

## Investigation of the effect of the combined methods on the rheological properties of high-paraffin oils

### Badanie efektu zastosowania metod łączonych na właściwości reologiczne rop wysokoparafinowych

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**ABSTRACT:** The impact of a magnetic field, the Difron-4201 depressor additive, a new composition with the conventional name N-1, and the synergistic effect of N-1 combined with a magnetic field on paraffin deposition and freezing temperature in high paraffin crude oil was studied for the first time. Laboratory experiments were conducted using the “cold finger” method at surface temperatures of 5, 10, 15, 20, and 25°C to assess paraffin deposition. The combined method (N-1 + magnetic field) demonstrated the most significant reduction in paraffin deposition across varying temperatures. The physical, chemical, and physicochemical effects on the freezing temperatures of high paraffin oil were evaluated following the RD standard method. Optimal usage rates were determined to be 600 g/t for the Difron-4201 depressor additive and 500 g/t for the N-1 composition. Similar to paraffin precipitation, the combined influence of the magnetic field and N-1 composition showed the most effective reduction in freezing temperature. It was also determined that the magnetic field, the Difron-4201 depressor additive, the new composition N-1, and the combined N-1 + magnetic field method affect the effective viscosity of high paraffin crude oil, with the combined method producing the most notable changes. Additionally, the bactericidal properties of the new composition N-1 were evaluated by studying its effect on sulfate-reducing bacteria over fifteen days under laboratory conditions using Postgate-B nutrient medium. N-1 exhibited the highest bactericidal effect at a concentration of 500 g/t, achieving a bactericidal effectiveness of 97%.

**Key words:** magnetic field, composition, cold finger method, high paraffinic oil, effective viscosity, freezing temperature, bactericidal effect, bacteria.

**STRESZCZENIE:** Po raz pierwszy zbadano wpływ pola magnetycznego, dodatku depresującego Difron-4201, nowej kompozycji o konwencjonalnej nazwie N-1 oraz synergicznego efektu N-1 + pola magnetycznego (metoda łączona) na osadzanie parafiny i temperaturę krzepnięcia w ropie naftowej o wysokiej zawartości parafiny. Eksperymenty laboratoryjne przeprowadzono przy użyciu metody „cold finger” przy temperaturze powierzchni palca wynoszącej 5, 10, 15, 20 i 25°C w celu oszacowania stopnia osadzania się parafiny. Wpływ fizyczny, chemiczny i fizykochemiczny na temperaturę krzepnięcia ropy o wysokiej zawartości parafiny oceniono zgodnie ze standardową metodą RD. Optymalny udział dodatków określono na 600 g/t dla dodatku depresującego Difron-4201 i 500 g/t dla kompozycji N-1. Podobnie jak w przypadku wytrącania parafiny, najbardziej skuteczną redukcję temperatury krzepnięcia wykazał połączony wpływ pola magnetycznego i kompozycji N-1. Ustalono również, że pole magnetyczne, dodatek depresujący Difron-4201, nowa kompozycja N-1 i połączona metoda N-1 + pole magnetyczne mają wpływ na efektywną lepkość ropy naftowej o wysokiej zawartości parafiny, przy czym połączona metoda wywołuje najbardziej zauważalne zmiany. Ponadto dokonano oceny właściwości bakteriobójczych nowej kompozycji N-1, badając jej wpływ na bakterie redukujące siarczany przez okres piętnastu dni w warunkach laboratoryjnych przy użyciu pożywki Postgate-B. N-1 wykazał najwyższy efekt bakteriobójczy w stężeniu 500 g/t, osiągając skuteczność bakteriobójczą na poziomie 97%.

**Słowa kluczowe:** pole magnetyczne, kompozycja, metoda „cold finger”, ropa wysokoparafinowa, lepkość efektywna, temperatura krzepnięcia, działanie bakteriobójcze, bakterie.

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## Introduction

One of the problems that complicate the operation of technological equipment, tanks, and pipelines during the extraction, collection, transportation, and storage of crude oil is asphaltene-resin-paraffin sediments (ARPS). The accumulation of paraffin ARPS crystals on the lower part of the inner surface of pipelines causes a sharp narrowing in the flow section (Aliyeva, 2003; Akramov and Yarkeeva, 2017). Currently, many methods are used quite effectively to combat asphaltene-resin-paraffin sediments, with the most economically and technologically effective being combined methods (Glushchenko, 2007; Espolov et al., 2016). Undoubtedly, all methods used in the extraction, transportation, and storage of high-paraffin oils aim to prevent the coagulation of small-sized oil deposits and their sedimentation due to gravity. As a result, small crystals remain suspended in the oil, which do not affect the flow rate (Ivanova, 2011; Gurbanov et al., 2020a). In other words, the increase in oil viscosity at low temperatures is prevented by combined methods. The rheological parameters of oils depend on their constituent components and the amount of mechanical mixtures (Gurbanov et al., 2020b; Ivanova et al., 2022). Thus, an increase in the amount of asphaltene-resin-paraffin components and mechanical mixtures in oil leads to higher viscosity and freezing points (Khidr, 2011; Matiev et al., 2018). It should be noted that the production share of oils with high rheological parameters is rapidly increasing in our country and in other countries with developed oil industries. Therefore, improving the flow of high-paraffin oils at low temperatures using effective combined methods is a crucial current issue (Wilde, 2009; Ramazanov et al., 2011).

The purpose of the research work is to study the effect of the physicochemical method on the rheological parameters of the high-paraffin oil sample.

## Research methodology

In order to conduct experiments under laboratory conditions, a sample of highly paraffinic oil was taken from a well in operation in the Narimanov field. The extracted oil sample is characterized by 10.5% of paraffin, 1.9% of asphaltene, 4.3% of resin and a freezing temperature of +18°C.

The freezing temperature of the high-paraffin oil sample was determined according to the temperatures given in RD 39-3-812-82 (1982). The percentages of asphaltene, resin, and paraffin in the studied oil were also determined using established methods (Khairov, 1996). The amount of asphaltene-resin-paraffin components precipitated in the high-paraffin oil sample was measured using the “cold finger” method, with temperature

variations (Jennings and Weispenning, 2005). During the laboratory experiments, the “cold finger” was set to temperatures of 0, 5, 10, 15, 20, and 25°C. A Reotest-2 rotary viscometer was used to determine the effective viscosity of high-paraffin oil. Experiments were conducted without any impact on the research object, simultaneously using different methods. As an individual reagent, the depressant additive Difron-4201 produced by the Russian company “EKOC”, the reagent MARZA-3, Difron-4201 + MARZA-3 = 59:1, and the new composition N-1 and magnetic field were also used as physical effects.

Postgate-B nutrient medium was used for the germination and development of sulfate-reducing bacteria (SRB), and the studies were conducted according to the NACE standard methodology (NACE, 1994). This nutrient medium is considered more suitable for the development of SRB, as it supports their intensive reproduction. The microscopic appearance of the bacteria was studied using an MBI-6 microscope. A limited dilution method was used to quantify viable cells. The growth of sulfate-reducing bacteria was optimized by adding special additives to the Postgate-B nutrient medium. Studies using different brands of steel samples were conducted under static and thermostatic conditions to ensure optimal SRB growth activity. The bactericidal properties of the reagents against sulfate-reducing bacteria were studied in Postgate-B nutrient medium. The reagents required for the preparation of the nutrient medium were calculated for one liter of water, and the pH of the medium was maintained in the range of 7–7.5, checked using universal indicator paper.

## Results and their discussion

During the experiments, the effects of a magnetic field, the Difron-4201 depressor additive, the N-1 composition, and the combined effect of the magnetic field and N-1 composition on paraffin precipitation, freezing temperature, and effective viscosity were studied. First, under laboratory conditions, using the “cold finger” method, at temperatures of 0, 5, 10, 15, 20, and 25°C, the effect of the Difron-4201 additive, N-1 composition, and magnetic field on asphaltene-resin-paraffin deposits formed in a sample of highly paraffinic oil, and the combined effect of N-1 composition + magnetic field was studied. The results obtained from numerous laboratory tests are summarized in tables 1–4.

As shown in table 1, the amount of paraffin deposits collected on the surface of the “cold finger” in the oil sample studied at temperatures of 0, 5, 10, 15, 20, and 25°C decreased from 14.30–1.30 g to 11.8–0.54 g due to the effect of the magnetic field. The effectiveness of the magnetic field ranged from 21.8% to 58.5%.

**Table 1.** Effect of magnetic field on paraffin precipitation**Tabela 1.** Wpływ pola magnetycznego na wytrącanie parafiny

Temperature	Amount of paraffin deposits in the oil	Amount of paraffin deposits after magnetic field (30 minutes)	Effectiveness of magnetic field method
[°C]	[g]	[g]	[%]
0	14.30	11.18	21.8
5	12.60	9.55	24.2
10	8.50	5.10	40,0
15	5.70	3.12	45.3
20	2.10	1.05	50,0
25	1.30	0.54	58.5

**Table 2.** Effect of Difron-4201 additive on paraffin precipitation**Tabela 2.** Wpływ dodatku Difron-4201 na wytrącanie parafiny

Temperature	Amount of paraffin deposits in the oil	Amount of paraffin deposits in oil after addition of Difron-4201	Effectiveness of Difron-4201 additive
[°C]	[g]	[g]	[%]
0	14.30	10.96	23.4
5	12.60	9.21	26.9
10	8.50	4.92	42.1
15	5.70	3.05	46.5
20	2.10	0.96	54.3
25	1.30	0.44	66.2

**Table 3.** Effect of composition on paraffin precipitation**Tabela 3.** Wpływ kompozycji na wytrącanie parafiny

Temperature	Amount of paraffin deposits in oil	Amount of paraffin deposits after adding N-1 composition	Effectiveness of the composition
[°C]	[g]	[g]	[%]
0	14.30	10.52	26.4
5	12.60	8.84	29.8
10	8.50	4.53	46.7
15	5.70	2.65	53.5
20	2.10	0.76	63.8
25	1.30	0.25	80.8

Table 2 shows that the amount of paraffin deposits collected on the surface of the “cold finger” in the oil sample studied at temperatures of 0, 5, 10, 15, 20, and 25°C without any effect was 14.30–1.30 g. After adding the optimal amount of Difron-4201 depressant additive of 600 g/t, the amount varied

**Table 4.** Effect of composition and magnetic field on co-paraffin precipitation**Tabela 4.** Wpływ kompozycji i pola magnetycznego na wytrącanie parafiny

Temperature	Amount of paraffin deposits in oil	Amount of paraffin deposits after the combined method	Effectiveness of combined method
[°C]	[g]	[g]	[%]
0	14.30	9.63	32.7
5	12.60	8.14	35.4
10	8.50	4.06	52.2
15	5.70	2.14	62.5
20	2.10	0.46	78.1
25	1.30	0.11	91.5

between 10.96–0.44 g. The effectiveness of the depressant additive ranged from 23.4% to 66.2%.

As shown in Table 3, the amount of paraffin deposits collected on the surface of the “cold finger” in the oil sample studied at temperatures of 0, 5, 10, 15, 20, and 25°C without any effect was 14.30–1.30 g. This amount varied from 10.52 g to 0.25 g due to the effect of the optimal amount of N-1 composition of 500 g/t. The effectiveness of the N-1 composition ranged from 26.4% to 80.8%.

According to Table 4, the amount of paraffin deposits collected on the surface of the “cold finger” in the oil sample studied at temperatures of 0, 5, 10, 15, 20, and 25°C without any effect is 14.30–1.30 g. This amount varied between 9.63–0.11 g due to the combined effect of N-1 composition + magnetic field. The effectiveness of the combined method ranged from 32.7% to 91.5%.

The combined effect of magnetic field, Difron-4201 additive, N-1 composition, and magnetic field with N-1 composition on the freezing temperature of high-paraffin oil was studied in laboratory conditions (Figure 1). The effect of the magnetic field was observed for 5, 10, 15, 20, 25, and 30 minutes. The amount of Difron-4201 depressant additive was 100, 200, 300, 400, 500, and 600 g/t, and the concentration of N-1 composition was 100, 200, 300, 400, and 500 g/t.

The results of numerous laboratory experiments given in Figure 1 can be summarized as follows:

1. When subjected to a magnetic field for 5, 10, 15, 20, 25, and 30 minutes, the freezing temperature of the high-paraffin oil sample decreased to +16, +12, +10, +8, +6, +5°C, respectively. The effectiveness of the magnetic field is 11.1%, 33.3%, 44.4%, 55.5%, 66.6%, 72.2%.
2. Adding 100, 200, 300, 400, 500, and 600 g/t of the Difron-4201 depressant additive to the high-paraffin oil sample resulted in freezing temperatures of +15, +10, +8,

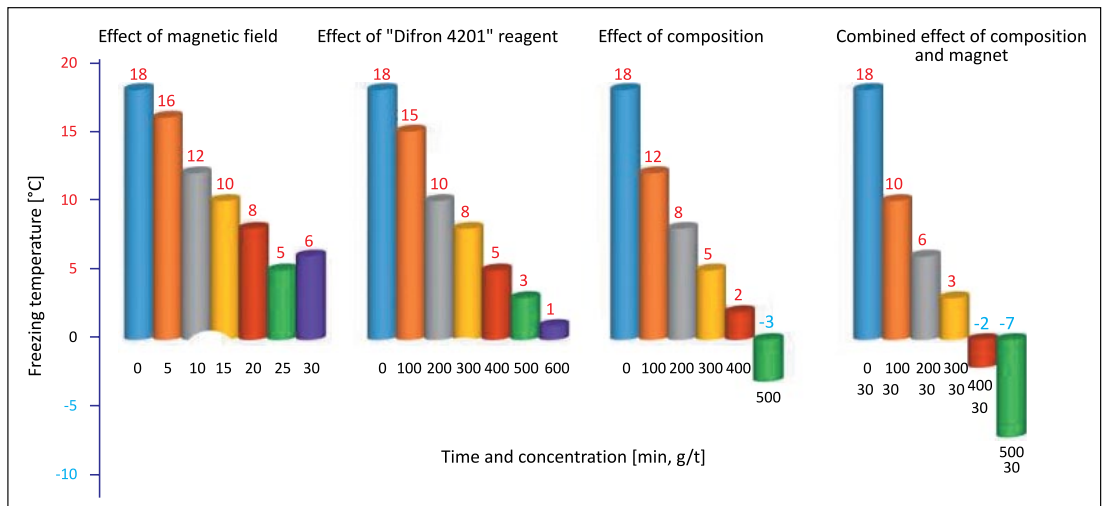


Figure 1. Results of the physical and physicochemical effects on the freezing temperature of oil

Rysunek 1. Wyniki oddziaływania fizycznego i fizykochemicznego na temperaturę krzepnięcia ropy naftowej

+5, +3, +1°C. The depressant effect of the additive is 16.6%, 44.4%, 55.5%, 72.2%, 83.3%, 94.4%.

- The addition of 100, 200, 300, 400, 500 g/t of the new N-1 composition to high-paraffin oil resulted in freezing temperatures of +12, +8, +5, +2, -3°C. The effectiveness of the reagent is 33.3%, 55.5%, 72.2%, 88.9%, 116.6%

With a combined application of the magnetic field + N-1 composition at concentrations of 100, 200, 300, 400, 500 g/t, and exposure to the magnetic field for 30 minutes for all concentrations, the freezing temperature was reduced to +10, +6, +3, -2, -7°C. The effectiveness of this combined method is 44.4%, 66.6%, 83.3%, 111.1%, 133.3%. From the comparative analysis of the results, it is evident that the combination of the magnetic field + N-1 composition has the most significant impact on high-paraffin oil with an initial freezing temperature of +18°C. The study also investigates the effects of the magnetic field, Difron-4201 additive, N-1 composition, and the combined

N-1 composition and magnetic field on the effective viscosity of the high-paraffin oil sample. The experimental results are summarized in table 5.

According to Table 5, the effective viscosity of the studied oil sample decreases in the temperature range of 5–25°C, both without reagents and under the influence of reagents. In general, the experimental results given in Table 5 can be summarized as follows:

- When the oil temperature changes in the range of 5–25°C, the effective viscosity decreases by 83.2%, reaching a value of 2.89 Pa·s.
- When the oil temperature changes in the range of 5–25°C with the presence of a magnetic field, the effective viscosity decreases by 85.1%, reaching a value of 1.54 Pa·s.
- With the presence of Difron-4201 additive, the effective viscosity decreases by 95.4%, reaching a value of 0.26 Pa·s when the oil temperature changes in the range of 5–25°C.

Table 5. Influence of magnetic field and composition on the effective viscosity of high-paraffinic oil at various temperatures.

Tabela 5. Wpływ pola magnetycznego i składu na lepkość efektywną ropy wysokoparafinowej w różnych temperaturach

Intensity/ [time]	Oil temperature [°C]	Effective viscosity [P·s]
0.00	5	17.2
0.00	10	11.34
0.00	15	8.58
0.00	20	4.97
0.00	25	2.89
Effect of magnetic field		
30 min	5	10.31
30 min	10	7.61
30 min	15	5.25
30 min	20	3.76
30 min	25	1.54

cont. Table 5/cd. Tabela 5

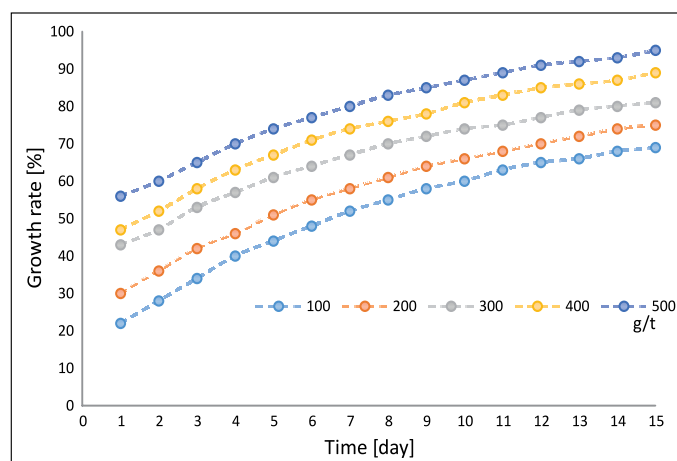
Intensity/ [time]	Oil temperature [°C]	Effective viscosity [P·s]
The effect of the additive Difron-4201.		
200	5	5.62
300	10	3.37
400	15	2.48
500	20	1.65
600	25	0.26
Effect of composition		
100 g/t	5	3.78
200 g/t	10	1.63
300 g/t	15	0.97
400 g/t	20	0.51
500 g/t	25	0.13
Combined effect of magnetic field and composition		
100 g/t / 30 min	5	0.4800
200 g/t / 30 min	10	0.1500
300 g/t / 30 min	15	0.0520
400 g/t / 30 min	20	0.0120
500 g/t / 30 min	25	0.0025

- When the oil temperature changes in the range of 5–25°C with the presence of the N-1 composition, the effective viscosity decreases by 96.6%, reaching a value of 0.13 Pa·s.
- The effective viscosity decreases by 99.5%, reaching a value of 0.0025 Pa·s when the oil temperature changes in the range of 5–25°C with the presence of both the N-1 composition and magnetic field.

During the research work, the effect of the N-1 composition against sulfate-reducing bacteria was studied. The bactericidal properties of the N-1 composition were tested in laboratory conditions using strains of *Desulfomicrobium* and *Desulfovibrio desulfuricans* bacteria. The sulfate-reducing bacteria used in the experiment were sourced from formation waters of the Bibiheybatneft OGES oil field. The effect of the N-1 composition on the incubation period of sulfate-reducing bacteria was studied over fifteen days. During this period, amounts of 100, 200, 300, 400, and 500 g/t of the composition were used. Based on the results of numerous experiments conducted over fifteen days, the effect of the N-1 composition on the growth rate of sulfate-reducing bacteria cells is shown in Figure 2.

The graphs given in Figure 2 can be characterized as follows based on the concentration of the N-1 composition:

- Due to the effect of CN-1 = 100 g/t, the growth factor N of bacterial cells varies between 22% and 69% over 1–15 days.
- Due to the effect of CN-1 = 200 g/t, the growth factor N of bacterial cells varies between 30% and 75% over 1–15 days.



**Figure 2.** Effect of N-1 composition on the growth factor (N [%]) of sulfate-reducing bacterial cells

**Rysunek 2.** Wpływ kompozycji N-1 na współczynnik wzrostu (N [%]) komórek bakterii redukujących siarczany

- Due to the effect of CN-1 = 300 g/t, the growth factor N of bacterial cells varies between 43% and 81% over 1–15 days.
- Due to the effect of CN-1 = 400 g/t, the growth factor N of bacterial cells varies between 47% and 89% over 1–15 days.
- Due to the effect of CN-1 = 500 g/t, the growth factor N of bacterial cells varies between 56% and 95% over 1–15 days.

Thus, the analysis of the results shows that as the concentration of the N-1 composition and the duration of the experiment



increases, the growth factor  $N$  of bacterial cells also increases, with the highest value observed at the concentration of 500 g/t of the composition.

Additionally, the bactericidal effect of the N-1 composition was determined by measuring the concentration of biogenic hydrogen sulfide in Postgate-B medium over fifteen days. The formation of hydrogen sulfide in the environment was determined by the iodometric titration method. Both the concentration of biogenic hydrogen sulfide and the number of microorganism cells were determined on a daily basis. Reagents were titrated using the iodometric method, and the amount of biogenic hydrogen sulfide formed in the Postgate-B environment was calculated. According to the amount of hydrogen sulfide found by the iodometric method, the bactericidal effect of the N-1 composition was calculated by the following formula:

$$S[\%] = \frac{C_0 - C_{inh}}{C_{inh}} 100\% \quad (1)$$

where:

$C_0$  – concentration of biogenic hydrogen sulfide in a non-additive environment.

$C_{inh}$  – concentration of biogenic hydrogen sulfide in its natural environment.

The coefficient of variation of hydrogen sulfide concentration is found by the following mathematical expression:

$$\gamma_c = \frac{C(H_2S)_0}{C(H_2S)_{inh}} \quad (2)$$

where:

$C(H_2S)_0$  – concentration of hydrogen sulfide in a non-treated medium,

$C(H_2S)_{inh}$  – concentration of hydrogen sulfide in the composition medium (NACE 1994).

The results of the bactericidal effects of the compositions based on the amount of biogenic hydrogen sulfide formed in the medium are given in Figure 3.

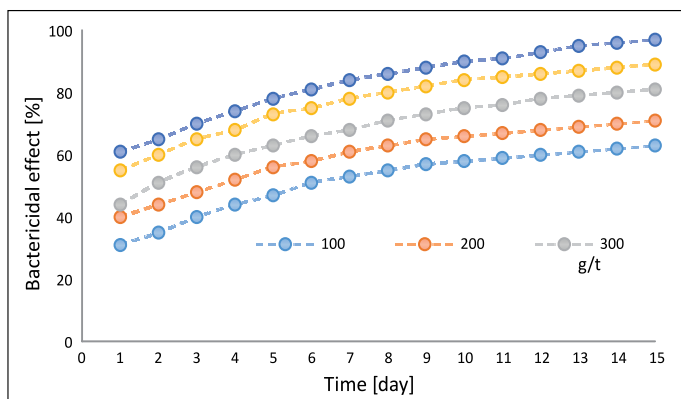


Figure 3. Bactericidal effect of composition N-1  
 Rysunek 3. Efekt bakteriobójczy kompozycji N-1

According to the results given in Figure 3, the bactericidal effect of the N-1 composition over 15 days at different concentrations is as follows:

1. With  $C_{N-1} = 100$  g/t, the bactericidal effect (S) of the composition ranges from 31% to 63% over 1–15 days.
2. With  $C_{N-1} = 200$  g/t, the bactericidal effect (S) of the composition ranges from 40% to 71% over 1–15 days.
3. With  $C_{N-1} = 300$  g/t, the bactericidal effect (S) of the composition ranges from 44% to 81% over 1–15 days.
4. With  $C_{N-1} = 400$  g/t, the bactericidal effect (S) of the composition ranges from 55% to 89% over 1–15 days.
5. With  $C_{N-1} = 500$  g/t, the bactericidal effect (S) of the composition ranges from 61% to 97% over 1–15 days.

Apparently, the new N-1 composition has high bactericidal properties.

### Conclusions

1. The influence of the magnetic field, Difron-4201 depressor additive, N-1 composition, and their combined effects, specifically the magnetic field combined with N-1 composition, on parameters such as freezing temperature, paraffin deposition, effective viscosity, and the proliferation of sulfate-reducing bacteria were investigated. The optimal consumption rates of reagents were determined based on density norms, revealing the most effective dosage to be 600 g/t for the Difron-4201 depressor additive and 500 g/t for the N-1 composition. Additionally, the optimal duration for the application of the magnetic field was found to be 30 minutes.
2. In the investigation of oil freezing temperature, the efficacy of the magnetic field, Difron-4201 depressor additive, and N-1 composition were individually examined, along with the combined method of N-1 composition with magnetic field application. The combined approach exhibited superior effectiveness in mitigating crystal nucleation in high-paraffin oil samples, reducing the freezing temperature from +18°C to +5, +1, -3, and -7°C, respectively. This phenomenon is attributed to the continuous agitation of sediment-forming components by electromagnetic waves induced by the magnetic field, thereby enhancing the reagent's efficacy on paraffin.
3. The impact of the magnetic field, Difron-4201 depressor additive, N-1 composition, and their combination with the magnetic field on viscosity was investigated from four perspectives. The effective viscosity of the oil sample ranged from 17.2 to 0.0025 Pa·s, with reductions to 1.54, 0.26, 0.13, and 0.0025 Pa·s, respectively. The significant decrease in effective viscosity can be attributed to enhanced

dispersion caused by the influence of electromagnetic waves, thereby minimizing viscosity.

4. Considering that MARZA-3, a component of the N-1 composition, functions as a microbiological anti-corrosion agent, the impact of N-1 composition on the development coefficient of sulfate-reducing bacteria was studied. The bactericidal effect of varying concentrations (100, 200, 300, 400, and 500 g/t) of the N-1 composition was observed to be 63%, 71%, 81%, 89%, and 97%, respectively.

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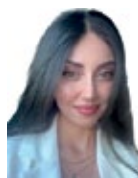
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