Continuous and semi-continuous industrial production of lubricants modified with graphene nanostructures

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Abstract. This article proposes one of the options for the production of graphene-containing suspensions and their modification of lubricants. It is based on the technology of obtaining graphene nanostructures by the method of liquid-phase shear exfoliation of graphite. The proposed technological scheme can operate in both semi-continuous and continuous modes. The main advantages of this technology are simplicity and reliability of equipment, as well as environmental friendliness of production.

1. Introduction

Currently, lubricants have high requirements regarding antifriction and anti-wear characteristics in friction units of many mechanisms and machines operating at variable and elevated speeds, pressures and under various temperature conditions. Various modifiers are used to improve the performance of lubricants. Many researchers argue that the addition of nanoparticles to lubricants, such as metal [1], metal oxide [2], metal sulfides [3], carbonate [4], borate [5], carbon materials [6, 7], organic materials [8] and rare earth compounds [9] are effective in reducing both friction and wear [10]. Friction reduction and antiwear properties are improved due to the individual characteristics of nanoparticles, for example, their
size, shape, and physicochemical nature [11]. One of the most promising modifiers is graphene plates [12].

The use of graphene plates as modifiers of lubricants on an industrial scale is constrained by the high cost and complexity of the technology for its production. At present, graphene plates, more precisely, partially recovered graphene oxide, are produced using one or another modification of the Hamers-Ofemann method. This technology has many disadvantages. In our opinion, the main disadvantages are environmentally hazardous production, since strong acids and high energy consumption are used, since ultrasound is used to exfoliate graphite oxide. In addition, using this technology, an aqueous suspension is obtained, which contains a mixture of graphene plates with a different number of layers. To obtain the modifier, an oil is added to this suspension and then the water is removed (evaporated). As a result, an oil-based modifier is obtained, which contains 10-15% graphene plates.

The method of liquid-phase exfoliation of graphite was developed relatively recently [13]. This method is environmentally friendly, since it does not use acids and has a low cost price, since it does not use ultrasonic processing of graphite. However, the problem of switching from an aqueous suspension to an oily suspension remains. We proposed to implement liquid-phase shear exfoliation of graphite in oil [14, 15]. Thus, it is advisable to continue improving the technology for the production of a lubricant modifier based on graphene plates obtained by liquid-phase shear exfoliation of graphite in oil.

The industry uses the following operating modes of equipment: periodic; continuous; semi-continuous. The choice of the mode mainly depends on the required performance and the specifics of the technological process. As many industries continue to accelerate the current paradigm shift from batch to continuous production of materials, options for continuous production of graphene wafers must now be considered to produce new materials with improved performance.

2. Technology of continuous and semi-continuous production of lubricants modified with graphene nanostructures

2.1 Functioning principle

By graphene nanostructures we mean a mixture of single-layer, two-layer, few-layer and multilayer graphene. There are two main options for modifying lubricants with graphene nanostructures. The essence of the first option is that first, an oil suspension with graphene structures is obtained and then, on this basis, you implement the entire production cycle of a particular lubricant. In the second variant, it is necessary to make a graphene concentrate in oil and then modify the finished lubricant.

From an economic point of view, at the first stage, it is advisable to implement the second option, since there is no need to make changes to the existing lines for the production of lubricants. Moreover, the equipment that will be used in the implementation of the second option can be fully used in the first option.
Previously, we developed a technological scheme for the preparation of graphene concentrate and modification of lubricants [15]. The results of further studies have shown a number of disadvantages, which are eliminated in the scheme, which is shown in figure 1.

This technology is implemented as follows. Powder of crystalline graphite by the metering device 1 is continuously fed into the rod drum mill 2. At the same time, the metering device 3 feeds into the mill either pure oil, which is the basis for the lubricant to be modified, or a clarified suspension from the filter 9. Mass concentration of graphite is from 10 to 20%. In the mill, graphite undergoes mechanical activation and partial exfoliation, that is, exfoliation of graphite particles into graphene nanostructures. After the mill, all particles have at least one size less than 100 nanometres. From the mill, the mixture enters tank 4, where either pure oil or clarified suspension from filter 9 is fed simultaneously by metering unit 5. Tank 4 has a mixer for distributing graphene nanoparticles and graphite particles throughout the volume of this tank. From tank 4 by pump 6, the suspension is fed into the rotary apparatus (exfoliator) 7. From the exfoliator 7, the suspension enters the exfoliator 8, etc. To organize continuous production in an industrial technological scheme, more than 10 exfoliators can be used (in figure 1, these exfoliators are not conventionally shown). After the cascade of exfoliators, the suspension enters the filter 9, where untreated graphite particles and large graphene particles are separated. The liquid part of the suspension enters the filter 10, where the graphene nanoparticles and oil are separated. The clarified part of the suspension, containing a very small amount of graphene, is fed to the dispenser 3. The precipitate from the filter 10 is fed to the mixer 11, where the modified lubricant is also supplied. From the mixer 11, the mixture of lubricant and graphene nanostructures is fed into the rotary homogenizer 12. After processing the mixture in the homogenizer, the lubricant modified with graphene nanostructures is fed to the packing section.
Figure 1. Functional diagram of the production of graphene nanostructures and the modification of lubricants

Despite the external complexity of the technological line for the modification of lubricants with graphene nanomaterials, all processes for processing the starting materials are purely mechanical and there are no pronounced chemical influences. During the mechanical activation of graphite in a drum rod mill 2, as well as during the movement of intermediate intermediates in high-gradient flows in the exfoliator 7 and rotary homogenizer 12, the planes of graphene plates and especially at their edges are defects. Among other things, dangling bonds can arise, due to which new chemical bonds can be formed, but there are much fewer of them than in the case of targeted functionalization of graphene, and even more so partially reduced graphene oxide.

2.2 Weight continuous feeding of graphite powder

In the presented technological scheme, in contrast to the one proposed earlier, a continuous weighing batcher is used to supply graphite powder to a rod drum mill. As in our work, we used a two-stage dosing technology. The essence of this method is that at the first stage, individual portions of bulk material with a certain weight ΔP are formed and at regular intervals ΔT are fed into a cylindrical tray, which performs circular oscillations about a longitudinal axis inclined to the horizon at an angle of 1 to 5 degrees. In the second stage, the portions are converted into a continuous flow due to the vibration of the tray. Figure 2 shows the conversion of individual batches to a continuous stream. Immediately after being fed into the tray, the portion of material has the shape shown in figure 2a. Under the action of vibration, the portion moves along the lok and simultaneously changes its shape (figure 2b). Before pouring from the vibrating tray, the portion turns into a uniform flow (figure 2c). The next portion is loaded into the tray when the previous portion is not completely emptied from the tray. The portions are connected to each other and thus a uniform continuous flow of bulk material with a given productivity is formed. The capacity of such a feeder Q is calculated as follows:
The results of experimental studies have shown that the error of continuous weight dosing of graphite powder at a productivity of 120 g / h does not exceed 0.25%.

3. Results and discussion
As noted earlier, in a real technological scheme, it is supposed to use several exfoliators sequentially. To check the effect of the number of exfoliators on the kinetics of the process and productivity of the line, we used two containers, similar to container 4 shown in figure 1. From the first container, the initial suspension was pumped with a fixed capacity into the first exfoliator (position 7 in figure 1) and then entered in the second exfoliator (item 8 in figure 1). From the second exfoliator, the treated suspension entered the second container. After the end of the suspension in the first container and the treated suspension stopped flowing into the second container, the exfoliator drives were turned off, i.e. one cycle of suspension processing ended. The treated suspension was pumped into the first tank by an additional pump and then the processing cycle was repeated. Every ten cycles, the concentration of graphene nanostructures in the suspension was determined and the productivity was calculated in terms of dry graphene. Similar experiments were performed with one exfoliator.

Figure 3 shows the dependence of the mass concentration of graphene nanostructures on the number of processing cycles. In this case, the initial concentration of graphite was 10%, the rotor speed was 10,000 rpm, the flow rate of the suspension by the pump when fed into the first exfoliator was 5 l / min. It can be seen from the graphs that when using two exfoliators (curve 2 in Fig. 3), a concentration of more than 6 mg / ml is reached approximately two times faster than when using one exfoliator (curve 1 in Fig. 3). With 30 exfoliators, this concentration can be achieved in one cycle.

![Figure 3](image3.png)

**Figure 3.** Dependence of the mass concentration of graphene nanostructures on the number of processing cycles, with a different number of exfoliators

![Figure 4](image4.png)

**Figure 4.** Dependence of the mass concentration of graphene nanostructures on the number of processing cycles at different pump flow rates
If the pump power is reduced by 2 times, the residence time of the suspension in each exfoliator will approximately double. In fig. 4 shows the dependences of the mass concentration of graphene nanostructures on the number of processing cycles at a pump capacity of 5 l/min (curve 1) and 2.5 l/min. It can be seen from the graphs that to achieve a certain concentration, for example 6mg/ml, with a pump capacity of 2.5 l/min, suspension processing cycles are required approximately 2 times less than with a capacity of 5 l/min. It should be especially noted that with an increase in the residence time of the suspension in each exfoliator, productivity will not increase. This technique allows to reduce the number of exfoliators in the production line, while ensuring the required performance for graphene.

Fewer exfoliators can be used with semi-continuous operation than with continuous operation. In this case, the outlet from the last exfoliator is connected to the inlet of the first exfoliator and until a certain concentration is reached, the suspension moves in a closed loop through all exfoliators. Thus, in a continuous mode, all devices of the circuit operate continuously, and in a semi-continuous mode, the suspension is processed continuously, and the lubricant is modified periodically.

4. Conclusion
The advanced technology for modifying lubricants with graphene nanostructures can operate in both continuous and semi-continuous modes. In addition, the graphene-containing suspension after removal of graphite particles and large graphene particles (after filter 9 in Fig. 1) can be used as a basis for the production of grease. In this case, it is not necessary to modify the existing production lines, but the end product is a grease modified with graphene nanostructures.

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