Satisfaction with the requirement of unbiasedness eliminates the systematic error, which depends on the sample size n and, in the case of consistency, tends to zero with $n \to \infty$. A parameter estimate is said to be consistent if, as the number of n observations grows, (i.e., when $n \to N$ in the case of a finite population of volume of N and at $n \to \infty$, in the case of an infinite population), the estimate tends to a theoretical value of the parameter. The estimate is effective if, among other estimates of the same parameter, it has the lowest variance.

The results of the calculation of sample characteristics are given in Table III (for a movable roller) and Table IV (for a fixed roller).

The relative variability index v is rather large (54.14% and 49.33%) – it exceeds 33%, which is a sign of a log-normal distribution [10] (for such distribution, regression analysis cannot be performed). After elimination of erroneous data, this indicator became equal to 17.99% and 12.07% for movable and fixed rollers, respectively. We took the greatest values of wear as erroneous both in the case of a movable roller and for a fixed roller (1.650 and 1.903, respectively).

TABLE III. SELECTED DISTRIBUTION CHARACTERISTICS (MOVABLE ROLLER)

Amount	4.29700
Sample mean $m_1 = \bar{x}$	0.477444
Variance S^2	0.229760
Unbiased variance $m_2 = \bar{S}^2$	0.258480
Standard deviation $\sqrt{S^2}$	0.479333
Standard deviation $m_3 = \sqrt{\bar{S}^2}$ (unbiased)	0.508410
The moment of the third order m_3	0.088878
The moment of the fourth order m_4	0.160536
The coefficient of variation v	54.14 %

TABLE IV. SELECTED DISTRIBUTION CHARACTERISTICS (FIXED ROLLER)

Amount	5.26600
Sample mean $m_1 = \bar{x}$	0.58511
Variance S^2	0.25656
Unbiased variance $m_2 = \bar{S}^2$	0.28863
Standard deviation $\sqrt{S^2}$	0.50652
Standard deviation $m_3 = \sqrt{\bar{S}^2}$ (unbiased)	0.53724
The moment of the third order m_3	0.234023
The moment of the fourth order m_4	0.343934
The coefficient of variation v	49.33 %

You can find a large number of different recommendations for the eliminating of gross errors of observation (anomalous values) [7]. We used the simplest methods for eliminating gross errors. Since we have a sample of a small volume of $n<25$, we used the method of calculating the maximum relative deviation [11-13]:

$$\frac{|x_i - \bar{x}|}{\bar{S}} \le \tau_{1-p} \quad (11)$$

where x_i is the extreme (largest or smallest) element of the sample, using which $\bar{x}$ and $\bar{S}$ have been counted; τ_{1-p} is the tabular value of the statistics, calculated at a probability belief q=1–p.

Thus, to distinguish the anomalous value, we calculate:

$$\tau = \frac{|x_i - \bar{x}|}{\bar{S}}, \quad (12)$$

which is then compared with the tabular value of τ_{1-p}:

$$\tau \le \tau_{1-p}. \quad (13)$$

If this inequality is observed, then the observation has not been eliminated, if not, then the observation has been excluded. After excluding a particular observation or several observations, the characteristics of the empirical distribution are re-read according to the data of the reduced sample.

Quantiles of the distribution of statistics at significance levels p = 0,10, p = 0,05, p = 0,025, p = 0,01 or probability belief q = 1 – p = 0,90, 0,95, 0,975, 0,99 are given in many references. In practice, the significance level usually used is p = 0.05 (the result is obtained with a 95% probability belief).

In our case $\bar{x}$ =0,477444, $\bar{S}$ =0,508410, x_i=1,650 (for the movable roller) and $\bar{x}$ =0,58511; $\bar{S}$ =0,28863; x_i=1,903 (for the fixed roller).

The elimination procedure can be repeated for the next maximum absolute deviation in absolute value, but $\bar{x}$ and $\bar{S}$ have previously been recalculated for a sample of the new volume n – 1.

We have also considered another method for eliminating gross errors for a small sample [14-18]. In this case we calculated:

$$\tau' = \frac{|x_i - \bar{x}|}{\sqrt{(n-1)/n}\ \bar{S}}, \quad (14)$$

and the result obtained was compared with a critical value taken from the reference guide with the corresponding n and 1 – p. In the formula (13) compared with the formula (11), a refinement coefficient is introduced:

$$\frac{1}{\sqrt{(n-1)/n}}. \quad (15)$$

For significance levels p = 0.05, p = 0.025, p = 0.01 for n = 9, we have τ_{1-P} equal to 2.24; 2.35 and 2.46. τ calculated is 4.57 and 4.54 for fixed and movable rollers, respectively. Thus, with a probability belief of 99%, the largest one is excluded from the sample. Calculated value τ' = 4.84 for fixed roller and τ' = 4.81 for movable one. Both techniques require the exclusion of the datum, largest in magnitude, from the samples. After exclusion, the sample characteristics were recalculated. The results are shown in Table V and Table VI. The new values of τ are 1.68 and 1.71 and τ' is equal to 1.80 and 1.83. For n = 8, τ_{1-P} are 2.17, 2.27, and 2.37. Inequality (12) is satisfied, therefore, we do not need to eliminate the data.

TABLE V. RECALCULATED SAMPLE DISTRIBUTION CHARACTERISTICS (MOVABLE ROLLER)

Sample mean $m_1 = \bar{x}$	0.330875
Variance S^2	0.05210
Unbiased variance $m_2 = \bar{S}^2$	0.05954
Standard deviation $\sqrt{S^2}$	0.22825
Standard deviation $m_3 = \sqrt{\bar{S}^2}$ (unbiased)	0.24400
The moment of the third order m_3	0.005208
The moment of the fourth order m_4	0.005508
The coefficient of variation v	17.99%

TABLE VI. RECALCULATED SAMPLE DISTRIBUTION CHARACTERISTICS (FIXED ROLLER)

Sample mean $m_1 = \bar{x}$	0.420375
Variance S^2	0.04439
Unbiased variance $m_2 = \bar{S}^2$	0.05073
Standard deviation $\sqrt{S^2}$	0.21069
Standard deviation $\sqrt{\bar{S}^2}$ (unbiased)	0.22524
The moment of the third order m_3	0.003565
The moment of the fourth order m_4	0.004238
The coefficient of variation v	12.07%

To improve the Miscibility of petroleum coke with NME and to achieve the desired consistency of the composition, a certain amount of spent diesel oil is added to it, from which mechanical impurities are removed by settling beforehand.

The composition developed in this way is a homogeneous black grease. The relationship between the individual components is determined by the conditions of application of the composition. The resulting composition has the following composition, wt. % [19-21]:

- petroleum coke 10 – 12;
- used diesel oil 15 – 25;

- low molecular weight polyethylene up to 100%.

Tests of this composition were carried out in the laboratory using the friction machine MI-1M (see Fig. (6) [22-23].

III. CONCLUSION

This composition has the following advantages:

1. The components of the composition are cheap, readily available products or waste products.

2. The composition is easily applied to the rail, does not drain from the side surface of the rail head, has a high protective effect.

3. When the rolling stock moves, the grease is spread by the wheels, ensuring uniform distribution on the side surface of the rail head.

4. Including in the composition of hydrocarbons can be biodegradable. This confirms the environmental safety and harmlessness of this composition.

5. The viscosity of the composition is regulated by the content of spent diesel oil.

6. The components of the composition are easily mixed to form a stable consistency during storage.

Thus, the composition to prevent wear in the wheel-rail friction pair, in which graphite is replaced by a cheaper component – petroleum coke, has high efficiency and minimal impact on humans and the environment.

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