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SELECTION AND STUDY OF DEPRESSANT ADDITIVES TO IMPROVE THE LOW-TEMPERATURE PROPERTIES OF HIGH WAXY CRUDE OILS FROM THE WESTERN REGION OF UKRAINE

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The effect of pour point depressants on crude oil properties is critical for ensuring smooth operations and efficient transportation. This paper presents experimentally determined characteristics of two high waxy crude oils from the Western region of Ukraine: Dolyna and Boryslav. The study demonstrates that selecting optimal additives can significantly enhance low-temperature properties, reducing the pour point and improving flowability. The selection process for depressant additives is justified, and their comparative characteristics are discussed. Considering efficiency, cost, and availability on the Ukrainian market, the depressant additives of Dodiflow brand manufactured by Clariant company and the depressant additive Rena 2210 of domestic production (Halychyna company) were chosen for the study. Among the Dodiflow variants, Dodiflow 5236 and Dodiflow 5773 exhibited the highest depressant effects for Dolyna and Boryslav high waxy oils, reducing the pour point by 15–21^{0}C at consumptions of up to 1000 ppm. The highest depressant effect of Rena 2210 additive (the pour point of oils with the additive decreased by 8–11^{0}C) was achieved only at its consumption of 1000 ppm. Further studies will investigate the effect of the most effective depressant additives on the rheological properties of oils from the Western region of Ukraine.

Keywords: depressant additive, high waxy oil, pour point, flowability, low-temperature properties.

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Introduction

The current state of the raw material base of Ukraine's oil industry is characterized by a significant deterioration in the structure of oil reserves. According to the Extractive Industry Data Portal of Ukraine [1], at the end of 2020, crude oil reserves amounted to almost 85 million tons. Half of this amount (51.18%) was in the Eastern region (Dnipro, Poltava, Kharkiv, Chernihiv, Sumy, Donetsk, and Luhansk regions); 35.77% were concentrated in the Western region (Lviv, Ivano-Frankivsk, Zakarpattia, Volyn, and Chernivtsi regions); and 13.05% were in the Southern region (Zaporizhzhia, Odesa regions, the Azov and Black Sea shelves).

Due to russia's occupation of a part of Ukraine's territory, hostilities, and the constant threat of missile attacks, the development of some fields has been virtually suspended. Therefore, an important part of Ukraine's energy strategy is to intensify or even restore production at brownfields (existing facilities). Given the current situation, studies of oils from the Western region of Ukraine are of particular relevance.

Most of oils from the Western region are high waxy and high-viscosity, so the main problem is their transportation. Facilitating the transportation of high-viscosity oils, reducing viscosity, and increasing the capacity of oil pipelines are important issues that are constantly in the spotlight [2,3]. Since the costs of maintenance, repair, and troubleshooting of transportation lines are very high, solving problems related to ensuring flow is becoming critical in the oil industry not only in Ukraine but also around the world. There are very few studies on the physicochemical characteristics of oils from the Western region and their flowability [4,5].

The peculiar physical and chemical properties of high waxy oils require the use of special pumping technologies or special additives. The most cost-effective way to improve low-temperature properties of oils is to use depressant additives, so-called pour point depressants (PPD), which prevent the formation of a spatial crystal lattice of paraffin in oil and, as a result, reduce the pour point and improve oil flowability.

To date, hundreds of compounds have been described that have a greater or lesser depressant effect. It is important to keep in mind that different types of depressants can have different effects depending on the composition of a particular oil and its transportation conditions. Therefore, the selection of optimal depressants for each specific case is a complex task that requires research and experimentation [6]. For high waxy oils from the Western region, no studies have been conducted on the selection of depressants, comparison of PPD of different types, as well as their effect on low-temperature properties.

This study aimed to substantiate the selection of PPD for high waxy oils from the Western region of Ukraine and to investigate their efficiency.

Experimental

The research objects were samples of commercial oil (hereinafter referred to as «Dolyna» oil) taken from Dolynanaftogaz (Ukraine) and commercial oil (hereinafter referred to as «Boryslav» oil) taken from Boryslavnaftogaz (Ukraine).

PPDs under study were a series of Dodiflow additives (Clariant company, Switzerland) and additive Rena 2210 (Halychyna company, Ukraine).

The analysis of the physical and chemical properties of the research objects was carried out according to standardized international methods (ASTM D1298-12b, ASTM D2502-04, ASTM D445, ASTM D97:2020, D 1266-18, ASTM D2892, ASTM D5853, and UOP46).

The low-temperature properties of the original oils and samples with PPD were determined using the UTZ-60 unit (Fig. 1). The unit consists of two parts: a hot bath and a cold bath located on a common base. The design allows the cold bath to be tilted by an angle of 45^0 to determine the aggregate state of the sample at any time.

A 50 ml sample of oil was heated to 55^0C to melt the paraffin hydrocarbons. Then PPD (dissolved in the solvent) was added in the amount converted to concentrate. The sample was cooled to room temperature, placed in the coupling of the instrument, and cooled to the specified temperature. The cold bath was tilted to an angle of 45^0 and incubated for 1 min. If the meniscus moved, it meant that the oil had not solidified. The procedure was repeated, cooling to a lower temperature.

Fig. 1. Appearance of UTZ-60 unit

For those oil samples with PPD that showed the best results, the pour point was re-determined after 20 days.

Results and discussion

Table 1 represents the main characteristics of investigated Dolyna and Boryslav oils.

The obtained experimental data (Table 1) confirm that the investigated oils from the Dolyna and Boryslav fields have high values of pour point (17–19^0C). The content of paraffinic hydrocarbons is 9.1–9.5 wt.% with a paraffin melting point of 52–53^0C. The oils are also characterized by a fairly high tar content and low sulfur content.

Table 1

Physicochemical characteristics of crude oils

Index	Value	
	Dolyna oil	Boryslav oil
density at 20^0C, kg/m^3	848	829
molecular weight	207	202
kinematic viscosity at 50^0C, cSt	4.1	2.9
pour point, ^{0}C	19	17
paraffin content, wt.%	9.5	9.1
melting point of paraffin, ^{0}C	53	52
sulfur content, wt.%	0.19	0.37
resins content, wt.%	19	10
percentage of fractions distilled to 200^0C	28.5	33.1
percentage of fractions distilled to 350^0C	54.0	61.2

These characteristics of oils create numerous problems during their transportation [7]. Several methods are used to reduce energy costs and the negative impact of paraffin deposits, such as non-isothermal pumping with heating, the use of depressants, and mixing oil with diluents. Each of them has its advantages and disadvantages. The effectiveness of depressants is beyond doubt, as evidenced by numerous publications and widespread use, although their use requires additional costs for their purchase.

Since, as mentioned above, the selection of a depressant for each specific oil is made on an experimental basis, even the best results of using a particular depressant for oils from other fields cannot be used for the high waxy oils from the Western region. Therefore, a thorough analysis of existing additives was carried out to make a reasonable selection of the most optimal depressants for improving the low-temperature properties of Dolyna and Boryslav oils.

In world practice, substances of various chemical natures are used as depressant additives [8,9]. The main types of PPD are as follows:

– ethylene copolymers with polar monomers (ethylene-vinyl acetate copolymers and their compositions, ternary copolymers based on ethylene and vinyl acetate, and ethylene copolymers with other polar monomers);

– polyolefin products (ethylene-propylene, ethylene-propylene-diene copolymers and their degradation products, alpha-olefin copolymers, and modified polyolefins);

– polyacrylate additives (polyalkyl(meth)acrylates, and copolymers of alkyl(meth)acrylates);

– bio-based depressants.

It is difficult to compare the effectiveness of different types of PPD because the published data are scattered and obtained on oils or oil products of different composition [10–14]. A significant part of publications does not pursue the goal of objective comparison of in-house produced additives and depressant additives developed by other authors or companies.

In Table 2, considering the synthesis parameters, we tried to compare the data of some types of depressant additives in terms of their effectiveness.

The consumption of copolymer depressant additives is the lowest among others. Copolymers and polyacrylates are the most effective in terms of depressing the pour point. From the standpoint of technological parameters, polyacrylates have undoubted advantages. The effect of using bio-based depressants is only manifested at high concentrations, and the efficiency is significantly lower than that of chemical PPD.

Given their widespread use, a large number of companies produce pour point depressants. The world leaders are Clariant, Afton Chemical, Evonik Industries, Infineum International Limited, Ecolab, Innospec, etc. The range of domestic PPD is extremely limited, with only a few companies producing them in Ukraine: AP Complex (Kyiv), Halychyna Research and Production Company (Drohobych).

Due to the differences in the physical and chemical properties of oils from different fields, as well as the conditions of their transportation, it is difficult to compare depressant additives produced by different manufacturers. We conducted a preliminary assessment of the market for depressants produced by various companies. First of all, we evaluated the data on the suitability of PPD for high waxy oils and their efficiency. We also took into account the price category and availability of additives in the Ukrainian market. Based on the analysis data, depressant additives of the Dodiflow brand manufactured by Clariant (Switzerland) and a domestically produced depressant Rena 2210 (Halychyna company) were selected for research. Among a wide range of Clariant depressants, the following concentrates in aromatic solvents were used for research:

– Dodiflow 5236 (branched polymer),

– Dodiflow 5773 (ethylene and vinyl acetate copolymer),

– Dodiflow 8150 (polymer mixture),

– Dodiflow 8151 (polymer mixture),

– Dodiflow 4138X (polyacrylate).

Table 2

Comparative data on the effectiveness of different types of depressant additives

Depressant	Molecular weight	Consumption, ppm	Depression effect, ^{0}C
ethylene copolymers with polar monomers	2000–3000	100–1000	25 and more
polyacrylates	26000–35000	500–1000	19–24
polyolefin products	2000–9000	300–1000	16–24
bio-based depressants	–	800–5000	2–15

The domestically produced Rena 2210 is a copolymer of high unsaturated compounds with vinyl acetate in a hydrocarbon solvent.

The characteristics of the PPD selected for the study are given in Table 3.

Since the commercial forms of depressant additives are highly viscous, to determine the pour point of oil and facilitate their introduction into the oil the concentrates must be pre-diluted. Studies on the solubility of PPD in several solvents (Table 3) showed that the best solvent is a mixture of xylenes. We prepared 10–30% solutions of PPD in the solvent. Taking into account the results of the evaluation experiments, the pour point of high waxy oils was determined using 30% solutions of depressants, the main characteristics of which are given in Table 4.

The effect of PPD on the low-temperature properties of oils was studied in the range of additive consumption of 100 to 1000 ppm. The range was selected based on the manufacturer's recommendations, taking into account that the depressant consumption of less than 100 ppm is impractical, since at such values, it practically does not reduce the pour point, and consumption above 1000 ppm is economically unprofitable. Moreover, according to the literature data [8,15], in some cases, additive consumption above 500 ppm no longer affects the depression of the pour point, and sometimes it can have a negative effect. This can be explained by the additive influence on the shape of the paraffin macromolecule. In dilute solutions, the additive molecules can be stretched into linear structures that are most optimal in terms of the additive's mechanism of action. In concentrated solutions, this possibility decreases, and the molecules are unbranched globules that are poorly sorbed on the surface of paraffin crystals.

Dependences of the pour point of Dolyna and Boryslav crude oil on PPD consumption are shown in Figs. 2 and 3, respectively.

According to the requirements of the technological regulations, for the existing Dolyna-Drohobych and Boryslav-Drohobych pipelines, which operate cyclically, the pour point of oil at the end of the transportation route must be at least 10^0C. Otherwise, oil solidifies in the summer within 8 hours without moving, and in the winter, depending on the heating temperature and ambient temperature, almost immediately. This is the biggest problem for the transportation of Dolyna and Boryslav oils because the «freezing» of oil pipelines may occur.

Table 3

Characteristics of depressant concentrates

Index	Value					
	Dodiflow 5236	Dodiflow 5773	Dodiflow 8150	Dodiflow 8151	Dodiflow 4138X	Rena 2210
color	yellow-brown	colorless	brown	yellow	pale yellow	brown
pour point, ^{0}C	24	20	21	21	18	18
flash point, ^{0}C	35	62	57	33	29	32
density at 40^{0}C, kg/m^3	880	880	880	876	890	870
water solubility	insoluble					
solubility in solvent (xylenes mixture)	soluble					
solubility in hexane solvent (P1-63/75 brand)	partially soluble					
solubility in white spirit (C4 150/200 brand)	partially soluble					
kinematic viscosity at 40^{0}C, cSt	450	220	182	251	120	95
boiling point, ^{0}C	134	187	200	210	67	135

Table 4

Characteristics of 30% PPD solutions in the solvent

Index	Value					
	Dodiflow 5236	Dodiflow 5773	Dodiflow 8150	Dodiflow 8151	Dodiflow 4138X	Rena 2210
pour point, ^{0}C	8	7	6	10	9	8
flash point, ^{0}C	30	29	31	26	26	25
density at 20^{0}C, kg/m^3	878	874	872	869	882	868
kinematic viscosity at 20^{0}C, cSt	8.0	9.7	7.9	10.6	6.9	9.5
boiling point, ^{0}C	132	134	133	131	129	129

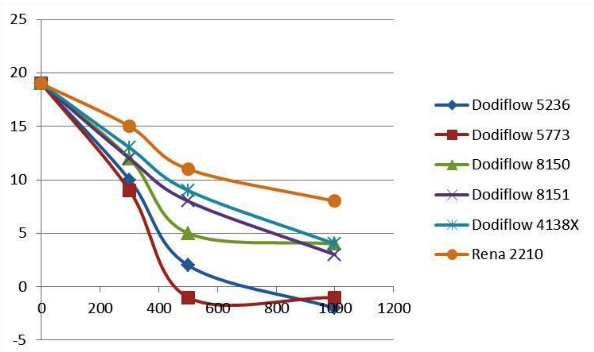

Fig. 2. Effect of different depressants on Dolyna oil pour point

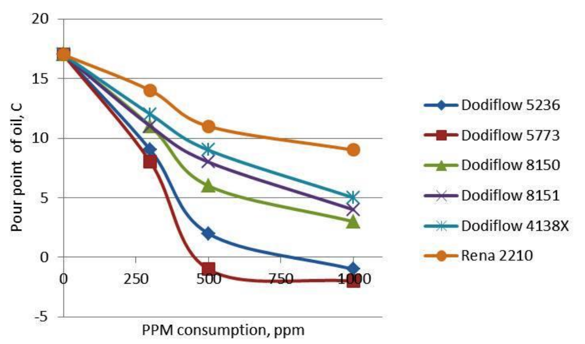

Fig. 3. Effect of different depressants on Borislav oil pour point

Therefore, the highest pour point of the studied oils with additives can be $+10^0$C. It was found that the addition of Dodiflow depressant additives in the amount of 500–1000 ppm reduces the pour point of both oils to +8...–2^0C (Figs. 2 and 3). Dodiflow 5236 and Dodiflow 5773 additives reduce the pour point to the required level even at a consumption of 300 ppm. After storage for 20 days the pour point of oil samples with 1000 ppm of depressants Dodiflow 5236 and Dodiflow 5773 decreased slightly (by 2–3^0C) even without repeated preheating.

The domestically produced depressant additive Rena 2210 reduces the pour point of Dolyna oil to $+8^0$C, and the pour point of Boryslav oil to $+9^0$C at additive consumption of 1000 ppm. This is the lowest depressant effect among all investigated PPD.

Thus, based on the experiments, it was determined that Dodiflow 5236 and Dodiflow 5773 additives have the highest depressant efficiency for Dolyna and Boryslav high waxy oils. In our opinion, the technology of their effect is that they change the shape, structure, and particle size of the dispersed phase of high waxy oil, thereby making the paraffin structure less stable and does not impede oil flow (Fig. 4).

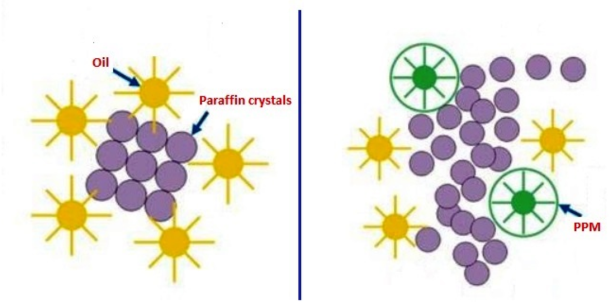

Fig. 4. Schematic representation of the PPD effect on high waxy oil (reprinted from ref. [16] with modification)

The additives modify the surface of paraffin crystals, as a result of which they stop sticking together, which is the main reason for oil solidification. The molecular structure and macromolecule size of the additives correspond to the geometry of the surface of the formed paraffin crystal.

Conclusions

The article deals with the physical and chemical characteristics of high waxy crude oils from the Dolynske and Boryslavske oil fields. The selection of depressant additives for these crude oils was substantiated and the characteristics of Dodiflow and Rena depressants were determined. It was found that the addition of Dodiflow depressant additives in the amount of 300–500 ppm reduces the pour point of both oils by 6–15^0C. The highest efficiency was shown by Dodiflow 5236 and Dodiflow 5773. Increasing the additive consumption to 1000 ppm reduces the pour point by 15–21^0C. The domestic depressant Rena 2210 proved to be effective only at consumption of 1000 ppm, reducing the pour point by 8–11^0C.

Since depressant additives affect not only the low-temperature but also the rheological properties of oil, this aspect is also important to consider when selecting the optimal depressant. Therefore, the study of the impact of depressants on the rheological properties of oil will continue to gain a more complete understanding of this process. Taking into account the physicochemical and safety characteristics of the depressant additives, the results obtained in terms of depressant efficiency, as well as the price, the research will continue using Dodiflow 5236 and Dodiflow 5773 depressants. Further experiments will provide additional data on the effectiveness of these PPDs. This approach will help improve the quality and safety of oil transportation through pipelines.

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ВИБІР І ДОСЛІДЖЕННЯ ДЕПРЕСОРНИХ ДОДАТКІВ ДЛЯ ПОКРАЩЕННЯ НИЗЬКОТЕМПЕРАТУРНИХ ВЛАСТИВОСТЕЙ ВИСОКОПАРАФІНИСТИХ НАФТ ЗАХІДНОГО РЕГІОНУ УКРАЇНИ

О.М. Шищак, П.І. Топільницький, В.Й. Скорохода

Вплив депресорів на властивості нафти є критичним для забезпечення її нормальної експлуатації і транспортування. У роботі наведені експериментально визначені характеристики двох високопарафінистих нафт західного регіону України – Долинської і Бориславської. Результати дослідження показали, що вибір оптимальних додатків може значно покращити низькотемпературні властивості нафт, знижуючи температуру застигання і полегшуючи їх текучість. Обгрунтовано вибір депресорних додатків для покращення низькотемпературних властивостей, наведено їх порівняльну характеристику. З врахуванням ефективності, ціни, і доступності на українському ринку, для проведення досліджень відібрано депресорні додатки марки Dodiflow виробництва компанії Clariant і депресор Рена 2210 вітчизняного виробництва. При дослідженні депресорної ефективності різних типів встановлено, що найвищий депресивний ефект для Долинської і Бориславської високопарафінистих нафт виявляють додатки Dodiflow 5236 і Dodiflow 5773. Їх застосування у кількості до 1000 ppm зменшує температуру застигання досліджуваних нафт на 15–21^{0}C. Найвищий депресивний ефект додатка Рена 2210 (температура застигання нафт з додатком зменшилась на 8–11^{0}C) виявився лише за його витрати 1000 ppm. В подальшому будуть проведені дослідження щодо впливу найефективніших депресорних додатків на реологічні властивості нафт західного регіону.

Ключові слова: депресорний додаток, високопарафіниста нафта, температура застигання, текучість, низькотемпературні властивості.

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Keywords: depressant additive; high waxy oil; pour point; flowability; low-temperature properties.

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