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INVESTIGATION OF THE EFFECT OF CRYSTALLIZATION CONDITIONS AND «DIFRON-4201» DEPRESSANT ADDITIVE ON THE COMPOSITION AND PROPERTIES OF PARAFFIN DEPOSITS

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For the first time in the laboratory, the physical and chemical characteristics of the model oil sample, the composition, and relative amounts of normal alkanes with carbon atoms from C_8 to C_{60} were determined by high-temperature liquid-gas chromatography. When Difron-4201 is added to the model oil, seven carbon atoms are displaced in the direction of the lower molecular weight distribution of paraffin hydrocarbons in the sediment. The effect of the Difron-4201 additive on the group composition of model oil and oil sediments obtained at different temperatures of the «cold finger» was studied. It was found that with the addition of the additive and with a decrease in the temperature of model oil and «cold pipe», the number of paraffin hydrocarbons in the group composition of sediment increases and the amount of resin and asphaltenes decreases. Microanalysis of the structure of asphaltene–resin–paraffin sediments obtained after the addition of the additive showed that the model oil sediments, separated at 30/150^{0}C and containing large amounts of high-molecular paraffin hydrocarbons, resin, and asphaltene components, have the highest proportion of amorphous structures. An increase in the share of dendritic modification of the crystalline structure is characteristic for paraffin hydrocarbons in sediments obtained with the addition of 900 g/t «Difron-4201» additive.

Keywords: model oil, depressant additive, Difron-4201, cold finger, oil sediment, n-alkanes.

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Introduction

One of the problems that complicates process equipment, capacities and pipelines during oil production, storage and transportation is asphaltene–resin–paraffin deposits. The systems productivity decreases sharply due to an increase in pressure differential and a decrease in the useful volume during the accumulation of oil deposits in the flow sections and tanks [1–3].

Despite the fact the fight against asphaltene–resin–paraffin deposits in the oil industry began 120 years ago, this issue is still relevant today. Currently, the number of oil fields rich in asphaltene–resin components and refractory paraffin hydrocarbons is growing, and high freezing temperatures and high viscosity characterize the resulting oils. In particular, during the storage and transportation of heavy oils in cold climates, the formation and accumulation of asphaltene–resin–paraffin deposits at the bottom of the tanks and on the pipelines' inner surface becomes intensive. This, in turn, leads to a decrease in the functional capacity of tanks and the oil recovery factor of pipelines [1–3].

The main factor influencing the formation and precipitation of solid phases in the dispersed oil system is the decrease in paraffin hydrocarbons' solubility. The solubility of paraffin hydrocarbons depends significantly on the temperature of the oil. Thus, the paraffin hydrocarbon crystals formed when the temperature decreases combine and create a robust structural lattice. The resulting large crystals dramatically increase the viscosity of the oil, resulting in a reduction of the flow rate of the oil and sometimes a complete loss of fluidity [4–6].

As a result of the local decrease in oil temperature in the subsurface layer, its ability to dissolve and resist the adhesion of sediment on the pipe surface decreases. The mechanism of formation and accumulation of asphaltene–resin–paraffin deposits on the surface of the equipment consists of the formation and growth of paraffin hydrocarbon crystals during direct mechanical cracking of surface cracks as well as the subsequent formation of crystals in the already formed paraffin–resin coating. Due to the diversity and complexity of the extracted oils, issues related to the prevention or removal of asphaltene–resin–paraffin deposits have not yet been resolved. This is the lack of systematic research in terms of the role of the component composition of the oil, taking into account the temperature factor in the process of sediment formation [6–9].

One of the most effective methods used to prevent or inhibit asphaltene–resin–paraffin deposits during oil production and transportation is chemical reagents. One of such chemical reagents is depressant additives, the function of which is to crystallize with paraffin hydrocarbons at the moment of formation of a new phase when the temperature drops, giving hydrophilicity to paraffin crystals with its polar group and weakening the adhesion of the solid phase on the metal surface. Depressor additives also keep the solid phase in a finely dispersed state in the environment. In general, factors such as the mechanism of formation of n-alkane crystals in a multi-component environment, the kinetics and thermodynamics of paraffin hydrocarbon crystallization, dielectric and other physical properties, the intermolecular interaction of additives with n-alkanes and other components of petroleum gives reason to say that determining the mechanism of action of additives is a very complex task.

Thus, the purpose of the work is to study the composition and properties of asphaltene–resin–paraffin sediments, depending on the temperature of the model oil and the adsorbing surface.

Experimental

The physical and chemical characteristics of the model oil sample developed for the laboratory research process are shown in Table 1.

The mass fraction of the asphaltene component in the model oil sample and the sediment separated from it was determined by Golden's «cold» separation of asphaltenes, and the resin content was determined by the chromatographic (column-adsorption) method.

Methodology for determining the mass fraction of asphaltenes

The investigated sample of the model oil was dissolved in 40 volumes of n-hexane and transferred to the flask, and the flask was closed with a stopper. The flask was stored in a dark place at a temperature of 15–20^{0}C for one day for complete precipitation of asphaltene components. At the end of the period, the solution was filtered. A new portion of the precipitate was filtered with n-hexane and washed with n-hexane until the solution was clear. The precipitate in the filter was then rapidly dissolved in hot benzene, and the filter was washed until the benzene became discolored. After the asphaltene components were completely dissolved in the benzene, the benzene was distilled, and the sample was brought to a constant weight at a temperature of 100–110^{0}C in a drying cabinet. In the end, the percentage of asphaltenes in the tested product (Z) was calculated by the following formula:

$$Z = \frac{100m}{M},$$

where m is the weight of obtained sediment (g), and M is the weight of the tested product (g).

Method for determination of the number of resinous substances

Gradual extraction of resin with different polar solvents allows the separation of neutral components (benzene resin) and acidic components (alcohol-benzene resins). The separation and distilling methods of resinous substances are based on different solubility and sorption capacities of these components. The deasphaltizate sample was dissolved in n-hexane and

Table 1

Physicochemical characteristics of model oil

Parameters	Quantity	Assignment method
The amount of water in the sample, %	0.2	GOST 2477-65
Density, ρ_4^{20} kg/m^3	894.3	GOST 3900-85
The amount of paraffin, %	11.6	GOST 11851-85
The amount of resin, %	10.2	GOST 11851-85
The amount of asphalt, %	5.2	GOST 11851-85
Freezing temperature, ^{0}C	16	GOST 20287-91
Saturation temperature of oil with paraffins, ^{0}C	28	–
Melting point of paraffin, ^{0}C	57	GOST 11858-83
The amount of sulfur, %	0.22	GOST 1437-75
A/R	0.509	–

placed in a 75 cm high and 1 cm diameter chromatographic column filled with dry silica gel. The sample was ignited at 250^{0}C for six hours. During the process, the paraffin-naphthene fraction was separated by dilution with the hexane-benzene solution in a ratio of 10:1. Benzene resins were desorbed from the chromatographic column with benzene, and a 1:1 methyl alcohol–benzene complex solvent was used to separate the alcohol-benzene resins.

Method for determination of the composition and relative amount of n-alkanes

A combination of liquid-adsorption chromatography and liquid-gas chromatography methods were used to determine the composition and relative amount of n-alkanes in the model oil and its sediments. During the liquid-adsorption chromatography method, the column was filled with aluminum oxide with a fourth activity rate of Al_2O_3 in a weight ratio of 1:50 and adsorbent soaked in hexane. In this case, the dilution process was carried out with n-hexane. Fraction output control was performed on a spectrophotometer with the automatic spectral recording by spectrophotometric method. Hexane fraction analysis was performed on a gas-liquid chromatography using a gas-ionization detector, and helium was used as the gas carrier. Shooting mode was a linear programming of the temperature at the speed of 4 degrees per minute at the temperature of 100^{0}C to 290^{0}C. Sample input was performed using a micro-syringe with a volume of 0.5 ml. The decryption of the obtained chromatograms was carried out with reference compounds and storage indices given in the literature. Molecular-mass distribution maxima for n-alkanes were determined on liquid-gas chromatograms. The individual composition of normal alkanes of oil sediments was determined by the high-temperature liquid-gas chromatography method.

Method for determination of the number of paraffin deposits by the «cold finger» method

Quantitative estimation of the formation of paraffin deposits in the model oil sample was carried out by the known «cold finger» method. Distilled water was used as the heat transfer agent during the experiment. Optimal regimes have been developed experimentally. For the experiment, a 40 g sample of model oil was taken, and the experiment lasts one hour. The amount of sediment formed on the surface of the pipe was determined by the gravimetric method. The final result was the algebraic mean of three parallel experiments.

Results and discussion

The process of crystallization of paraffin begins immediately upon contact of oils with the surface of the pipe, which has a temperature close to the initial temperature of crystallization of paraffin hydrocarbons (turbidity temperature). Paraffin's turbidity temperature in the studied model oil varies in the range of 34–60^{0}C. Therefore, a temperature regime covering the entire crystallization range of paraffin was selected during the experiments. The temperature of the model oil (T_{mn}) varies from 60 to 300^{0}C, and the temperature of the «cold pipe» (T_{sb}) varies from 30 to 15^{0}C [8]. The composition and relative amounts of normal alkanes with carbon atoms from C_8 to C_{60} in the model oil were determined by high-temperature gas-liquid chromatography. The model oil sample is characterized by a monomodal distribution of paraffinic hydrocarbons with a wide maximum in the C_{10}–C_{16} field (Fig. 1).

As can be seen from Fig. 1, the amount of n-alkanes decreases with increasing molecular weight.

The total amount of low-molecular ΣC_8–C_{16}

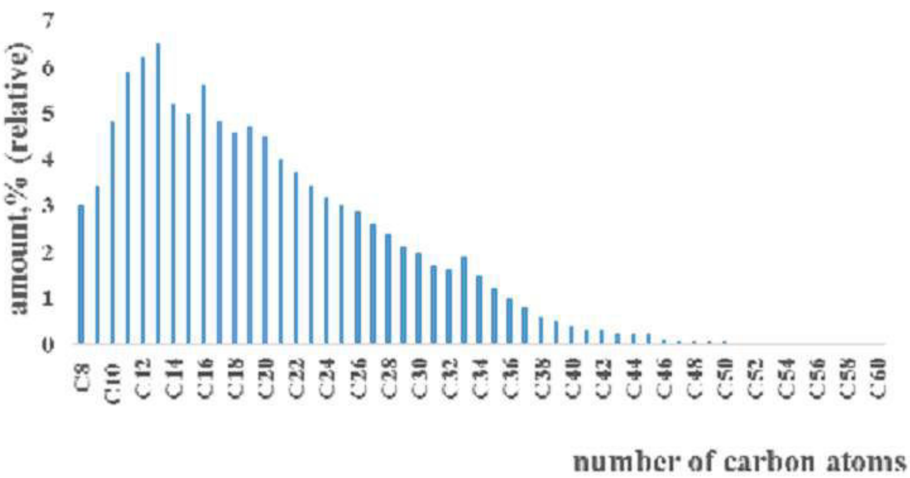


Fig. 1. Molecular-mass distribution of n-alkanes in model oils

and high-molecular $\Sigma C_{17}-C_{40}$, $\Sigma C_{41}-C_{60}$ alkanes and their ratio $\Sigma C_8-C_{16}/\Sigma C_{17}-C_{60}$ were calculated for the model oil sample (Table 2).

Table 2

The number of n-alkanes in the model oil

Parameter		Value
amount of n-alkanes,% (relative):		
	ΣC_8-C_{16}	45.6
	$\Sigma C_{17}-C_{40}$	59.1
	$\Sigma C_{41}-C_{60}$	1.32
ratio	$\Sigma C_8-C_{16}/\Sigma C_{17}-C_{60}$	0.8

The results of gas-liquid chromatography and group analysis showed that the studied model oil is characterized by low and high molecular paraffin hydrocarbons, resin-asphaltene components, which are directly involved in the process of sedimentation. The more paraffin, resin and asphaltenes in the oil, the stronger the oil deposits will be.

Determination of the number of oil deposits

To determine the effect of asphaltene–resin–paraffin components on the properties of sediment formation in model oil and their structural and rheological properties, experiments were performed in the laboratory at different oil sample and temperatures of the «cold finger». Numerous experiments have shown that the formation of sediments from high-paraffin model oil begins at the temperature of 60^0C in oil and the temperature of 35–45^0C in the «cold» rod one-tenth of a percent. When the temperature of the model oil is 30^0C and «cold finger» temperature is 15^0C, the maximum amount of paraffin deposits on the surface of the cold finger is observed. The formation of oil deposits is often described in the literature as an adsorption process due to the formation and growth of crystals at the liquid(oil)–solid(«cold finger») phase separation boundary as well as a direct mechanical connection on cracks and surface irregularities [10].

As a result of adsorption on the surface of a solid, molecular and atomic layers are formed that have the ability to remain stable. Paraffins, resins, and asphaltenes present in the oil during contact with the «cold finger» are considered active in terms of adsorption. They are mainly adsorbed on that surface. First of all, due to their high melting point, paraffin is adsorbed. The higher the content of high molecular paraffin hydrocarbons in oil, the more sediment is formed. Then low-molecular paraffin hydrocarbons are adsorbed. The crystals of the separated paraffin hydrocarbons combine to form a solid structural lattice, to which the liquid oil phases are attached. The higher the number of paraffin hydrocarbons and surfactants in the oil, the stronger the cage, the higher the viscosity, the higher the static displacement stress, and the higher the oil's freezing point. At the same time, there is an increase in the number of oil sediments formed; its rheological properties deteriorate as well as its bond strength to metallic surfaces increases. It was found that in addition to the temperature of the oil and the temperature of the adsorbing surface, the amount of low and high molecular paraffin hydrocarbons in the oil as well as resins and asphaltenes, has a strong influence on the sedimentation process.

Study of group composition of oil sediments

The group composition of asphaltene–resin–paraffin sediments is determined by their formation temperature and the composition of high-paraffin oil. Analysis of the group composition of oil deposits

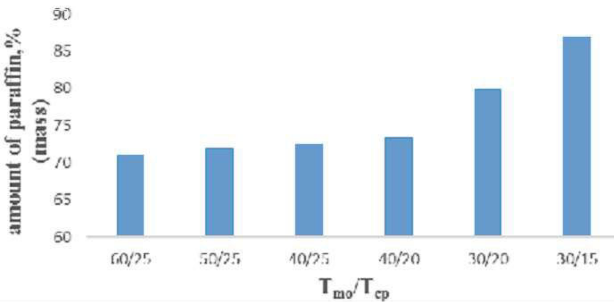


Fig. 2. The effect of model oil and «cold finger» temperature on the number of precipitated paraffin hydrocarbons

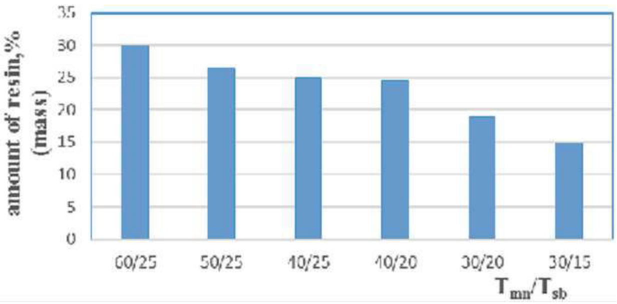


Fig. 3. The effect of model oil and «cold finger» temperature on the number of precipitated resin components

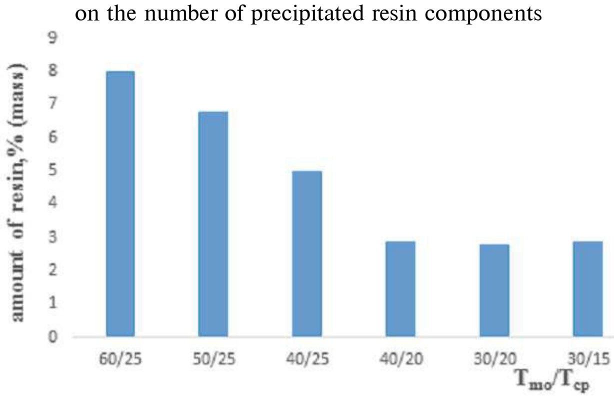


Fig. 4. The effect of model oil and «cold finger» temperature on the number of deposited asphaltenes

showed that 70–85 wt.% of the deposits consisted of paraffinic hydrocarbons (Figs. 2–4).

A gradual increase in the number of paraffin hydrocarbons in the sediments obtained with a decrease in the model oil temperature and the «cold finger» was observed. As can be seen in Figs. 3 and 4, when the model oil temperature changes from 60^0C to 30^0C and the temperature of the «cold finger» from 25^0C to 15^0C, the amount of resin and asphaltenes in the sediment decreases by 2 times and by 2.5 times, respectively. Analysis of the results shows that the molecular processes of phase transitions in the temperature range of sediment formation are associated with asphaltenes and resins. When the concentration of surfactants in the oil increases, first the supermolecular structures are formed, and then the asphaltenes are separated in a separate phase. The resistance of these colloidal systems to stratification is determined by the thickness of the solvate coating formed from resin molecules, which are considered to be structural and mechanical barriers to the association. The aggregation and deposition of asphaltenes depend primarily on the value of the forces of interaction between their fragments. The presence of active centers in asphaltene molecules that determine Van der Vaals bonds, Coulomb interactions, electric charge transitions, induction forces and volume interactions with ion repulsion leads to the growth of particles that cause colloidal instability in the systems [10]. Formation of small associations requires a stabilizing agent, which is also played by resins that form a curtain around the asphaltene core [11–13]. It is clear that at temperatures of 60^0C in model oil, asphaltenes include larger associations due to their increased reactivity and the mobility of molecules in a low-viscosity environment. As a result, the number of asphaltenes and resins in oil deposits increases. The decrease in the temperature of oils leads to the formation of small associations, ensuring their high durability. Thus, it was determined that changes in temperatures of model oil's and the «cold finger» affect the group composition of the sediments separated from the high-paraffin model oil. At high oil temperatures, the amount of resin and asphaltenes in the sediments increases. When the temperature of the model oil and the «cold finger» drops to a temperature close to the freezing point of the oil, the share of paraffin hydrocarbons increases due to the separation of low-molecular paraffin in the sediment group.

Study of the composition of paraffin hydrocarbons in sediments separated at different temperatures

Molecular-mass distribution of n-alkanes in separated sediments depends on the composition of the oil and the temperature conditions of their formation. The individual composition of n-alkanes was determined on a chromatograph by high-temperature gas-liquid chromatography (Fig. 5).

The sediments contain low-molecular n-alkanes (Table 3), and the maximum amount is released in the form of a solid phase at a temperature gradient of $30/15^0$C.

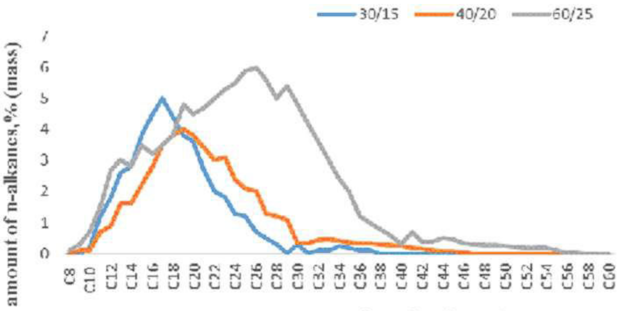


Fig. 5. Molecular-mass distribution of n-alkanes in sediments separated at different temperatures of the model oil and «cold finger»

As the temperature decreases, the structure of the liquid phase changes based on the regularity of the dispersed phase molecules' location. Pre-formed molecular complexes tend to be densely structured.

The liquid phase molecules that form the solvate film around the crystallization centers precipitate due to recrystallization with the solid phase [12]. As the temperature of the model oil and the «cold finger» rises, the number of solid paraffin in the oil sediments and the share of high-molecular n-alkanes with a number of carbon atoms C_{41}–C_{60} increase.

As the model oil temperature rises to 60^0C and the temperature of the «cold finger» rises to 25^0C,

Table 3

The number of n-alkanes in the sediments separated at different temperatures of the model oil and the «cold finger»

Sediments	amount of n-alkanes,% (relative)			ΣC_8–C_{16}/ΣC_{17}–C_{60}	ΣC_{17}–C_{59}/ΣC_{18}–C_{60}
	ΣC_8–C_{16}	ΣC_{17}–C_{40}	ΣC_{41}–C_{60}		
30/15	2.2	38.1	0.2	0.06	1.6
40/20	1.3	41.3	0.8	0.03	1.7
60/25	0.5	79.6	4.4	0.005	1.5

the total amount of $C_{17}-C_{40}$ doubles and the amount of high-molecular paraffin hydrocarbons of the order $C_{41}-C_{60}$ increases by 22 times. Low-molecular C_8-C_{16} alkanes are present in small amounts in the sediment at these temperatures. In the «cold finger» at a constant temperature of 20^0C and an increase in the temperature of the oil, the total amount of n-alkanes and the share of an odd number of hydrocarbons increase. An increase in the temperature of the «cold finger» to 25^0C and model oil temperature to 60^0C leads to a decrease in these values.

Thus, changes in the temperature of the high-paraffin model oil and the temperature of the «cold finger» have a significant effect on the content of n-alkanes in oil sediments.

Study of the microstructure of model oil and its sediments

Depending on the crystallization conditions, different modifications of paraffin hydrocarbons' crystal structures can occur: dendrite, spherical and mixed dendrite-spherical. Spherolite and rhombic crystallization are characteristic of polymer compounds as well as high molecular paraffin hydrocarbons. Low molecular paraffin hydrocarbons, as a rule, form a dendritic crystalline structure [14].

During the dilution of sediments, the microphotographs of model oil sediments were taken to determine the type of crystalline modification of paraffin hydrocarbons, High-paraffin model oil deposits obtained at a temperature of 60^0C of model oil and 25^0C of «cold finger» are characterized by a coarsely dispersed structure. A decrease in the oil temperature to 40 and 30^0C leads to the formation of finely dispersed structures (Fig. 6).

Thus, it was determined that the type of crystallization of paraffin hydrocarbons depends on the amount of high-molecular alkanes, resins and asphaltenes in the sediment. Paraffin deposits obtained at the temperature gradients of $60/25^0$C and characterized by the maximum amount of alkanes in the series $C_{41}-C_{60}$ should form spherulite-shaped crystals. However, under the same conditions ($60/25^0$C), asphaltene-resin components cause a radical change in the shape of paraffin crystals and form coarsely dispersed structures instead of spherulitic systems. A decrease in temperature leads to a reduction in the share of high-molecular $C_{41}-C_{60}$ n-alkanes, responsible for regular-shaped crystals in deposits, and an increase in the amount of low-molecular C_8-C_{16} alkanes, which cannot form regular-shaped crystals due to low melting points.

Effect of «Difron-4201» additive on the number of paraffin hydrocarbons in oil deposits and their group composition

The molecular-mass distribution of paraffinic hydrocarbons in the non-additive model oil sediments has a monomodal distribution with a maximum of C_{24}. When «Difron-4201» is added to the model oil, seven carbon atoms are displaced in the direction of the lower molecular weight distribution of paraffin hydrocarbons in the sediment (Fig. 7).

It was found that the content of $C_{17}-C_{40}$ and $C_{41}-C_{60}$ n-alkanes in the sediments of the additive model oil decreased by 0.8 and 10 times, respectively. Still, the share of low-molecular C_8-C_{16} paraffin

a b c

Fig. 6. Formation of paraffin hydrocarbon crystals in sediments separated at different temperatures of the model oil and «cold finger» (^{0}C): a – 60/25, b – 40/20, and c – 30/15

Table 4

Effect of «Difron-4201» depressant additive on the content of n-alkanes in model oil sediments

Sample	Quantity,% (mass)		
	ΣC_8-C_{16}	$\Sigma C_{17}-C_{40}$	$\Sigma C_{41}-C_{60}$
Model oil	2.2	38.1	0.2
Model oil+900g/t "Difron-4201"	32.56	30.48	0.02

hydrocarbons increased by 14.8 times (Table 4).

In the laboratory, the effect of the «Difron-4201» additive on the group composition of the oil

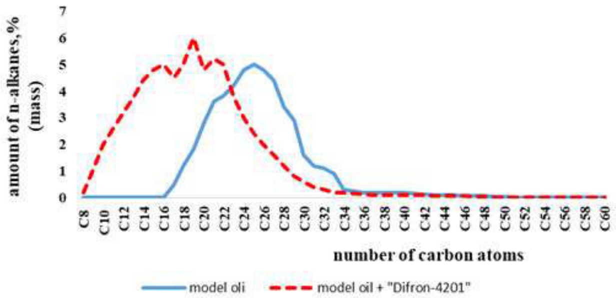


Fig. 7. Molecular-mass distribution of n-alkanes in sediments separated by the addition of «Difron-4201» additive (900 g/t)

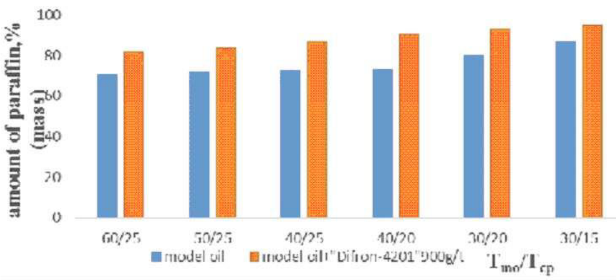


Fig. 8. Changes in the group composition of model oil deposits at the addition of 900 g/t «Difron-4201» additive:
1 – model oil; 2 – model oil+«Difron-4201» 900 g/t

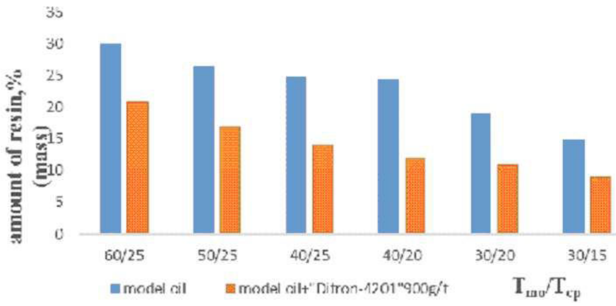


Fig. 9. Changes in the group composition of model oil deposits at the addition 900 g/t «Difron-4201» additive:
1 – model oil; 2 – model oil+«Difron-4201» 900 g/t

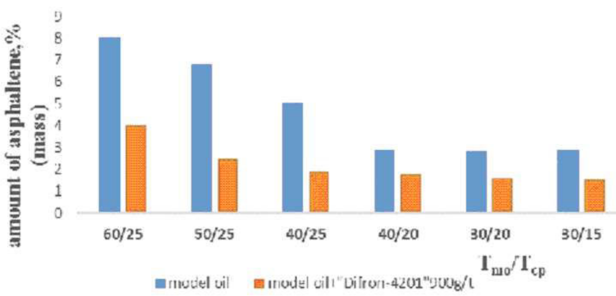


Fig. 10. Changes in the group composition of model oil deposits at the addition 900 g/t «Difron-4201» additive:
1 – model oil; 2 – model oil+«Difron-4201» 900 g/t

sediments obtained at different temperatures of the model oil and the «cold finger» was studied (Figs. 8–10). It was found that with the addition of the additive, the amount of paraffin hydrocarbons in the sediment group increases, and the amount of resin and asphaltenes decreases as the temperature of the model oil and the «cold finger» decreases.

This dependence is explained by the fact that along with paraffin hydrocarbons, asphaltenes are directly involved in the formation of oil deposits [7], indicating a high tendency of individual particles to mix with larger systems until they separate out from the environment to a new phase.

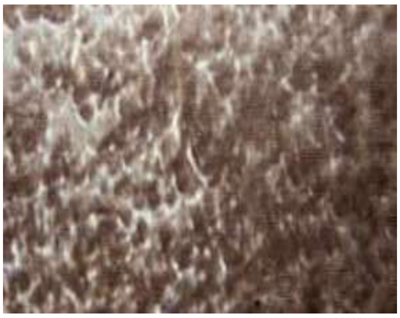
Resins together with asphaltenes are included in oil sediments in the form of associations.

Under the influence of «Difron-4201», the growth of paraffinic hydrocarbon crystals is blocked in the oil, but the association of asphaltenes is weakened, i.e. large associations are not formed and some asphaltenes do not precipitate and remain dependent on the oil system. Besides, the formation of associative complexes between resins and asphaltenes is inhibited, so there is a decrease in the amount of asphaltene-resin components in the sediment. An increase in the number of paraffin hydrocarbons occurs due to a reduction in the temperature of the oil and the «cold finger». However, in this case, mainly low-molecular paraffin hydrocarbons are precipitated because the additive «Difron-4201» prevents the formation of large molecules. Thus, the addition of «Difron-4201» additive to the model oil leads to a change in the molecular weight distribution of n-alkanes and a change in their content in the sediments to lower molecular weight alkanes as well as a decrease in the amount of asphaltene-resin components in the sediments. In addition, the composition of oil sediments affects their structural and rheological properties.

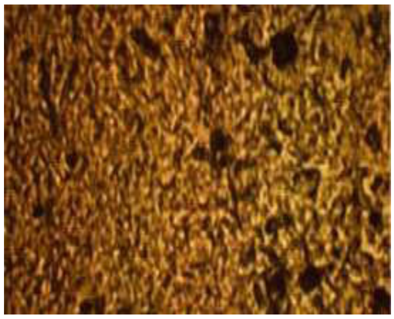
The microstructure of model oil sediments formed in the additive environment

Microanalysis of the structure of asphaltene–resin–paraffin deposits obtained after adding the additive showed that the deposits of model oil, separated at 30/15^{0}C and containing a large amount of high molecular weight paraffinic hydrocarbons (11.6 wt.%), resin (10.2 wt.%) and asphaltene (5.2 wt.%) components have the highest part of amorphous structures. With the addition of 900 g/t «Difron-4201» additive, the share of dendritic modification of the crystalline structure for paraffinic hydrocarbons increases in the sediments (Fig. 11).

Thus, the results of the experiments showed that when the temperature of the model oil and the



a



b

Fig. 11. Microphotography of model oil deposits with and without additives: a – model oil, b – model oil+«Difron-4201»

«cold finger» changes, the additive «Difron-4201» affects the formation of oil deposits as well as their group composition, the number of paraffinic hydrocarbons in the deposits and structural and rheological properties.

Conclusions

1. Analysis of the results of the gas-liquid chromatography study showed that the model oil sample is characterized by a monomodal distribution of paraffinic hydrocarbons with a wide maximum in the C_{10}–C_{16} field, and their amount decreases with the increasing molecular weight of n-alkanes. During the study of the group composition of the oil sediments separated at different temperatures of the model oil and the «cold finger», we determined that the change in the temperature of the model oil and the «cold finger» affects the group composition of the paraffin sediments. A decrease in the oil temperature leads to a reduction in the amount of resin and asphaltenes.

2. The composition and molecular-mass distribution of n-alkanes in oil sediments change due to the release of low-molecular paraffin hydrocarbons when the temperature of the model oil and the «cold finger» drops to temperatures close to the freezing point of the oil. In addition, when the temperature of the model oil changes from 60^0C to 30^0C and the temperature of the «cold finger» changes from 25^0C to 15^0C, the amount of released paraffinic hydrocarbons increases by 1.3 times and the amounts of resin and asphaltenes decrease by 2 and 2.5 times, respectively.

3. The results of measuring the molecular weight distribution of n-alkanes in the separated sediments showed that when the oil temperature rises to 60^0C and the temperature of the «cold finger» rises to 25^0C, the total amount of C_{17}–C_{40} doubles and the amount of high-molecular paraffinic hydrocarbons C_{41}–C_{60} increases by 22 times. At these temperatures, low-molecular C_8–C_{16} alkanes are present in the sediment in small amounts. The study of the microstructure of the model oil and its sediments showed that the sediments obtained at an oil temperature of 60^0C and a «cold finger» of 25^0C have a coarsely dispersed structure. The decrease in oil temperature to 40^0C and 30^0C leads to the formation of finely dispersed structures.

4. When the «Difron-4201» depressant additive is added to the model oil, the share of paraffinic hydrocarbons with the number of carbon atoms C_{17}–C_{40} in the sediment decreases and the number of n-alkanes with lower molecular weight increases. The number of resins and asphaltenes in the group composition of the sediment decreases. Microanalysis of the structure of asphaltene–resin–paraffin sediments obtained after adding the additive showed that the part of dendritic modification of the crystal structure of paraffinic hydrocarbons in the sediments separated at $30/15^0$C increases.

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ДОСЛІДЖЕННЯ ВПЛИВУ УМОВ КРИСТАЛІЗАЦІЇ ТА ДОБАВКИ-ДЕПРЕСАНТУ «DIFRON-4201» НА СКЛАД І ВЛАСТИВОСТІ ПАРАФІНОВИХ ВІДКЛАДЕНЬ

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Вперше в лабораторії методом високотемпературної рідинно-газової хроматографії визначені фізико-хімічні характеристики модельного зразка масла, склад і відносні кількості нормальних алканів з кількістю атомів вуглецю від C_8 до C_{60}. При додаванні в модельну олію «Difron-4201» сім атомів вуглецю заміщуються в напрямку меншого молекулярно-масового розподілу парафінових вуглеводнів в осаді. Досліджено вплив присадки «Difron-4201» на груповий склад модельної нафти та нафтових відкладень, одержаних при різних температурах «холодного пальця». Встановлено, що з додаванням присадки та зі зниженням температури модельного масла та «холодної труби» кількість парафінових вуглеводнів у груповому складі осаду збільшується, а кількість смоли та асфальтенів зменшується. Мікроаналіз структури асфальтен-смоло-парафінових відкладень, одержаних після додавання добавки, показав, що модельні нафтові відкладення, відокремлені при 30/150^{0}C і які містять велику кількість високомолекулярних парафінових вуглеводнів, смоли та асфальтенових компонентів, мають найвищий рівень частки аморфних структур. Збільшення частки дендритної модифікації кристалічної структури характерне для парафінових вуглеводнів в осадах, одержаних з додаванням добавки «Difron-4201» у кількості 900 г/т.

Ключові слова: модельне масло, добавка-депресант, Difron-4201, холодний палець, нафтовий осад, н-алкани.

INVESTIGATION OF THE EFFECT OF CRYSTALLIZATION CONDITIONS AND «DIFRON-4201» DEPRESSANT ADDITIVE ON THE COMPOSITION AND PROPERTIES OF PARAFFIN DEPOSITS

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For the first time in the laboratory, the physical and chemical characteristics of the model oil sample, the composition, and relative amounts of normal alkanes with carbon atoms from C_8 to C_{60} were determined by high-temperature liquid-gas chromatography. When Difron-4201 is added to the model oil, seven carbon atoms are displaced in the direction of the lower molecular weight distribution of paraffin hydrocarbons in the sediment. The effect of the Difron-4201 additive on the group composition of model oil and oil sediments obtained at different temperatures of the «cold finger» was studied. It was found that with the addition of the additive and with a decrease in the temperature of model oil and «cold pipe», the number of paraffin hydrocarbons in the group composition of sediment increases and the amount of resin and asphaltenes decreases. Microanalysis of the structure of asphaltene–resin–paraffin sediments obtained after the addition of the additive showed that the model oil sediments, separated at 30/150^{0}C and containing large amounts of high-molecular paraffin hydrocarbons, resin, and asphaltene components, have the highest proportion of amorphous structures. An increase in the share of dendritic modification of the crystalline structure is characteristic for paraffin hydrocarbons in sediments obtained with the addition of 900 g/t «Difron-4201» additive.

Keywords: model oil; depressant additive; Difron-4201; cold finger; oil sediment; n-alkanes.

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