Method of indirect estimation of lubricating properties of petroleum products

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Abstract. In this research, a new method for evaluating the lubricating properties of prophylactic agents was developed. For the method, specialized metal models and a press with a strain-gauge s-shaped gauge, using for recording shear load indicators, were designed. Using the new method, prophylactic agents based on mixtures of light and heavy gas-oil catalytic cracking and delayed coking with the addition of tar or cracking residue as depressor additives were analyzed. A research of the hydrocarbon composition of the prophylactic agent, which was correlated with the removed shear load diagrams, was also made. As a result, the dependencies of the lubricating properties of fuels with a change in their fractional composition were identified, and the most effective PAs were determined.

1. Introduction
When moistened minerals and loose materials are transported, they adhere and freeze to the metal surfaces of the dump cars and car bodies, and the pieces of material regelate. This leads to a significant increase in labor costs when unloading cars and incomplete unloading of vehicles, which leads to significant economic losses. Thus, preventing of sticking, adfreezing and regelating of loose and lumpy materials and rocks is an important task [1-3].

To solve these problems, prophylactic agents (PAs) were developed. These agents were classified into bulk, liquid and solid. The most widespread currently received liquid PAs. Their effect was based on the formation of a hydrophobic film on the surfaces of particles of materials and metal surfaces, which led to the displacement of water in a separate phase, as a result of which it formed a weak ice [4,5].

There are 4 PAs groups: oligoorganosiloxanes (silicone fluids), PAs based on hydroxyl-containing compounds, salts of inorganic and organic acids, oil-based PAs.

Methyl and ethyl siloxanes are most common in group of organosilicon fluids. They satisfy all physico-chemical and operational indicators, but have a high cost.

Hydroxyl-containing compounds are represented by products based on glycerol, alcohols, glycols and their esters, as well as bottoms from their production. In terms of environmental safety, the use of propylene glycol is most preferred.

To improve the performance properties of glycols, it is possible to add in them small amounts of inorganic salts. In addition the solutions of inorganic salts can be used as independent PAs. The most common use of a solution of CaCl₂, in the concentration range of 25-30% of its freezing temperature reaches -40°C. When transporting materials in conditions up to -10°C, other salts can be used: NaCl, K₂CO₃, NaNO₃, Na₂SO₄ and also CO(NH₂)₂ [6].

In the climatic conditions of the continental zones, it is preferable to use petroleum-based products, since they are able to withstand temperatures below -20°C.

The main requirements for PAs, relate to their physico-chemical and operational properties, as well as efficiency of use. First of all, they must effectively prevent adfreezing and regelation in conditions of low temperatures, be non-toxic, do not cause environmental damage, and also have multifunctional use.
(for various materials, minerals and ores). In addition, they must have a satisfactory viscosity for ease of spraying through the nozzles, do not have a corrosive effect and a negative impact on the materials transported [7]. Thus, the most important characteristic is the lubricity.

To assess the lubricating properties of fuels, oils and other petroleum products, the indicator is used - the wear scar diameter, which is measured using a four-ball wear test machine. With the help of this tribological analyzer, it is able to estimate the ability of substances to reduce the loads arising in the process of friction. However, to evaluate the lubricating properties of PAs, the main task of which is to prevent the adfreezing of materials to metal surfaces, this indicator is not sufficiently informative. This is due to the fact that, in addition to the lubricating properties, they must have a low pour point, a high adhesion index and an optimal chemical composition [8].

Given the diversity of PAs, it is necessary to develop a method that will allow evaluating their effectiveness, regardless of their state of aggregation or chemical composition.

Since PAs are most often used for transportation of various minerals (coal, ores, sludge), it is proposed in the methodology to simulate the conditions of transportation at low temperatures. The main cause of sticking and freezing of loose materials to the walls of cargo compartments is water contained in the material itself. During transportation, water accumulates in the lower part of the car, forming a layer of liquid phase between the car wall and the material. The strength of the freezing of the material is influenced by the chemical composition of solid phases (the presence of oxygen atoms in the structural lattice, which causes the formation of hydrogen bonds with water molecules) and the thickness of the water layer [9,10].

2. Materials and Equipment

Further, a new method for evaluating of lubricating properties of PAs was developed. For testing, a metal (steel grade St3) car model was developed and manufactured (Fig. 1). The gate for unloading was represented by a metal plate, which was subjected to processing by PA.

![Figure 1. Experimental model][1]

![Figure 2. Press][2]

The models were placed in the freezer for 24 hours. As a result of the ongoing processes of adhesion and crystallization of water on the surface of the metal and the material was frozen. Since the task of the PA is to prevent these phenomena, an assessment of their effectiveness can be carried out by extruding the plate. When the plate is shifted, the ice layer is destroyed and the material comes off the wall. Thus, it is necessary to extrude the plate and measure the force applied to shift it. This load characterizes the strength of freezing and allows indirect evaluating the lubricity of PA.

To measure the forces, a press with a DYLY-104/300 tensile-compression strain gauge was used (Fig. 2).

Initially, the sensor was connected to a laptop using the Arduino Uno programmer and the data was displayed on the screen in the Arduino program. Thus, the press required additional equipment. Then a
display was connected to the programmer, as a result of which the work of the press became completely autonomous.

3. Analysis of Results and Experimental Data
Before evaluating the lubricating properties of PA, the humidity of the transported materials was measured, since it has a great influence on the degree of adfreezing and freezing [11, 12, 13, 14]. For coal, depending on whether it is pit or brown, this parameter will vary widely from 10% to 55%. The internal humidity, that is, the water molecules that make up the lattice of crystallohydrates of the mineral part, is not taken into account, since it does not affect the freezing.

In order to analyze the effect of humidity content of the tested materials on the freezing strength, a series of tests were carried out according to the previously described procedure with quartz sand (95–99.8% silicon oxide SiO$_2$), pit coal (86% carbon; 0.5% sulfur; 9.2% volatile matter; ash 4.3%) and urtite (ore for the production of alum slate and a number of by-products (soda, cement), containing metal oxides SiO$_2$ (from 40% by weight), Al$_2$O$_3$ (from 20%), Na$_2$O (from 10 %), as well as Fe$_2$O$_3$ + FeO, MgO, CaO, K$_2$O, TiO$_2$) [15].

The purpose of the test was to build a graphic dependence on the freezing strength of the humidity of the material. The experiments with urtite did not give a positive result, since the crushed processed material with a particle size of <40 microns participated in the tests. In the course of the experiment, it was impossible to obtain a homogeneous mixture; the applied layer of urtite was pelletized and irregularly froze. The tests with coal and quartz sand were successful, since the sizes of particles from mixed fractions were in the range of 100 μm ÷ 1 mm. The test results are shown in Figures 3 and 4.

![Figure 3. Dependence of shear load on coal moisture.](image-url)
In the process of freezing, the humidity content of the material changed. In the study, two series of values were obtained: the initial humidity before testing (Fig. 4, black branches) and the humidity found at the end of the test after measuring the freezing strength (Fig. 4, grey branches). To measure the humidity after freezing, two weights of the material were taken from both sides of the model gate. The arithmetic average was taken as the true value. Taking into account the change in the moisture content of the material in the freezing process, more accurate graphical dependencies were obtained and empirical equations were derived using approximation.

For coal and quartz sand, linear and quadratic dependencies were derived:

\[
P_{\text{coal}} = 0.0884w; \quad P_{\text{sand}} = 0.0222w^2 - 0.2584w + 2.9612;
\]  

where \(P_{\text{coal}}\) and \(P_{\text{sand}}\) - the strength of freezing of coal and sand, MPa; \(w\) - moisture content of the material, % wt.

The result obtained is explained by the presence of oxides in the structure of building sand, mainly silicon oxide (Fig. 5). Hydrogen bonds are formed between the water molecules and the oxide centers of silicon oxide in the sand and iron oxide in the steel wall of the car. Coal is almost pure carbon, so this phenomenon is not typical for it.

Based on practical data, the following humidity was taken: 15% for sand and 20% for coal.

Using a new method, PA based on light and heavy gas oil catalytic cracking and delayed coking (LGCC, HGCC, LGDC, HGDC) with the addition of tar (T) or cracking residue (CR) as depressor additives were analyzed. As a result of the tests, the following shear load values were obtained in kilograms, which were then converted into units of pressure (see Table 1).
Figure 5. Hydrogen bonds in the phase section of a Sol-L-Sol.

| Table 1. Dependence of the load for shear on the composition of the lubricant. |
|-------------------------------------------------------------|
| **Prophylactic agent** | **Shear load, MPa** | **Coal with 20% moisture** | **Sand with 15% moisture** |
|------------------------|---------------------|-----------------------------|-----------------------------|
| Without agent          | 3.16                | 7.95                        |                             |
| Blend HGCC:LGCC+0%T    | 0.94                | 1.77                        |                             |
| Blend HGCC:LGCC+2%T    | 1.46                | 0.88                        |                             |
| Blend HGCC:LGCC+5%T    | 0.65                | 0.17                        |                             |
| Blend HGCC:LGCC+10%T   | 1.17                | 5.0                         |                             |
| Blend HGDC:LGDC+0%RC   | 1.72                | 3.84                        |                             |
| Blend HGDC:LGDC+2%RC   | 0.25                | 5.03                        |                             |
| Blend HGDC:LGDC+5%RC   | 1.24                | 2.46                        |                             |
| Blend HGDC:LGDC+10%RC  | 1.31                | 5.24                        |                             |

4. Conclusions
According to the table, it is possible to determine the optimal PA compositions, using which a minimum shear load of the plate is required for a model filled with moistened sand or coal. The new method allows successful conducting a comparative assessment of the lubricating properties of prophylactic agents. It is also easier to use it than using a four-ball wear test machine. The method showed that mixtures based on vacuum gas-oils with the addition of heavy residues can be used as PA. To prevent sticking, adfreezing and regelation of wet loose materials, it is recommended to use preventive lubricants based on catalytic cracking gas-oil and delayed coking with a cracking residue content of 2%, or tar 5%.

In addition, the production of these mixtures will expand the range of commercial petroleum products produced at refineries, and will improve the efficiency of refining through the rational use of heavy oil refining residues.

References
The work was carried out within the framework of the state assignments 0792-2018-0002 «Rational use and deep processing of raw hydrocarbon to produce marine fuels and carbon materials».

References
[1] Oshchepkov I A and Khudonosova Z A 1999 Prevention of freezing of overburden rocks to the walls of vehicles *Mining information and analytical bulletin* 3 75-76
[2] Koulyandin G A, Omelyanenko A V and Fedorova L L 2013 Georadar researches of structural features and water cutting of overburden rocks for coal open-cast mining *Journal of Mining Institute* 200 49-53
[3] Gushchin A A, Ermakov A Yu and Miroshnikov A M 2016 The study of coal congealing during storage and transportation Mining information and analytical bulletin 4 140-154
[4] Kondrasheva N K, Zyryanova O V, Kireeva E V and Ivkin A S 2016 Refinery byproducts in dust suppression and the prevention of rock adhesion and freezing at mines Coke and Chemistry 59 338-344
[5] Korshunov G I, Kovshov V P, Kovshov S V and Yerzin A H 2014 A new chemical method of dust suppression for the storage of the rock mass Journal of Mining Institute 207 116-120
[6] Gushchin A A, Ermakov A Yu and Miroshnikov A M 2017 Analyses of crystallization and consolidation of aqueous reagent solutions to prevent congelation Mining information and analytical bulletin 4 403-8
[7] Vasiliev A L, Lavrenko S L and Gruszczynski M 2018 Experimental studies of rheological properties of stowing pulps Journal of Physics: Conference Series 1118.
[8] Dashko R E and Lange I Y 2017 Engineering-geological aspects of negative effects associated with contamination of disperse soils by oil products International Multidisciplinary Scientific GeoConference Surveying Geology and Mining Ecology Management 17 617-625
[9] Goldstein R V and Epifanov V P 2011 To the measurement of adhesion of ice to other materials Bulletin of the Perm National Research Polytechnic University. Mechanics 2 28-41
[10] Matsumoto K and Kobayashi T 2007 Fundamental study on adhesion of ice to cooling solid surface International Journal of Refrigeration 30 851–860.
[11] Adam J, Meuler J, Smith D, Varanasi K K, Mabry J M, McKinley G H and Cohen R E 2010 Relationships between Water Wettability and Ice Adhesion ACS Applied materials & interfaces. Americal Chemical Society
[12] Cai CZ, Li GS, Huang ZW, Shen ZH and Tian SC 2014 Rock pore structure damage due to freeze during liquid nitrogen fracturing Arabian journal for science and engineering 39 9249-9257
[13] Qin L, Zhai C, Xu JZ, Liu SM, Zhong C and Yu GQ 2019 Evolution of the pore structure in coal subjected to freeze-thaw using liquid nitrogen to enhance coalbed methane extraction Journal of petroleum science and engineering 175 129-139
[14] Shakhnazarov K Y, Prykhin E I and Pomeranets I B New version of Kurnakov's law about relationship between properties of binary alloys and phase diagrams balance 2017 IOP Conference Series: Earth and Environmental Science 87
[15] Davidson Gp and Nye JF 1985 A photoelastic study of ice pressure in rock cracks Cold regions science and technology 11 141-153