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THE APPLICATION OF DEPRESSOR ADDITIVES TO IMPROVE THE RHEOLOGICAL OIL PROPERTIES AND INHIBIT THE BOTTOM SEDIMENTS FORMATION IN STORAGE TANKS

Abstract. The possibility of using depressant additives to improve the rheological oil properties and inhibit the bottom sediments formation during storage in the *Kazakhstan's* oil refinery tanks is investigated. It is shown that the introduction of depressant additives makes it possible to reduce the temperature of oil fluidity loss by 3-6 °C. It was found that the introduction of depressant additives significantly improves the oil fluidity as comparison with the oil without heat treatment and the oil with heat treatment. Analysis of bottom sediments from the storage tanks for the content of the sum of asphalt-resinous compounds and mechanical impurities showed that the test sample belongs to type P1. Chromatographic paraffins determination in oil and bottom sediments showed a higher total content of hard melting paraffins from C18 in the bottom sediments of the storage tanks - 34.69% than in oil entering reservoir parks - 21.04%. A high-molecular alkanes predominate in the sediments up to C₄₀, and the total amount of paraffins in the sediments exceeds their content in the initial oil by 15 %.

Key words: rheological oil properties, asphalt-resin-paraffin deposits, tank, depressor additives.

Introduction. On the Kazakhstan territory highly paraffinic oils, containing along with the branched alkanes a significant paraffins number of a normal or slightly branched structure, are extracted for the most part [1, 2]. A feature of this oil type is the high chilling temperature, which causes the rheological properties (mobility, fluidity, etc.) deterioration of both the oil itself and the products of its processing [3, 4]. During the oil extraction, transportation and storage with a high content of paraffins, intensive formation of asphalt-resin-paraffin deposits occurs on the inner surface of oilfield and refinery equipment, which leads to a decrease in the efficiency of pumping units, a reduction in the capacity of pipelines, the useful capacity of oil storage tanks and reduction of maintenance periods of equipment operation [5-8]. ARPD are highly disperse suspensions of crystals of paraffin-naphthenic hydrocarbons, asphaltenes and mineral impurities in oils and resins [9, 10]. The ARPD composition and properties can vary in a wide range, depending on the oil properties and composition, the development conditions, the surface equipment characteristics, etc., which causes additional difficulties arising during its removal (inhibition) [11, 12].

At the present time, there are a number of methods and technologies for lowering the chilling temperature and improving the rheological characteristics of high-viscosity paraffin oil and inhibiting the ARPD formation: heat treatment and other physical impact methods, dilution with light oil fractions or various solvents, as well as the additives introduction regulating viscoelastic oil properties [13, 14]. The most effective way to improve the rheological characteristics are the chemical methods of treating oils with the application of depressor, inhibiting and detergent additives [15, 16, 19-21].

The introduction of additive, even in small amounts, to highly paraffin oils can significantly alter the rheological oil (chilling temperature, viscosity, shear stress) properties and as a consequence, prevent the paraffin deposition [17, 18].

The work purpose is to investigate the depressor additives efficiency to improve the rheological properties of oil entering the tank farm of an oil refinery and to inhibit the ARPD deposits formation during storage in tanks. To carry out these researches, oil sample of entering the refinery for the refinery tank

farm and a sample of bottom sediments from the tanks were selected. The investigated oil is the oil mixture from the South Turgai trough deposits and refers to paraffin hardening oil. Oil characteristics at the sampling time are presented in table 1.

Table 1 – Oil characteristics

The indicator name	Testing method	Testing result
Oil temperature, °C		17,1
Oil pressure, MPa		0,23
Oil density of under measurement and pressure conditions, kg / m ³	KR ST 2.153	820,3
Oil density at temperature 20 ⁰ C, kg / m ³	KR ST 2.153	818,0
Oil density at temperature 15 ⁰ C, kg / m ³	KR ST 2.153	822,5
Mass sulfur content, %	KR ST ASTM D 4294	0,09
Vapour pressure, kPa (mm Hg)	GOST 1756	29,4 (220,4)
Mass water content, %	GOST 2477	0,03
chloride salts concentration, mg / dm ³	GOST 21534	39,3
Mass chloride salts content, %	GOST 21534	0,0048
Mass mechanical impurities content, %	GOST 6370	0,0085
Total mass ballast content, %		0,0433
Organochlorine compounds content, mln ⁻¹ (ppm)	KR ST ASTM D 4929	1,4
Mass paraffin content, %		
no-flow point, °C	KR ST ASTM D 5853	3,0
Yield fractions % at the temperature up to 200 ⁰ C at a temperature up to 300 ⁰ C	GOST 2177	33,0 53,0
Mass content of hydrogen sulphide, mln ⁻¹ (ppm)		
Mass methyl content - and ethyl mercaptans, mln ⁻¹ (ppm)		
Kinematic viscosity, mm ² / s (cSt) at a temperature of 14.5 °C	KR ST ASTM D 445	10,7

Research methods. At the first research stage it was appropriate to analyze the oil sample and bottom sediment samples to obtain an idea of the percentage of paraffins, asphalt-resin compounds and mechanical impurities ratio.

Determination of the total content of resin-asphalt substances was carried out using the Marcuson adsorption method. This method is based on the ability of resin-asphalt substances, as compounds of unsaturated and containing groups of atoms with large chemical energy, to be retained on the adsorbent surface. As an adsorbent, silica gel, previously dried at a 250°C temperature was used.

Determine the asphaltene content allowed their insolubility in low-boiling limiting hydrocarbons. With sufficient dilution of the sample weighed with a solvent (in our case in a 40-fold volume) the asphaltene precipitate. As a solvent, gasoline was used that did not contain aromatic hydrocarbons and boiling within the 65 - 95 °C range.

The mechanical impurities amount was determined in accordance with GOST 6370-83. The method essence is consists in filtering the tested products with preliminary dissolution of slowly filtering products in toluene, filter washing on the solvent, followed by drying and weighing [22].

Chromatographic paraffins determination in oil and bottom sediments was carried out using the AutoSystem LX gas chromatograph, the Perkin-Elmer 3012 SIMDIS model according to ASTM D2887 with the programmable temperature of the column thermostat and a universal capillary column injector, pneumatics and an autosampler for liquid samples. The AutoSystem LX chromatograph is equipped with a flame ionization detector with a digital signal amplifier, a pneumatics for supplying hydrogen and air, automatic ignition and flame detector monitoring. Before the analysis, the conditioned samples were kept for at least half an hour. In the chromatograph, the same oil samples were introduced in an amount of 0.3 µl. Oil samples chromatographic analysis was carried out on a capillary column ELITE PS 2887. The carrier gas (He) flow rate through a quartz capillary and analytical column was 50 cm/min.

In the second study phase effect of various additives (DP2G, DMN 1005 sample 1, DMN 1005 sample 2, NHT-I, PAO 80072 and PAO 82004) to the dynamic viscosity of the oil was investigated. The oil temperature of fluidity loss (TFL) was also determined by the ASTM D5853 method.

To determine the dynamic viscosity, shear stress, shear stress limit, it was used an Anton Paar-rheometer viscometer (Austria) of the RheolabQC model with the Rheoplus software using the DGR-42 measuring system (12ml), a double-slotted cylinder and the CC-17 measuring cylindrical element (5 ml). Dynamic (apparent) viscosity and shear stress measurements were carried out in a linear temperature measurement mode (cooling rate 25 °C / h) at a constant shear rate (10s^{-1}), and a linear change in shear rate (from 0 to 100s^{-1}) at constant temperature. The flow temperature was used to determine the transition temperature of a Newtonian fluid to a non-Newtonian fluid, a limiting shear stress, and a dynamic (apparent) viscosity.

The oil temperature of fluidity loss (TFL) values without heat treatment, with heat treatment and when various additives were added to the oil were determined according to the ASTM D5853 method at the TFL measurement facility. As cooling baths, 2 thermostats were used: LAUDA RE-420 (with temperature 0 °C maintained - thermostat 1), LAUDA RA-8 (with maintaining the temperature -18 °C - thermostat 2).

Results and discussion. The samples analysis results of bottom sediments showed that the content of resin-asphalt substances in ARPD is in percentage ratio higher than the content of asphaltenes and the content of mechanical impurities is 0,18 % (Table 2).

Table 2 – RA, asphaltenes and mechanical impurities content (%) in the analyzed samples

Analyzed sample	Content RA, %	Asphaltenes content, %	Mechanical impurities content, %
ARPD sample	10,42	6,57	0,18

Chromatographic paraffins determination in oil and bottom sediments indicates a higher total content of hard melting paraffins from C_{18} in the bottom sediments of the tank 34,69 % (Figure 1) than in oil entering the storage tanks 21,04% (Figure 2). It should also be noted that high-molecular alkanes predominate in the sediments up to C_{40} , and the total amount of paraffins in the sediments exceeds their content in the initial oil by 15 %.

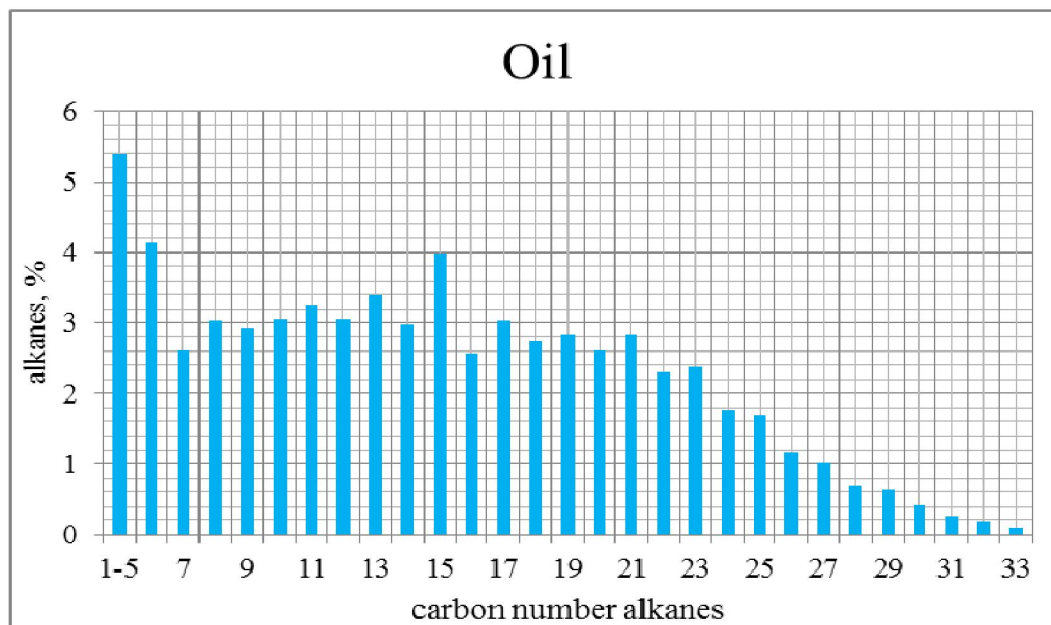


Figure 1 – n-alkanes distribution in oil

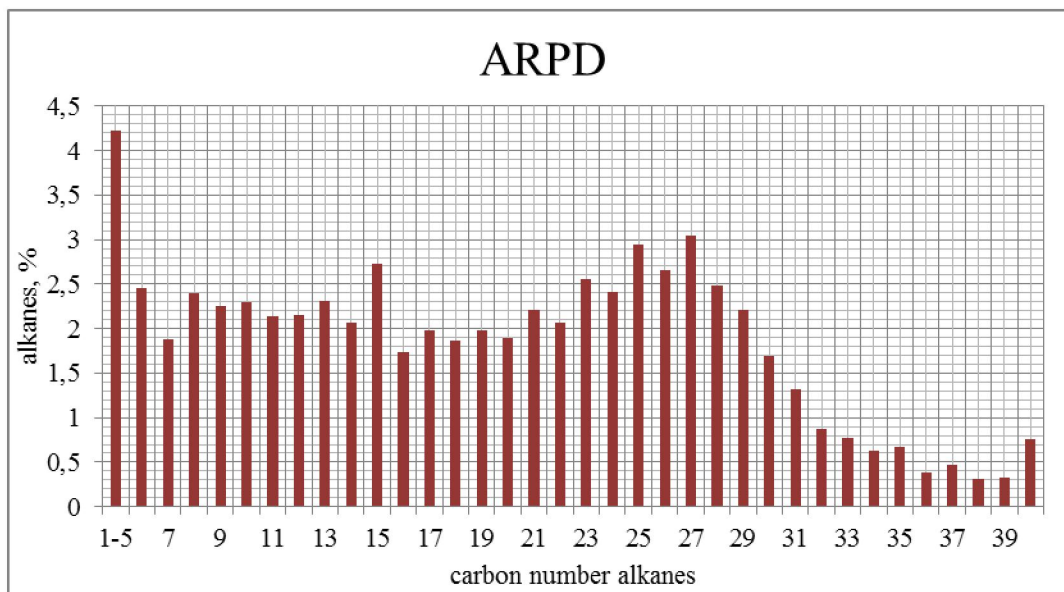


Figure 2 – n-alkanes distribution in the ARPД sample

Thus, it can be concluded that when storing paraffin oil in a tank farm, bottom sediments are formed with a predominant content of high melting paraffins with an increase in their quantity compared to the original oil. In this connection, solid oil sludge is formed in the process of precipitation of hard melting paraffins with asphaltenes and high temperatures are required to destroy them with the use of solvents and surfactants that allow the washing of solid paraffins and asphaltenes from slimes. The selection of solvents and surfactants, as a rule, is carried out according to the type of ARPД. Depending on the content of paraffin hydrocarbons, resins, asphaltenes and their ratio ($\beta = PH/RAS$), oil deposits are divided into the following types: paraffin $\beta > 1,1$; Mixed $\beta \approx 0,9-1,1$ and asphaltenic $\beta < 0,9$ (Table 3) [23].

Table 3 – ARPД classification

ARPD group	Subgroup ARPД	The paraffin ratio (P) content to the sum resins (R) and asphaltenes (A), $P/(R + A)$	Mechanical impurities content, %
Asphaltenic (A)	A ₁	<1	0-0,2
	A ₂	<1	0,2-0,5
	A ₃	<1	>0,5
Mixed (M)	M ₁	≈1	0-0,2
	M ₂	≈1	0,2-0,5
	M ₃	≈1	>0,5
Paraffin (P)	P ₁	>1	0-0,2
	P ₂	>1	0,2-0,5
	P ₃	>1	>0,5

The ratio paraffins content (P) to the resins sum (R) and asphaltenes (A) for the sample of bottom sediments is 3.32, the content of mechanical impurities is 0.18 %, which, in accordance with table 3 allows them to be classified as paraffinic P₁.

The study of the various additives effect (DP2G, DMN 1005 sample 1, DMN 1005 sample 2, NHT-I, PAO 80072 and PAO 82004) on the dynamic viscosity of crude oil showed that the introduction of depressant additives significantly improves the oil fluidity compared to oil without heat treatment and heat treatment. In this case, additives DP2G and DMN 1005 sample 1 are much more effective than other additives (figure 3).

Table 4 shows the results of determining the temperature of fluidity loss. The flow temperature values for oil samples without heat treatment, with heat treatment and the optimum dosage of additives give reason to believe that the introduction of depressant additives allows to reduce the temperature of pour point in comparison with oil without heat treatment by 9 °C.

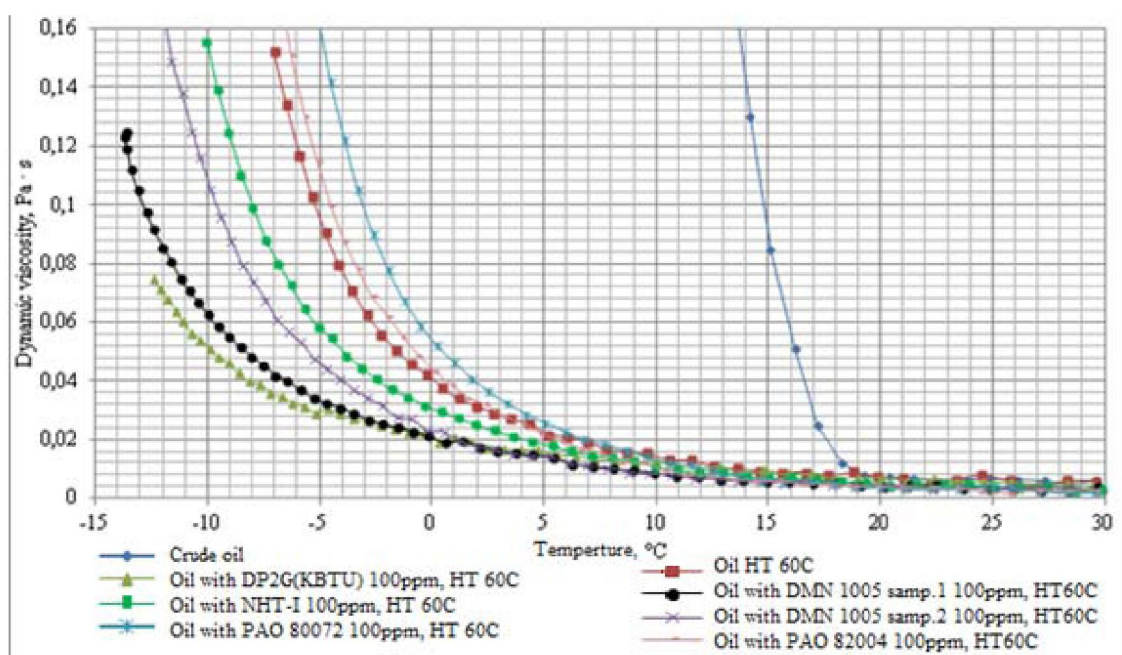


Figure 3 – Rheological oil curves: without heat treatment, with heat treatment and with additives

Table 4 – The temperature of fluidity loss (TFL): without heat treatment, with heat treatment, with an optimum additives dosage

Additive name	Concentration, ppm	TFL, °C
Crude without additive	–	+12
HT 60 °C	–	+3
DP2GKBTU	100	+3
DMN 1005 sample 1	100	+3
NHT-I	100	+6
DMN 1005 sample 2	100	+3
PAO 80072	100	+6
PAO 82004	100	+6

Conclusions. Investigations have shown that when storing paraffin oil in a tank farm, bottom sediments with a predominant content of high melting paraffins are formed with an increase in their amount compared to the initial oil, which leads to the formation of solid oil sludge. Based on the ratio of the content of paraffins (P) to the resins sum (R) and asphaltenes (A), the investigated sediments are related to the paraffin type of deposits, subgroup II. The introduction of various additives into oil improves the fluidity of oil compared to oil without heat treatment and with heat treatment. The most effective additives for the test samples are DP2G and DMN1005 sample 1. The results of the obtained values of flow temperatures for oil samples without heat treatment, with heat treatment and optimal additives dosage have shown that the depressant additives introduction allows to reduce the temperature of oil flow loss in comparison with oil without heat treatment at 9 °C.

REFERENCES

- [1] Vasil'janova L.S. Nekotorye osobennosti neftej Kazahstana // *Nef't' i gaz*. 2006. N 2. P. 83-90.
- [2] Bakirova S.F., Bujanova N.S., Muhanova M.B. Spektral'naja harakteristika neftej i prirodnyh bitumov jugo-vostoka Prikaspijskoj vpadiny // *Nef't' i gaz*. 2001. N 1. P. 65-68.
- [3] Mahmotov E.S., Sigitov V.B., Ismurzin O.B., Kondrat'ev V.V., Boranbaeva L.E. Fiziko- himicheskie i reologicheskie parametry neftej Respubliki Kazahstan. Spravochnik na 3-h jazykah (kazahskij, russkij i anglijskij). Ch.1. Almaty: Zhibekzholy, 2008. 629 p.

- [4] Ilyin S.O., Arinina M.P., Polyakova M.Yu., Kulichikhin V.G., Malkin A.Ya. Rheological comparison of light and heavy crude oils // *Fuel*. 2016. Vol. 186. P. 157-167.
- [5] Ivanova L.V., Burov E.A. Asfal'tosmoloparafिनovыe otlozheniya v processah dobychi, transporta i hraneniya // *Jelektronnyj nauchnyj zhurnal «Neftegazovoe delo»*. 2011. N 1. URL: <http://www.ogbus.ru>
- [6] Hizhnjak G.P., Usenkov A.V., Ust'kachincev E.N. Oslozhnjajushhie faktory pri razrabotke Nozhovskoj gruppy mestorozhdenij OOO «LUKOIL-PERM» // *Vestnik Permskogo nacional'nogo issledovatel'skogo politehnicheskogo universiteta. Geologija. Neftegazovoe i gornoe delo*. 2014. N 13. P. 59-68. DOI: 10.15593/2224-9923/2014.13.6
- [7] Markin A.N. Neftepromyslovaja himija / A.N. Markin, R.Je. Nizamov, S.V. Suhoverhov // *Prakticheskoe rukovodstvo*. Vladivostok: Dal'nauka, 2011. 288 p. 6.
- [8] Hassanean M.H., Awad M.E., Marwan H., Bhran A.A., Kaoud M. Studying the rheological properties and the influence of drag reduction on a waxy crude oil in pipeline flow // *Egyptian Journal of Petroleum*. 2016. Vol. 25. P. 39-44.
- [9] Osobennosti sostava asfal'tosmoloparafिनovыh otlozhenij v skvazhinah mestorozhdenij Zapadnoj Sibiri / A.N. Sadykov, R.Sh. Nigmatullina, D.F. Fazlyev, F.R. Farrahova, R.G. Shakirzjanov // *Nauchnye trudy "Problemy himii nefti"*. Novosibirsk: Nauka, 1992. P. 302-305.
- [10] Sharifullin, A.V. Composition and structure of asphalt-resin-paraffin deposit of Tatarstan / A.V. Sharifullin, L.R. Baibecova, R.F. Khamidullin // *Tekhnologiinefti i gaza*. 2006. N 4. P. 34-41.
- [11] Boukadi A., Philp R.P., Thanh N.X. Characterization of paraffinic deposits in crude oil storage tanks using high temperature gas chromatography // *Applied Geochemistry*. October 2005. Vol. 20, issue 10. P. 1974-1983.
- [12] Beshagina E.V., Judina N.V., Prozorova I.V., Savinyh Ju.V. Sostav i svojstva nef'tjanyh osadkov // *Himija v interesah ustojchivogo razvitiya*. 2007. Vol. 15, N 6. P. 653-658.
- [13] Nasyrov A.M. Sposoby bor'by s otlozhenijami parafina. M.: VNIIOJeNG, 1991. 44 p.
- [14] Volkova G.I., Loskutova Ju.V., Prozorova I.V., Berezina E.M. Podgotovka i transport problemnyh neftej (nauchno-prakticheskie aspekty). Nacional'nyj issledovatel'skij Tomskij gosudarstvennyj universitet, 2015. 138 p.
- [15] Sara M. Hashmi, Abbas Firoozabadi. Self-assembly of resins and asphaltenes facilitates asphaltene dissolution by an organic acid // *Journal of Colloid and Interface Science*. 15 March 2013. Vol. 394. P. 115-123.
- [16] 16Irina V. Litvinets, Irina V. Prozorova, Natalya V. Yudina, Oleg A. Kazantsev, Alexey P. Sivokhin. Effect of ammonium-containing polyalkyl acrylate on the rheological properties of crude oils with different ratio of resins and waxes// *Journal of Petroleum Science and Engineering – V.146 (2016)-p. 96–102*
- [17] Auezov A.B., Zhumadilova G.T., Karabaeva B.A., Gabsattarova G.A., Bizhanov Zh.A., Mahmotov E.S. Prirodnye depressanty iz chisla kazahstanskih neftej i ih aktivnaja sostavljajushhaja. *Nef't' i gaz*. 2004. N 4. P. 84-90.
- [18] Jafari Behbahani Taraneh, Golpasha Rahmatollah, Akbaria Hassan, Dahaghin Alireza. Effect of wax inhibitors on pour point and rheological properties of Iranian waxy crude oil // *FUEL PROCESSING TECHNOLOGY*. 2008. Vol. 89. P. 973-977.
- [19] Estrella Rogel, Cesar Ovalles, Janie Vien, Michael Moir Asphaltene characterization of paraffinic crude oils // *Fuel*. 15 August 2016. Vol. 178. P. 71-76.
- [20] Cesar Ovalles, Estrella Rogel, Harris Morazan, Michael E. Moir Synthesis, characterization, and mechanism of asphaltene inhibition of phosphoropoxylated asphaltenes // *Fuel*. 15 September 2016. Vol. 180. P. 20-26.
- [21] Uojld Dzh. Himicheskaja obrabotka dlja bor'by s otlozhenijami parafinov (per. s ang. Klepinin V.) / Dzh. Uojld // *Neftegazovye tehnologii*. 2009. N 9. P. 25-29. 35
- [22] GOST 6370-83 Nef't', nefteprodukty i prisadki. Metod opredelenija mehanicheskikh primesej.
- [23] Ibragimov G.Z., Sorokin V.A., Hisamutdinov N.I. Himicheskie reagenty dlja dobychi nef'ti: Spravochnik rabochego. M.: Nedra, 1986. 240 p.

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ПРИМЕНЕНИЕ ДЕПРЕССОРНЫХ ПРИСАДОК ДЛЯ УЛУЧШЕНИЯ РЕОЛОГИЧЕСКИХ СВОЙСТВ И ИНГИБИРОВАНИЯ ДОННЫХ ОТЛОЖЕНИЙ В РЕЗЕРВУАРАХ

Аннотация. Исследована возможность применения депрессорных присадок для улучшения реологических свойств нефти и ингибирования процесса образования донных отложений в процессе хранения в резервуарах казахстанских НПЗ. Показано, что введение депрессорных присадок позволяет снизить температуру потери текучести нефти на 3–6°C. Установлено, что ввод депрессорных присадок значительно улучшает текучесть нефти по сравнению с нефтью без термообработки и с термообработкой. Анализ донных отложений с резервуаров на содержание суммы асфальтосмолистых соединений и механических примесей показал, что исследуемый образец относится к типу П₁. Хроматографическое определение парафинов в нефти и донных отложениях показало более высокое суммарное содержание твердоплавких парафинов от С₁₈ в донных отложениях резервуара – 34,69%, чем в нефти, поступающей в резервуарные парки – 21,04%. В отложениях преобладают высокомолекулярные алканы вплоть до С₄₀, а общее количество парафинов в отложениях превышает содержание их в исходной нефти на 15%.

Ключевые слова: реологические свойства нефти, асфальтосмолопарафиновые отложения резервуар, депрессорные присадки.

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**РЕЗЕРВУАРЛАРДАҒЫ МҰНАЙДЫҢ РЕОЛОГИЯЛЫҚ ҚАСИЕТТЕРІН ЖАҚСARTУҒА
ЖӘНЕ РЕЗЕРВУАР ТҮБІНДЕГІ ШӨГІНДІЛЕРДІ ИНГИБИРЛЕУГЕ АРНАЛҒАН
ДЕПРЕССОРЛЫҚ ПРИСАДКАЛАРДЫҢ ҚОЛДАНЫСЫ**

Аннотация. Қазақстанның МӨЗ резервуарларындағы мұнайды сақтау барысында, оның реологиялық қасиеттерін жақсарту және резервуар түбінде шөгінділердің пайда болу үдерісін ингибирлеу үшін депрессорлық присадкалар пайдалану мүмкіндіктері зерттелді. Мұнда, депрессорлық присадкаларды енгізу кезінде мұнайдың аққыштық қасиетін жоғалту температурасын 3–6°C төмендетуге мүмкіндік берді. Депрессорлық присадкаларды енгізу, мұнайды термоөңдеумен және термоөңдеусізбен де салыстырғанда, оның аққыштығын едәуір жақсартатыны анықталды. Резервуар түбіндегі шөгінділердің асфальтты-шайырлы қосылыстарға және механикалық қоспаларға жүргізілген құрамдық жиынтығының талдаулары, зерттеліп отырған үлгінің П1 түріне жататынын көрсетті. Мұнайдағы және шөгінділердегі парафиндерді хроматографиялық жолмен анықтау нәтижелері бойынша С18 жоғары қиын еритін парафиндердің жиындық құрамы резервуар паркіне түсетін мұнайда – 21,04% құраса, ал бұнымен салыстырғанда резервуар түбіндегі шөгінділерде өте жоғары – 34,69% көрсетті. Шөгінділерде жоғары молекулалы алкандар басым С40 дейін, ал шөгінділердегі парафиндердің жалпы мөлшері бастапқы мұнай құрамындағыдан 15% артық.

Түйін сөздер: мұнайдың реологиялық қасиеттері, асфальтты-шайырпарафиндішөгінділер, резервуар, депрессорлық присадкалар.