Reduction of airborne particulate matter emissions associated with petroleum coke production

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Abstract. This article presents the results of studies on production based on products of secondary oil refining processes of agents for dust suppression and reduction of losses from blowing out of wet bulk carbon-containing materials, in particular petroleum coke, as well as against freezing and adhesion during their transportation at low temperatures. The use of the developed dust suppression-antifreeze agent will reduce exposure to dust of the employees at the delayed coking unit in the course of petroleum coke production and improve its freeze resistance. It will have a positive impact on the solution of the problem of petroleum coke transportation at subzero temperatures, and will also allow expanding the range of marketable products, and increasing production efficiency.

1. Introduction

Today, the delayed coking process is one of the most rapidly developing and promising processes for crude oil deep conversion, since commissioning of a delayed coking unit at a refinery leads to an increase in the main indicator - oil conversion ratio up to 95%.

To ensure safe conduct of the process, it is necessary to strictly comply with the requirements of industrial and fire safety, labor protection, in addition, the working conditions of the workers of the plant are changing, as there is an additional harmful production factor - dust, due to the release of coke dust into the air of the working area, which has the ability to smouldering, spontaneous combustion and self-ignition. Exceedence of the maximum allowable concentrations for petroleum coke dust in the air of the working area of production facilities (MAC in the working area is 5 mg/m³) can lead to development of occupational lung diseases [1, 2, 4-6]. In terms of human exposure, petroleum coke dust is classified as 4 hazard class. According to GOST 22898, the smouldering temperature of spontaneous combustion of dust with a particle size of 50-100 µm is 205-235ºC, the self-ignition temperature is 535-625ºC. Dust with a particle size of 50-160 µm is not explosive: the lower limit of airborne dust ignition is absent up to 500 g/m³.

Coke production refers to industries that pose a potential danger due to the high likelihood of contact with raw materials, coke dust products and auxiliary reagents during work and adverse physical factors (noise, vibration, thermal and electromagnetic radiation, presence of radioactive sources from nuclear level gauges on coke drums and fractionation column, etc.). Main sources of air pollution are: tube furnaces section, heat exchangers section, coke drums section, pumping stations section, rectification and stabilization section, and section for transferring petroleum coke from
conveyor to conveyor, screening section, hoppers for unloading petroleum coke from silos, petroleum coke wagon loading line, petroleum coke crushing, handling and storage section [2, 3].

Alongside with that, the high humidity of petroleum coke creates difficulties in coke handling at the delayed coking unit, resulting in low efficiency of screen sizing. Transportation of petroleum coke with high humidity is associated with intense adhesion in autumn period and adfreezing of cargo and its freezing to the metal surface of dump cars, gondolas, hoppers, dump truck bodies in winter. As a result of this, up to 50% of the rock mass remains unloaded, which necessitates additional cleaning, while the cost of transportation increases by 20%. To prevent dust loss, adhesion, adfreezing, freezing of rocks with high humidity various means are used, the most widespread industrial applications in recent years have been gained by preventive means of petroleum origin - Niogrin and Universin [4-14].

Currently, the task of combating dust formation, losses from blowing, adhesion, adfreezing and freezing to working metal surfaces of automobile and railway vehicles during transportation of petroleum coke at subzero temperatures is an critical task for oil refining industry, which determined the purpose of this research. Patent search showed that a number of preventive agents have been developed for treatment of carbon-containing bulk cargos during transportation, for example:

- Preventive agent, including as a solvent the kerosene-gasoil fraction of secondary processes (thermal cracking of residual oil, or delayed coking, or catalytic cracking) with boiling range of 195-270°C 70-78% wt., and the rest is tar [15]. This preventive agent is characterized by low pour points: minus 58 - minus 65°C with assumed viscosity at 50°C of 1.33°AV.
- Preventive agent containing as a solvent the kerosene-gasoil fraction of catalytic cracking with boiling range of 200-275°C, 50-60% wt., and the rest is tar [16]. This preventive agent is characterized by low pour points: minus 49 - minus 61°C with assumed viscosity at 50°C 2.63-2.85°AV.
- Preventive agent containing a 0.8-2.0% solution of low molecular weight polyethylene in the kerosene-gasoil fraction of secondary processes with boiling range of 190-270°C 50-60% wt. and tar 40-50% wt. [17]. This preventive agent is characterized by low pour point of minus 42 - minus 47°C with assumed viscosity at 50°C 1.83-2.83°AV.

The disadvantage of the considered preventive agents [15, 16, 17] is their high viscosity, due to the significant content of a thickening additive of oil origin (tar of 22-50% wt.). As a result, a sharp increase in viscosity at temperatures below minus 20°C leads to increased consumption of the agents, makes their spraying by nozzles difficult at low temperatures and complicates the technology of their application to obtain a uniform coating.

- There are various compositions for treatment of working surfaces of transport containers to reduce freezing of bulk materials to the working surfaces [18]: according to the first variant, the composition contains a fraction of high-temperature thermal cracking of high severity (pyrolysis), distilled off within 140-600°C (pyrolysis resin) as a wide oily fraction of thermal origin in the amount of 10-95% wt. and a fraction of straight run low-viscosity fuel oil as a middle distillate hydrocarbon fraction obtained in the process of atmospheric distillation of crude oil in the amount of 5-90% wt. The compositions have pour points of minus 29 - minus 45°C with assumed viscosity at 50°C of 2.1-3.3°AV. The closed-cup flash point is 45-74°C. The disadvantage of the compositions specified in [18] for treatment of the working surfaces of transport containers to reduce the freezing of bulk materials to the working surfaces is the high value of the assumed viscosity at 50 °C, which leads to difficulty in spraying the compositions with nozzles at low temperatures. At the same time, with a decrease in viscosity by increasing the content of low-boiling fractions (kerosene fraction and high-temperature thermal cracking fraction of high severity), the closed-cup flash point decreases, converting the proposed compositions into more flammable liquids: from “combustible” to “flammable”. The disadvantage is also the need to use expensive depressant additives to obtain the composition according to the third variant.
- Preventive agent against adfreezing and freezing of bulk materials to transport equipment containing light catalytic cracking gasoil with boiling range of 180-360 °C 80-90% wt. and tar
from sour oils 10-20% wt. [19]. This preventive agent is characterized by low pour points: minus 58 - minus 60 ° C. However, this preventive agent does not have sufficiently high dust-suppression properties.

- Universin-S dust-suppression composition containing light catalytic cracking gasoil with boiling range of 190-320°C 45-60 %wt., the residue from thermal cracking of heavy aromatic distillates of secondary processes 15-20% wt., residue from thermal cracking tars from sour oils 5-10% wt., light coking gasoil with boiling range of 190-350°C - the rest [20]. The composition has pour points of minus 55 - minus 62°C with an assumed viscosity at 50°C of 1.30-1.46°AV. The disadvantage of the composition is its complexity (multi-component composition). The components included in the composition are obtained in the course of various petroleum refining processes. In case of absence of one of the units within the process flow scheme of the plant: catalytic cracking, delayed coking or thermal cracking, the possibility of preparing a preventive agent of the required quality is excluded.

The objective of this study is to involve a minimum amount of a thickening additive of petroleum origin (tar or fuel oil), sufficient for the manifestation of a depressant effect due to the structural organization of macromolecular associates of resinous-asphaltene substances of residues in kerosene-gasoil fractions of secondary processes without a significant increase in viscosity and with the possibility of uniform application of a preventive agent on cargo in a finely dispersed state, using nozzles for this purpose, which will reduce the costs of their transportation and unloading. The implementation of the task will make it possible to achieve the goal of the study to reduce the employees’ exposure to coke dust by using dust suppression-antifreeze.

2. Research methods

Compounding of thickening additive with solvent was carried out, the selection was made and the optimal ratio of initial raw components was determined to obtain a dust suppression-antifreeze agent with a complex of required properties.

Dust suppression and anti-freeze agent was obtained in a cylindrical mixer with a mechanical mixing device with adjustable heating of the entire outer surface, a thickening additive in the amount of 3 ... 5% wt. was heated in a cylindrical metal mixer to (85 ± 5)°C, 95 ... 97% wt. of solvent was added and the mixture was stirred for 10 minutes at (85 ± 5)°C to obtain a homogeneous mass, then the resulting mixture was subjected to isothermal aging for 60 min at (85 ± 5)°C.

As thickening additives for dust-suppression and antifreeze preventive agents the following was used:

- fuel oil from the AVT-6 Crude Distillation Unit of Naftan OJSC with density at 20°C according to GOST 3900 equal to 939 g/cm 3, open cup flash point according to GOST 4333 equal to 173°C;
- tar from the VT-1 Unit of Naftan OJSC with density at 20°C according to GOST 3900 equal to 1002 g/cm 3, open cup flash point according to GOST 4333 equal to 275°C.

Secondary process kerosene-gasoil fractions were used as solvents in dust suppression-antifreeze preventive agents:

- side cut of C10+ aromatic hydrocarbons from the Pseudocumene Unit of Naftan OJSC with boiling range of 180-330 ° C (Solvent 1).
- kerosene-gasoil fraction of the visbreaking process from the Visbreaking-Thermal Cracking Unit of Naftan OJSC with boiling point of 195-245°C (Solvent 2).

The characteristics of the used kerosene-gasoil fractions of the secondary processes are shown in the table 1.

The obtained dust-suppression anti-freezing agents were studied by standard methods to determine the pour point (GOST 20287-74), closed cup flash point (GOST 6356), assumed viscosity at 50°C (GOST 6258), density 20°C (GOST 3900), mass content of mechanical impurities and water (GOST 6370 and GOST 2477, respectively).
Table 1. Physical and chemical characteristics of the solvent components.

| Indicators                                      | Solvent 1 | Solvent 2 |
|------------------------------------------------|-----------|-----------|
| Density at 20°C, GOST 3900, g/cm$^3$           | 0.902     | 0.819     |
| Assumed viscosity at 50°C, GOST 6258, °AV      | 1.096     | 1.092     |
| Flash point, GOST 6356, °C                     | 62        | 69        |
| Pour point, GOST 20287, °C                     | below -65 | -54       |
| The content of mechanical impurities, GOST 6370, wt.% | none     | none     |
| Fractional composition, GOST 2177:             |           |           |
| IBP                                            | 180       | 195       |
| 50%                                            | 193       | 212       |
| EBP                                            | 330       | 245       |

3. Results and discussion

Table 2 shows a comparison of the technical and economic indicators of the three proposed samples of dust suppression-antifreeze agents with industrial analogues (Niogrin PS-35S Technical specifications TU 0258-002-38507925, Universin-S PS Technical specifications TU 38.1011142, Severin-2 Technical specifications TU 38.101863):

- Sample 1: Visbreaking diesel with 5% wt. fuel oil from AVT-6;
- Sample 2: Visbreaking diesel with 3% wt. tar from VT-1;
- Sample 3: total aromatics fraction C$_{10+}$ 5% wt. fuel oil from AVT-6.

Table 2. Physical and chemical properties of the dust-suppression antifreeze.

| Indicators                                      | Niogrin PS-35S | Universin-S PS | Severin-2 |
|------------------------------------------------|----------------|----------------|-----------|
| Assumed viscosity at 50°C, GOST 6258, °AV      | 1.0 – 3.0      | 1.1 - 3.5      | 1.12      |
| Pour point, GOST 20287, °C, not higher         | minus 35       | minus 40       | minus 50  |
| Flash point, GOST 6356, °C, not less            | 40             | 80             | 80        |
| Mass fraction of water, GOST 2477, %, max       | 2.0            | 0.5            | 0.5       |
| The content of mechanical impurities, GOST 6370, wt.% | 1.0     | 0.3            | 0.2       |
| Copper strip test, GOST 6321                    | passes         | -              | -         |
| Color, visually                                | light brown to black |            |           |
| Cost $ / ton                                   | 180-200        | 180-200        | 210-1100  |

The obtained dust-suppression antifreeze agents are a thin dark brown oily liquid based on a solvent and a thickening additive of petroleum origin, and with a small thickening additive content they have good low-temperature properties, which allows their use in severe climatic conditions. In this case, 3 ... 5% wt. is the optimal concentration of a thickening additive (tar or fuel oil) to achieve the maximum depressant effect in kerosene-gasoil fractions.

The analysis of the corrosion effect on metals (Steel 10, aluminum, copper) according to GOST 9.080 has been performed. It was found that all samples stand the test.
The process of freezing and sticking to the surface of open wagons was simulated in laboratory conditions with artificial watering (moisture content of 10%) of petroleum coke or coal in freezers at the temperature of -30 °C during 48 hours. The experiments were carried out in special metal models of railway gondola cars (material - Steel 20), simulating railway cars used to transport coal, reduced by 1225 times [21]. Treatment of the inner surface of the gondola car was carried out using a spray gun. The volume of petroleum coke or coal was treated by spraying the reagent through a nozzle. In practice, for treatment of gondola car walls, a flow rate of 10 liters per gondola car is taken; for comparative tests, a flow rate of 8 ml per one model of a gondola car is accepted, according to the scale factor of this object. Unloading of petroleum coke or coal after holding the containers in the freezer at the temperature of -30 °C for 48 hours was carried out after mechanical impact on the side wall of the gondola car model with impacts of a weight of 1 kg tied to a cord 35 cm long and with the incidence angle of 45° with subsequent flipping. After each impact and turning over, visual assessment of the volume of coal discharged was carried out as a percentage. The simulation results of the process of freezing and sticking to the surface of gondola cars showed that all samples can reduce the adhesion (adfreezing) of petroleum coke or coal to the metal surface, significantly reduce the freezing of petroleum coke or coal and facilitate their unloading from prototype containers, the compositions show sufficient adhesive properties with respect to dust, which allows to reduce losses from blowing out of wet bulk carbon-containing materials during their transportation and to reduce the impact of the dust factor on the staff.

When liquid is applied to the inner surfaces of dumpcars, open wagons, wagons and dump trucks, as well as the inner surfaces of excavator buckets, graders and other mining equipment, a solid hydrocarbon layer forms on a metal surface that prevents direct contact between pieces of bulk material and metal as a result of which the adhesion and adfreezing strength of the carbon-containing mass is reduced. When treating the mass of bulk material, a thin film is also formed on its surface, which prevents the freezing of pieces of material into a single monolith. It is recommended to spray dust-suppression and anti-freezing agents during transportation of petroleum coke simultaneously directly onto the inner metal surface of vehicles and onto coke moving along the conveyor with a total consumption of 1-3% wt. by weight of petroleum coke.

Air pollution with coke dust was evaluated by the mass method. It was found that dust suppression and anti-freeze agents based on diesel fractions of secondary oil refining processes with the addition of 5% wt. fuel oil from AVT-6 Unit (sample 1) reduces dust content of air by 7.4 times, and 3% wt. tar (sample 2) from VT-1 Unit – by 3.5 times.

The simulation of the dust loss process of petroleum coke was carried out to prevent blowing out during transportation by open method. The wind speed in the laboratory wind tunnel was determined using a mechanical cup anemometer. A dry and treated weighted sample of petroleum coke dust was placed in a wind tunnel for 30 minutes at the wind speed of 30 km/h. The weighed sample without treatment with a preventive agent showed that dust removal is 58%, while dust removal for weighed samples treated with a sample is 1 - 12%, thus, losses during the blowing process are reduced by 4.8 times.

Analysis of the technical and economic indicators of the proposed dust suppression and antifreeze agents in comparison with industrial analogues showed that they are not inferior to the “Niogrin-PS 35C” in basic operational properties and are more than three times cheaper.

4. Conclusion
The developed dust suppression-antifreeze agents do not show corrosiveness with respect to metal surfaces, do not contain mechanical impurities and water, have sufficiently high flash points that meet fire safety requirements, are characterized by low pour points, allowing them to be used at ambient temperatures below minus 30 °C; have good wettability, adhesive ability and rheological properties; low consumption of about 1.5% wt. per the mass of the transported cargo. The proposed dust-suppression and anti-freeze agents from local raw materials can be recommended for use to combat dust formation and to prevent freezing and adhesion of rocks and bulk carbon-containing cargoes to
metal surfaces and cavities of automobile and railway vehicles. The use of kerosene-gasoil fractions of secondary processes in optimal proportions with residual oil products (tar or fuel oil) will increase the raw material base for the production of preventive agents, as well as expand the scope of use of petroleum by- and co-products. Industrial implementation of the proposed agents for preventing freezing, adhesion as well as for dust suppression of bulk carbon-containing materials will decrease the cost of their transportation and unloading and reduce the impact of the dust factor on personnel.

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