Calculation of parameters of the rotary apparatus for the production of graphene concentrate based on synthetic oils

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Abstract. This article presents the results of a study of the process of liquid-phase shear exfoliation of graphite in oil. The result is a suspension containing graphene structures. It was experimentally established that when designing industrial devices, the concentration of graphene structures in oil can be considered directly proportional to the following parameters: graphite concentration in the initial suspension; rotor radius; rotational speed; number of moving blades; suspension processing time. A relationship, allowing to calculate the performance or parameters of industrial rotary devices based on the results of experiments on a laboratory setup, was obtained.

1. Introduction
Friction is an important characteristic of the motion of contacting surfaces, because the friction are among the main causes of failures of engines, gears, bearings, etc. and wear of items, the uninterrupted performance of which depends on the quality of mechanical system operation, especially in the transport, industrial and energy sectors [1]. Analysis of the real situation showed that up to a third of the fuel energy is lost due to the friction of moving fragments, such as transmission, tires, brakes, etc. [2]. Such a large energy loss is associated with high values of friction and wear coefficients.

At the present level of development of science and technology, there are two options to reduce the friction coefficient and reduce energy loss: the creation of anti-friction materials for parts that are included in the friction units; the creation of new high-performance lubricants that reduce the coefficient of friction, friction and wear parts. Both of these problems are trying to solve thousands of scientists and engineers around the world. Since there are a huge number of mechanisms that work and will work for many years in the industry, the second solution to the problem of friction today seems to us to be more realistic and relatively quickly implemented in real life.

There are a huge number of lubricants of different consistency (liquid, plastic, etc.), composition and method of use. But all these lubricants contain a base (natural or synthetic) and antifriction additives. There are a huge number of bases and additives, but we focus on synthetic oils and graphene derivatives as additives.

Graphene is one of the newest nanoscale carbon allotropes, has unique properties associated with minimizing friction and wear, and also has good thermal and mechanical properties. So, this 2D material can serve as a solid or colloidal (liquid) lubricant [3,4]. It has now been established that the
tribological characteristics of graphene and its derivatives depend on many factors, including morphology, a thickness of graphene layers, the method of manufacture and surface chemistry [5-7].

Research results both at the micro level [8] and at the macro level [9] showed that graphene and graphene oxide (GO) is really very much lower friction coefficient.

It should be noted that graphene and its derivatives are environmentally friendly products, and this fact increases the prospects of their use as an effective nano-additive for oils and plastic lubricants [10]. In this work, the tribological properties of GO in SAE20W-50 engine oil were investigated, and a decrease in wear rate of 60-80% was observed, and the minimum value of the friction coefficient (0.057) was determined by adding 0.5 wt.% GO. A review of recent advances in the production and study of the tribological characteristics of graphene is given in [11].

The results of studying the tribological characteristics of crumpled graphene balls seem to be very interesting [12]. It was found that these balls are very stable in the solid state and when dispersed in liquids, they do not open and do not collapse even after heating or granulation. Besides, they can be particularly dispersed in different solvents (for instance, in lubricating oils), without employing any additional procedure such as chemical functionalization, due to the fact that they are attracted to each other through the weak van der Waals forces [13]. It is noteworthy that base oils containing only 0.01-0.1 wt.% of these balls appear to be more efficient in decreasing friction and wear than conventional commercial lubricants. This fact was established after determining the tribological properties of graphene and the other carbon-based materials – graphite, reduced graphene oxide (r-GO, or chemically modified graphene), and carbon black – using a pin-on-disk tribometer. A base oil (e.g., polyalphaolefin) was mixed with 0.01-0.1 wt.% of these materials and then sonicated until the solid particle residue disappears and complete dispersion occurs. It was found that the crumpled graphene balls, added to the oil at the above-mentioned concentrations, provide consistently good performance and the lowest friction and wear coefficients: their 20-and 85-% reduction is achieved, respectively, compared to the unmodified oil. Moreover, the graphene-modified base oil outstrips the 5W30 lubricant due to its reduced friction and wear.

Similar results on the reduction of friction and wear coefficients were obtained when modifying greases with graphene plates, which consist of several layers (up to 25 layers) [14,15].

Graphene plates were not balls, but their shape was very different from the plane, which was confirmed by their image, obtained by SEM.

Thus, an analysis of the literature on the use of graphene as an antifriction additive showed that graphene and its derivatives are very promising materials. In our opinion, the results of laboratory studies have so far not been widely applied on an industrial scale, mainly due to the high cost of graphene and its derivatives. The articles [16,17] published the results of the production of few-layers graphene using a high-speed stator-rotor mixer. The fact of obtaining double-, few- and multi-layered graphenes as one-atom-thick carbon platelets is confirmed by electron microscopy and Raman spectroscopy. In [18], we experimentally proved that using liquid-phase shear exfoliation it is possible to obtain graphene structures (a mixture of graphene, few-layer and multilayer graphene).

As a result of experimental studies, we found [15] that when 0.1-% multi-layered graphene (up to 25 layers) is added to a comprehensive calcium lubricant, the wear spot diameter decreases by 50%, the scoring index increases 2.9 times, and the bearing capacity increases 3.8 times.

Currently, there exist no methods for calculating the parameters of industrial rotary devices. Thus, the aim of the present research is to study the process of liquid-phase shear exfoliation of graphite and to obtain dependences for calculating the performance or main parameters of a rotary device intended for manufacturing graphene masterbatches.

2. Preliminary experiments

We used the improved rotary device, as described elsewhere [19]. Its main difference from the device used in [16] is that its rotor blades are able to move in the radial direction under the action of centrifugal forces during rotation of the rotor. This technical solution provides contact of the blades with the inner surface of the stator and increases the efficiency of shear exfoliation.
As parameters that can affect the intensity of the process of exfoliation of graphite were chosen: the radius of the inner surface of the stator; rotor speed; the number of moving blades. To determine the type of dependences of the effect of these parameters on the exfoliation intensity, several series of experiments were conducted with a discrete change in one of the parameters.

Experiments were performed as follows. Preparing 3-6 liters of oil suspension of crystalline graphite GSM-2 with a concentration from 2.5 to 10%. The suspension was poured into a cylindrical container, a rotary apparatus was installed, and the processing of the suspension began. Every 5 cycles of suspension processing, samples were taken to determine the concentration of graphene structures.

Figure 1 shows the dependence of the concentration of graphene structures on the number of suspension processing cycles. The rotor speed was 10,000 rpm, the concentration of graphite in the initial suspension was 50 mg/ml.

![Graph showing the dependence of the concentration of graphene structures on the number of processing cycles.](image)

**Figure 1.** The dependence of the concentration of graphene structures on the number of suspension processing cycles.

As can be seen from the graph, at the beginning of the exfoliation process, during 15 processing cycles, the dependence is almost linear. In the case of industrial production, it is not economically feasible to process the suspension more than 15 times. Thus, to design industrial rotor devices, the dependence of the concentration of graphene structures on the number of processing cycles can be considered linear. It should be especially noted that since the time of one cycle is constant, the dependence of the concentration of graphene structures on time is also linear.

3. **Determination of the main parameters of the exfoliation process**

In our opinion, the intensity of liquid-phase shear exfoliation depends on the magnitude of shear stresses that arise between graphene layers when a graphite particle enters the zone between the stationary inner surface of the stator and the moving blade. Thus, in the industrial rotary device, it is required to ensure tangential stress values not less than those taking place in the laboratory device.
3.1 Determination of normal and tangential stresses

The graphite particle in the zone between the stator and the rotor is acted upon by centrifugal forces that move and ultimately press this particle to the inner surface of the stator. If the particle mass is equal to \( m \), the angular velocity of rotation of the rotor is \( \omega \), the inner radius of the stator is \( R \), then the centrifugal force \( F_{CP} \) acts on the particle, the numerical value of which is:

\[
F_{CP} = m\omega^2 R. \tag{1}
\]

Normal stresses \( \sigma_{CP} \), which act between the graphene layers that make up a particle, generally depend on the shape of the particle and its lateral dimensions, more precisely, the area. In the first approximation, the magnitude of the tangential stresses can be estimated using the average value of the area of the graphene layers \( S_M \). In this case, the normal stresses \( \sigma_{CP} \) will be equal to:

\[
\sigma_{CP} = F_{CP} / S_M. \tag{2}
\]

To determine the stresses arising between the graphene layers in the particle from the action of the moving rotor blade, we use the scheme of action of the forces from [19], which is given in figure 2.

\[\text{Figure 2. Diagram of forces acting on a particle located between the blade and the inner surface of the stator.}\]

First of all, we define the centrifugal force \( F_C \), which acts on the blade:

\[
F_C = m_{PL} \omega^2 R_{CT}, \tag{3}
\]

where \( m_{PL} \) is the mass of the blade, \( \omega \) is the angular velocity of rotation of the rotor, \( R_{CT} \) is the distance from the center of gravity of the blade to the axis of rotation of the rotor.

If we consider the forces acting on the particle, then \( N = F_C \). Normal stresses in the contact zone, particles with a blade will be equal to:

\[
\sigma_p = N / S_p, \tag{4}
\]

where \( \sigma_p \) is the normal stresses in the contact zone, \( S_p \) is the contact area of the particle with the blade.

The average value of normal stresses that occur between graphene layers is equal to:

\[
\sigma_G = N / S_G, \tag{5}
\]

where \( S_G \) is the contact area between adjacent graphene layers.

The shearing force \( G \) acting on the particle is equal to:

\[
G = N \cdot \tan \alpha_p, \tag{6}
\]

The tangential stresses that arise in the zone of contact of the blade with the particle will be equal to:

\[
\tau_p = G / S_p. \tag{7}
\]

The average value of the tangents stresses that occur between adjacent layers is:

\[
\tau_G = G / S_G. \tag{8}
\]
The obtained dependences (5) and (8) are necessary in order to ensure minimum values of normal and tangential stresses between graphene layers during exfoliation of graphite particles when designing new rotary apparatuses since we are successfully exfoliated under laboratory conditions at given values of stresses.

3.2 Calculation of the current concentration of graphene structures

Initially, it can be assumed that all the parameters of the process and the device for its implementation are interconnected. The main task is to find the functional dependence of the concentration of graphene nanoplates, which was formed in suspension as a result of the separation of particles of graphite. Taking into account that in practical calculations we will use a linear section of the dependence of the concentration of graphene structures on the number of cycles shown in Figure 2, we made the assumption that the current concentration linearly depends on: graphite concentration in the initial suspension \( c_0 \), mg/ml; radius of stator \( R \), m; \( n \) is the number of blades; velocity of rotation of the rotor \( \omega \), rpm. Since, ultimately, the resulting dependence will need to be associated with similar parameters of the laboratory setup; we introduce the index to the above parameter designations – \( L \), and obtain the following designation parameters of the laboratory installation: \( t_L \); \( c_{LO} \); \( R_L \); \( n_L \); \( \omega_L \). We will look for the indicated dependence in the following form:

\[
c = k c_L \left[ \left( \frac{c_0}{c_{LO}} \right) \frac{R}{R_L} \left( \frac{\omega}{\omega_L} \right) \left( \frac{n}{n_L} \right) \frac{t}{t_L} \right],
\]

where \( k \) is the proportionality coefficient.

The numerical value of the coefficient \( k \), apparently depends on the properties of graphite and oil. If the designed apparatus will process a suspension of the same graphite and oil that was used in the laboratory setup, \( k \) is equal to 1.

4. Results and discussion

The parameters that we used when obtaining the dependency presented in figure 2 will be considered the parameters of the laboratory setup: \( c_L = 6 \) mg/ml; \( c_{LO} = 50 \) mg/ml; \( R_L = 20 \) mm; \( \omega_L = 10000 \) rpm; \( n_L = 4; \ t = 2700 \) sec. It is these parameters that we will use when calculating the concentrations according to (9). The concentration of graphene structures was determined by the specific gravity of the suspension using the technique given in [20].

Figure 3 shows the dependence of the concentration of graphene structures on the rotor speed. In this graph, the points show the experimental values, and the line is a calculation by the formula (9). Line 1 is a calculation at a concentration of graphite in the initial mixture of 50 mg/ml, and a straight line 2, at a concentration of 100 mg/ml. As you can see, the calculation satisfactorily coincides with the results of the experiment, up to a rotor speed of 12,000 rpm, but with a further increase in speed, the real intensity of the exfoliation process of graphite decreases. Since from a practical point of view it is impractical to carry out the process with reduced intensity, dependence (9) can be used in the design of industrial rotary apparatuses.

The linear nature of changes in the concentration of graphene structures depending on the rotational speed of the rotor is experimentally confirmed by the results obtained for the graphite exfoliation in water using a rotor device of the similar design [21].

Figure 4 shows the dependence of the concentration of graphene structures on the concentration of graphite in the initial suspension. On this graph, the points stand for the experimental values, and the line represents the calculation according to equation (9). As can be seen, the calculated and experimental values satisfactorily coincide.

A comparison of the calculated and experimental values of the concentrations showed that the calculated values differ from the average experimental values by no more than 15%.

The results of experiments with two movable blades showed that the intensity of the exfoliation process decreased by approximately two times. Unfortunately, the design of our device did not allow us to change the diameter of the rotor, so we are going to decide on the influence of the number of blades and the diameter of the rotor in the near future.
Figure 3. The dependence of the concentration of graphene structures on the rotor speed.

Figure 4. The dependence of the concentration of graphene structures on the concentration of graphite in the initial suspension.
5. Conclusion
The process of liquid-phase shear exfoliation of graphite in oil is investigated. Dependences are obtained that allow us to determine the normal and tangential stresses that occur in a graphite particle, when processed in a rotary apparatus with moving blades and which must be provided in the designed apparatus. It was established experimentally that the concentration of graphene structures in suspension is directly proportional to the speed of rotation of the rotor and the concentration of graphite in the initial suspension. A dependence is proposed for calculating the concentration of graphene structures from the results of a limited number of experiments on a laboratory setup. Comparison of calculated and experimental values of concentrations was carried out and it was found that the discrepancies between these values do not exceed 15%.

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