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RECEIVING AN ANTIFREEZING AGENT FOR TRANSPORTING COKE BY RAIL

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The article presents the research findings of obtaining and analyzing the properties of antifreezing agent from products and semi-products of JSC Naftan to prevent sticking and freezing of coke to metal surface of open wagons during the transportation of petroleum coke from JSC Naftan to Belarusian Cement Plant in the wintertime.

Introduction. In autumn and especially wintertime, when coke, minerals and other loose rocks with high humidity are transported, there is sticking and freezing of a significant part of the solid mass to metal surfaces of wagons, and there is also freezing in a bulk cargo. In this regard, up to 50% of the bulk is not unloaded, which necessitates additional cleaning by means of excavators or manually and leads to a decrease in the productivity of quarry equipment by 15-20%. Accordingly, the cost of transportation increases by 20-25%.

To address the challenge of sticking and freezing of bulk cargo during transportation, there are various preventive means of oil origin, such as Nyogrin, Universin, Severin, produced by adding residual products of oil refining and petrochemistry. However, they all are produced in foreign countries and have a sufficiently high price. Due to a prompt commissioning of a delayed coking unit at JSC Naftan, there will be a problem of transporting petroleum fuel coke to Belarusian Cement Plant in Klimovichi at low temperatures.

The purpose of this study is to select component composition and to research the properties of Nyogrin-type preventive agents based on the residual products of JSC Naftan.

Preventive lubricants of petroleum origin should meet the following requirements [1, 2]:

– to have a low yield point;
– to lubricate a metal surface well;
– not to cause corrosion of metal surfaces;
– not to be toxic and fire-hazardous;
– to have a low cost;
– to be obtained in quantities necessary to meet the needs.

Methodology. A light vacuum gas oil with AVT-6 was chosen as the basic component of the preventive product from Naftan products and semi-products. For LVGO in the laboratory conditions, fractional distillation is performed. Density, kinematic viscosity, conditional viscosity, viscous flow activation energy, refractive index, flash points and surface tension are determined by Rebinder method.

High-molecular, heavy oil residues, such as: tar from VT-1, fuel oil with AVT-6, bitumen of oil building BN-90/10, semi-solid non-distilled residue of heavy pyrolysis resin, residual extract of selective purification of oils with phenol and residues from a Thermocracking unit are used as thickening, adhesive, anticorrosive and frost-proof additives to light vacuum gas oil. The content of asphaltenes is determined for high-molecular residues. The maximum content of asphaltenes in the form of a stable colloidal solution is characteristic of bitumen as the most severe residual product of oil refining. The minimum content of the residual extract is selective, which is associated with the preliminary removal of asphaltenes from tar, as it is deasphalted by propane. In addition to asphaltenes, crystals of high molecular weight, highly condensed aromatics, such as naphthalene, anthracene, and their derivatives, are formed in the pitch of the heavy pyrolysis resin.

Anti-freezing agents were obtained by mixing the residual products with a light vacuum gas oil and subsequent heat treatment at a temperature of up to 100°C for 1.5 – 2 hours by means of a mechanical paddle mixer. The residues were added in concentrations of up to 5% by weight to a LVGO.

Results, discussion and conclusion. Viscosity is an important indicator for preventive measures, at low ambient temperatures it should be low, which allows to apply the formulations on the surface of the transport equipment in a finely dispersed state using nozzles. Viscosity decreases relatively to the initial light vacuum gas oil when fuel oil and tar are involved, probably because the molecules of oil residues cause an increase in the compactness of dispersed particles and formation of nanoaggregate clusters.

For all samples, indicators such as flash temperature, an indicator characterizing the fire safety of the oil product and the refractive index are determined by which one can judge the prevalence of individual groups of hydrocarbons. The refractive index increases with increasing content of aromatic hydrocarbons. The flash point of petroleum products, depending on their volatility and vapor pressure when various additives were involved,

was in all cases not lower than 125 ° C. According to this parameter, the obtained compositions are not inferior to the industrially produced preventive compositions Nyogrin and Universin, the flash point for which should not be lower than 75 and 80°C respectively. The obtained flash points meet the technical requirements, this is one of the main parameters, because the treatment of transport equipment with preventive measures should be carried out in open areas, or in closed rooms in compliance with fire safety standards.

The protective properties of preventive compositions in the presence of water are associated with the ability to create an adsorption-chemisorption membrane on the metal surface. The degree of corrosion on copper plates was determined by visual inspection of the surface of copper plates after 5 hours of testing them for corrosion. As a result of investigations, it was found that corrosion spots were not found on the surface of copper plates immersed in oil products. Corrosion degree 1a is established, which indicates insignificant corrosion for all test samples.

The analysis of the specific interfacial surface is performed on a spectrophotometer. The optical density of preventive agents increases in proportion to the increase in the concentration of the residue in the compositions. Molecules of oil residues cause an increase in the compactness of dispersed particles. Instead of a spatially loose structure, a finely dispersed compact structure is formed, which is accompanied by an increase in the specific interfacial surface.

Asphaltenes are strong surfactants that can adsorb at the phase interface and lower the surface tension. It was found that with a slight increase in the concentration of the residue, the surface tension of their solutions decreases sharply, further decrease in surface tension slows down with increasing concentration, and starting with the saturation concentration the new addition of the residue practically does not reduce the surface tension.

When heavy oil residues are mixed with gas oil fractions, the asphaltenes contained in them form mixed crystals with paraffins and cycloparaffins, which impedes their growth and the formation of a structural skeleton from solid hydrocarbon crystals due to the weakening of coagulation bonds between them. The nature of the curves for the change in the yield point of mixtures based on gas oil fractions is extreme. The extremum corresponds to 3% of the sediment concentration in the composition (the yield point is reduced by 29°C with tar involved and by 22°C when the fuel oil is involved), which corresponds to the optimum concentration of tar-asphaltene substances, at which the adsorption of the latter on the surface of all solid hydrocarbons available in the system.

The physicochemical properties of the antifreezing agent and industrial analogues are presented in Table 1.

Table 1. – Physico-chemical properties of the proposed antifreezing agent and industrial analogues

Antifreezing agent name	Yield point, ° C	Flash point, ° C	Conditional viscosity at 50 °C, ° VC	The content of H_2O, in a bulk %	The content of mechanical impurities, in a bulk %
Nyogrin-45	not higher -45	not less 40	1,0-3,0	no more 2,0	no more 1,0
University-40	not higher -40	not less 80	1,3-3,0	no more 0,5	no more 0,3
Severin-50	not higher -50	not less 80	1,1-1,5	no more 0,5	no more 0,2
Light vacuum gas oil with 3% tar mass (proposed product)	-29	148,8	1,49	0,01	traces

Simulation of the freezing process and adherence to the surface of open wagons was carried out under laboratory conditions with artificial coke watering in freezing chambers at a temperature of -25°C. A uniform thin layer of a chilled preventive agent was applied on the surface of pre-cooled metal trays (30 x 20 x 15 cm) with a brush, preventing the lubricant from flowing onto the metal surface. After 5-10 minutes after applying the preventive, an equal amount of bulk material was loaded into all containers. After using a pulverizer, the coal was moistured with water in amount of 5% to the bulk of coal. To create conditions that are as close as possible to loading conditions, after filling the containers with coke, an additional packing of loose rock was carried out. The filled trays were placed in freezing chambers for two days at a temperature of -25 ° C.

After the test time, the trays were emptied by overturning, then the metal surface of the laboratory open wagons was inspected, the degree of unloading of loose rock in percentage terms was estimated. For the tests, a sample of the antifreezing agent containing 97% of the light vacuum gas oil with 3% tar mass was taken. Laboratory tests showed that the processing of laboratory open wagons did not reveal a frozen product and no additional manual unloading was required.

Thus, the conducted researches made it possible to conclude that the antifreezing agent containing a light vacuum gas oil with 3% tar mass can be effectively used to prevent sticking and freezing of coke to the metal surface of open wagons. It is recommended for use in the transportation of petroleum coke from JSC Naftan to Belarusian Cement Plant in Klimovichi in winter.

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