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INTENSIFICATION OF PARAFFIN WAX SEPARATION FROM OILSTOCKS BY STATIC CRYSTALLIZATION

The possibility of paraffin wax separation from the high-boiling slack wax by static crystallization has been studied. Gas chromatographic analysis of individual hydrocarbon composition of the high boiling slack wax and its structural-group composition by the method of IR Fourier spectroscopy has been determined, experiments on the de-oiling on installation that simulates the operation of industrial crystallizers has been done. It is established that the de-oiling process of the high-boiling slack wax by static crystallization is obtained tightened in time and economically impractical.

It has been proposed to introduce the paraffin oil from low-boiling slack wax as a diluent for the high boiling slack. Physical and chemical analysis of individual raw material components and their mixtures has been determined, the process of de-oiling by static crystallization has been done.

The introduction of the paraffin oil from low-boiling slack wax into the high-boiling slack wax reduces the time and the temperature of partial melting phase of static crystallization without worsening the quality of the melt. As a result, the static crystallization goes faster and different technological costs are reduced.

Key words: slack wax, paraffin oil, deoiling, crystallization, paraffin, chromatography, spectroscopy, paraffinicity.

Introduction. In organic chemistry under the definition of “wax” saturated hydrocarbons of the alkane series having the formula C_nH_{2n+2} is understood, where n is the number of carbon atoms regardless of the physical properties and chemical structure.

In the engineering the term “wax” means a product which is a mass, consisting mainly of hydrocarbons of the marginal series containing 18 to 35 carbon atoms, and having a white or yellowish color depending on the presence of oils and resins.

Paraffin wax is widely used in different sectors of the economy. The largest consumer of paraffin is a petrochemical industry where they are used as raw materials for basic organic synthesis. In the Republic of Belarus main consumers are enterprises of the rubber and tire industry. Paraffin wax is widely used in woodworking for hydrophobization of wood, in the manufacture of candles, in food industry, medicine and cosmetics [1, 2].

Main part. All ongoing industrial methods of separation of the solid paraffins from slack wax obtained in dewaxing refined selective treatment of oil fractions containing significant amounts of oil can be divided into two types:

– de-oiling with the use of selective solvents;

– de-oiling by way of sweating.

The most versatile are methods of crystallization with the use of selective solvents, as they can be used for almost any material – from distillate diesel fuels to heavy residual products. However, this method is characterized by high energy costs for cooling the raw material mixture and the solvent recovery, high consumption of solvents for dilution of raw materials, a low rate of filtration of raw materials and low yield of the target product [3]. Therefore, relevant technologies in order to improve the quality of the wax, reducing energy and material costs become up to date. Among such plants are the technology of separation of the solid paraffins by crystallization, which does not require solvents.

In the Republic of Belarus the only manufacturer of paraffin wax is JSC “Factory of mountain wax”, where for de-oiling of slack wax by static crystallization system, developed by firm “Sulzer Chemtech” (Switzerland) is used.

This method has the following advantages:

– lack of use of technology in polar solvents;

– no expensive nodes, filtration and centrifugation of the product;

– environmental safety of the process, allowing to locate production in small sanitary zones of the enterprises;

– a small area occupied by the equipment, allowing to locate production in the building.

The static crystallization process consists of three sequentially repeated steps: obtaining paraffin oil (stage 1); raw material processing (stage 2); the receipt of the product (stage 3). Each stage consists of phases of crystallization, partial melting and full melting, during which the coolant temperature is changed according to predetermined dependence “temperature – time”. The resulting fractions depending on content of oil merge into a well-defined capacity (balance, intermediate power stages or product) according to the material balance.

However, this most advanced and environmentally friendly method of producing a paraffin wax at the moment does not allow effective to recycle high boiling slack wax having high viscosity and containing more than 20% of hydrocarbons C_{35+} normal and isomeric structures. The process of de-oiling such slack waxes is tightened in time and economically unfeasible [4].

The aim of this work was to develop technological methods, allowing to expand the raw material base for the production of solid paraffin.

The object of the study was the high boiling slack wax, obtained in JSC “Naftan” (Novopolotsk) in dewaxing refined selective treatment of oil fractions. In Table 1 shows the main physical-chemical characteristics of the slack wax.

Experiments on the de-oiling of crude oil was carried out on a laboratory setup simulating the operation of industrial crystallizers.

Table 1

Physical-chemical parameters of high-boiling slack wax

Parameters	Value
Mass fraction of oil, %	9.21
Melting point, °C	55
Kinematic viscosity at 100°C, mm^2/s	4.93
Chromatographic analysis, the content of, %:	
– n-paraffins	46.44
– isoparaffins	53.56
– hydrocarbons C_{35+}	26.17

Individual hydrocarbon composition of n- and isoalkanes was determined on gas chromatograph Chromatek – Crystal 5000.1 with a flame ionization detector. The metal column length of 30 m with an internal diameter of 0.53 mm and a film thickness of 0.25 μm was used.

By the IR Fourier spectroscopy method the structural-group composition of the investigated samples of slack wax, sweats and melts were determined. Studies of the IR spectra is performed on an infrared spectrometer FSM 1202 (Infraspek) in the range 4,000–400 cm^{-1} with resolution of 4 cm^{-1}.

As a technological reception, allowing to expand the raw material base for the production of solid paraffin, it was proposed to enter as a diluent for high-boiling slack wax paraffin oil, obtained by de-oiling low-boiling slack waxes, in the amount of 10%.

Main physical and chemical parameters of the mixture of high boiling slack wax and paraffin oil are given in Table 2.

Table 2

Physical-chemical characteristics of mixture of high-boiling slack wax and paraffin oil

Parameters	Value
Mass fraction of oil, %	9.80
Melting point, °C	54
Kinematic viscosity at 100°C, mm^2/s	4.89
Chromatographic analysis, the content of, %:	
– n-paraffins	44.79
– isoparaffins	55.21
– hydrocarbons C_{35+}	24.58

Individual hydrocarbon composition of n- and isoalkane mixture of high-boiling slack wax and paraffin oil are presented in Figure.

The ratio of normal and isoparaffins is 45 and 55%, respectively, of which hydrocarbons C_{35+} make up 24.6%, which is 1.5% less than that of the sample of high-boiling slack wax.

The process of de-oiling of high-boiling slack wax and its mixtures with the paraffin oil was carried out by one of the process stages of static crystallization stage processing of raw materials. The heating rate according to the given dependence “temperature – time” in the collection of the first sweat was 1.2°C/h, while collecting second sweat – 1.5°C/h. The output of the first sweat was 21%, second sweat 27%, and melt – 52%.

Introduction paraffin oil of low boiling slack wax in an amount of 10% reduced the time for the stage of processing at 2 h in comparison with the processing of high-boiling slack wax without additives, and reduce the temperature of the phase selection sweats at 1°C.

Physico-chemical characteristics of melts obtained when carrying out de-oiling of high-boiling slack wax and its mixture with the paraffin oil are given in Table 3.

Table 3

Physical-chemical characteristics of melts

Parameters	Melts	
	slack wax	slack wax + + 10% paraffin oil
Mass fraction of oil, %	6.61	6.04
Melting point, °C	58	58
Kinematic viscosity at 100°C, mm^2/s	5.07	5.06
Chromatographic analysis, the content of, %:		
– n-paraffins	50.77	50.10
– isoparaffins	49.23	49.90
– hydrocarbons C_{35+}	27.11	24.68

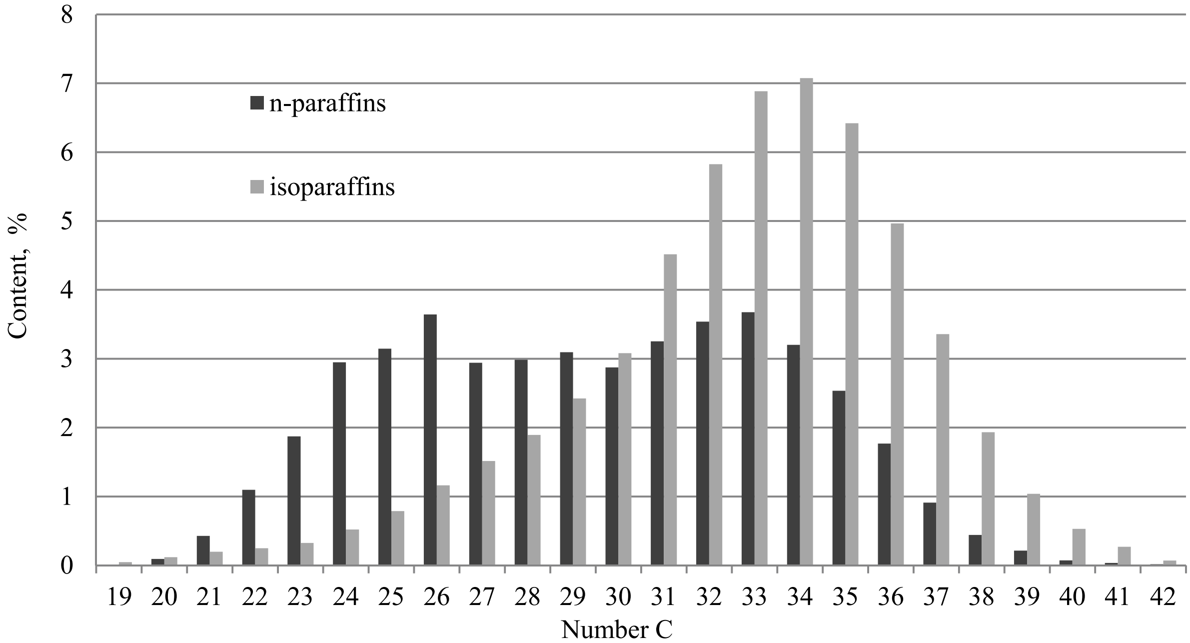
As follows from the data Table 3, the mass fraction of oil in the melt when the de-oiling of the high-boiling slack wax with the addition of paraffin oil is 0.5% lower than the same experiment without additives. The contents of high boiling hydrocarbons C_{35+} in the melt when the de-oiling of the high-boiling slack wax with the addition of paraffin oil is by 2.5% lower, that should have a positive impact on the subsequent stages of a product.

With the method of IR Fourier spectroscopy peculiarities of the chemical structure of the investigated samples [5] were studied.

Table 4

The relative intensity of the characteristic absorption bands in the IR spectra

Analyzed sample	Degree of branching	Degree of aromaticity	Content of paraffin hydro-carbons, %
The high-boiling slack wax	1.635	0.133	83.84
Paraffin oil of low boiling slack wax	1.476	0.060	86.26
The mixture of slack wax and paraffin oil	1.558	0.073	89.20
The melt after the de-oiling of slack wax	1.500	0.099	86.08
The melt after the de-oiling of mixture	1.525	0.015	96.30



Chromatogram of a mixture of high boiling slack wax and paraffin oil

The degree of branching of the paraffin hydrocarbon chains can be characterized by the coefficient representing the ratio of the intensities of the most characteristic absorption bands for the CH_3- and CH_2-groups:

$$\beta_{1464}^{720} = \frac{\nu_{1464}}{\nu_{720}}.$$

The degree of aromaticity can be characterized by the coefficient representing the ratio of the intensities of the most characteristic absorption bands for aromatic structures relative to the methylene groups of paraffinic structures:

$$\beta_{1600}^{720} = \frac{\nu_{1600}}{\nu_{720}}.$$

Group composition was calculated from the optical densities in the IR spectra of the samples to the absorption bands characterizing the deformation vibrations ties C–H and C–C: 1,450, 1,370 and 720 cm^{-1} (alkanes); 1,030 and 970 cm^{-1} (naphthenes); 1,600, 870, 810, and 750 cm^{-1} (arenes); 1,700 cm^{-1} (oxidation products) [6].

The calculation of the values of relative intensities of characteristic absorption bands in the IR spectra of the analyzed samples are given in Table 4.

Conclusion. It is established that the introduction of an additive to high-boiling slack wax paraffin oil of low-boiling slack wax allows to reduce the time and temperature of reference process, without compromising the quality of the melt. Thus, by introducing additives, which influence the intensity of intermolecular interactions, it is possible not only to improve the quality allocated to paraffin, but to accelerate the process of static crystallization, and consequently, to reduce various types of costs in the implementation process.

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