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# THE STUDY OF THE CORROSION PROTECTION EFFECT OF AN INHIBITOR-BACTERICIDE BASED ON SULFONATES AND AMINES IN PRODUCED WATERS

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Corrosion not only increases maintenance costs but also poses environmental and safety risks. The use of sulfonate- and amine-based inhibitors for protecting oilfield infrastructure against corrosion is a critical advancement in the oil and gas industry. The present study investigates the development and effectiveness of a newly formulated bactericidal inhibitor, NS-41A, for mitigating hydrogen sulfide-induced corrosion and microbiologically influenced corrosion in reservoir waters. Chemical and microbiological analyses were performed on water samples from production wells of the «Neft Daslari» Oil and Gas Production Unit. Well No. 2425 was identified as the most aggressive, exhibiting a corrosion rate of 1.2870 $g/m^2 \cdot h$, a hydrogen sulfide content of 91.56 $mg/dm^3$, and bacterial counts of $10^5$—$10^6$ cells/ml. The effectiveness of NS-41A was evaluated at concentrations ranging from 25—250 mg/l. At the optimal dosage of 200 mg/l, the corrosion rate decreased by a factor of 64.38, achieving 96.4% protection efficiency, while sulfate-reducing bacteria, iron bacteria, and hydrocarbon-oxidizing bacteria were entirely eradicated. The inhibitor was synthesized in two stages using heavy gas oil, sodium sulfonate, and aminoethylethanolamine. Laboratory experiments demonstrated that a 4:1 ratio of sodium sulfonate to aminoethylethanolamine (NS-41A) exhibited significant inhibitory and biocidal activity. This research highlights the potential of NS-41A as a cost-effective and efficient inhibitor for industrial applications. It also provides a valuable framework for future innovations in the field of corrosion protection, with potential adaptability to other industrial contexts.

**Keywords**: sodium sulfonate, aminoethylethanolamine, inhibitor-bactericide, corrosion rate, iron bacteria, hydrocarbon-oxidizing bacteria, sulfate-reducing bacteria, isopropyl alcohol.

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## *Introduction*

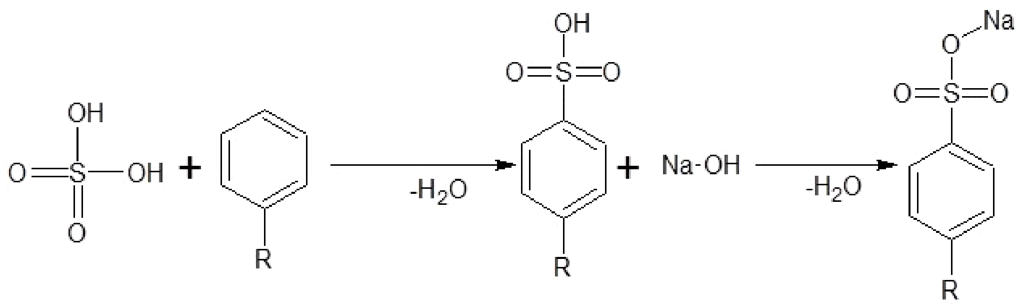
The operation of oil and gas fields presents significant challenges due to the corrosive nature of reservoir environments, exacerbated by drilling fluids and injected water used to maintain reservoir pressure. These substances, although effective in their intended functions, often contribute to heightened corrosion aggressiveness when inadequately treated. Such conditions compromise the reliability and efficiency of oilfield equipment, emphasizing the critical need for ongoing monitoring and protective measures [1,2]. Understanding the role of various chemical and biological factors in corrosion processes is crucial for maintaining operational safety and extending the lifespan of infrastructure in the oil and gas industry. Produced water in oil and gas fields typically contains substances such as carbon dioxide, oxygen, and hydrogen sulfide, as well as microorganisms that contribute to corrosion. Among the microorganisms contributing to corrosion, sulfate-reducing bacteria

(SRBs), iron bacteria (FeB), and hydrocarbon-oxidizing bacteria (HOB) are particularly influential due to their metabolic activities. SRBs reduce sulfates to hydrogen sulfide, creating a highly corrosive environment that accelerates metal degradation. Iron bacteria oxidize ferrous ions to ferric ions, promoting the formation of corrosive deposits [3–6]. Hydrocarbon-oxidizing bacteria metabolize hydrocarbons present in reservoir fluids, often producing organic acids that lower pH levels and exacerbate corrosion. These biological activities form complex biofilms that shield bacterial colonies, making them resilient to conventional treatments and amplifying their impact on pipeline integrity. Understanding and mitigating these processes is crucial for designing effective, adaptive strategies to manage microbiologically influenced corrosion (MIC) in oil and gas fields [7]. These microorganisms play dominant roles due to their adaptability and rapid multiplication and catalyze chemical transformations that accelerate the deterioration of pipelines and equipment. Monitoring and mitigating the impact of these factors is an ongoing priority in reservoir management. In oil fields such as Neft Daslari, one of Azerbaijan's oldest and most significant offshore oil production units, the combination of high $H_2S$ content, acidic water conditions, and bacterial proliferation creates a particularly aggressive environment for corrosion. As oil fields mature and water injection for enhanced recovery increases, the challenge of corrosion intensifies, necessitating the development of effective mitigation strategies.

Chemical inhibitors and biocides are widely employed to control both $H_2S$-induced and microbial corrosion. However, many traditional inhibitors are either partially effective, environmentally hazardous, or uneconomical for large-scale applications. Therefore, there is a growing need to develop new, cost-effective, and environmentally acceptable inhibitors that can simultaneously reduce $H_2S$ corrosion and control microbial growth in aggressive oilfield environments. Bactericidal corrosion inhibitors have emerged as a practical and effective solution to counteract these challenges. These inhibitors not only reduce the rate of metal degradation but also target microbial-induced corrosion by suppressing the activity of harmful bacteria. Their affordability and ease of application make them one of the most widely used methods in the industry. However, studies show that prolonged use of a single inhibitor can lead to microbial resistance [8].

Over time, specific microbial groups adapt to the inhibitor and may even metabolize it, diminishing its effectiveness. This necessitates the periodic introduction of new inhibitors and biocides, tailored to the evolving conditions of the oilfield environment. Advanced research and development in this area focus on creating inhibitors with enhanced durability and effectiveness, capable of mitigating corrosion while adapting to changing microbial ecosystems. Addressing these challenges through innovative corrosion management strategies ensures the continued reliability of oilfield operations and minimizes economic and environmental risks. By implementing comprehensive monitoring systems and adopting novel inhibitors, the oil and gas industry can effectively combat the persistent issue of corrosion [9]. These measures contribute not only to operational efficiency but also to the sustainability of valuable resources and infrastructure. The primary goal of this study was to develop and implement new inhibitors and biocides in oil and gas fields to counteract the challenges posed by microbial adaptation and reduced effectiveness of existing reagents. This ensures the continued efficacy of corrosion management strategies, enhances the durability of equipment, and minimizes operational disruptions caused by microbial-induced corrosion in dynamically evolving reservoir environments [10].

In the preparation of the inhibitor biocide, heavy gas oil obtained from the coking unit of the Heydar Aliyev Baku Oil Refinery was used. In the first stage, sulfuric acid sulfonation of the heavy gas oil and the production of the sodium salt of sulfuric acid were carried out (Scheme). In the second stage, compositions




Scheme. Sulfonation and neutralization reaction of sodium sulfonate and aminoethylethanolamine (AEEA) in various ratios were prepared in a mixture of water and isopropyl alcohol. Laboratory studies revealed that a composition with a 4:1 ratio of sodium sulfonate to AEEA (NS-41A) was more effective against both hydrogen sulfide and microbiological corrosion. The physicochemical properties of the NS-41A reagent were determined (Table 1), and the bactericidal-inhibitor effect was studied in the most aggressive water sample taken from well No. 2425 of the «Neft Daslari» oil field.

In the research work, water samples from the following production wells of the «Neft Daslari» Oil and Gas Production Unit (OGPU): 2167, 2416, 2568, 819, 2417, 966, 2425 from OGPU No. 1, respectively, were subjected to chemical and microbiological analysis under laboratory conditions based on current regulatory documents. The corrosion aggressiveness was determined, and the most aggressive water sample was selected for further experimentation.

***Experimental, results and discussion***

The amount of hydrogen sulfide in the water samples was determined according to the OCT 39-234-89 standard using the iodometric method (Table 2). According to the standard, the hydrogen sulfide content (mg/l) was calculated using the following formula:

$$C_S = \frac{17040 \cdot (V_1K_1 - V_2K_2) \cdot K_r \cdot N}{V_r},$$

where $V_1$ is the amount of iodine added (ml); $K_1$ is the correction factor for expressing iodine concentration correctly; $V_2$ is the amount of sodium thiosulfate used for back titration (ml); $K_2$ is the correction factor for expressing thiosulfate concentration correctly; N is the normality of the titrated thiosulfate or iodine solution; and $V_r$ is the volume of the water sample taken for analysis (ml).

The corrosion aggressiveness of the reservoir water sample was determined using the gravimetric method in accordance with the state standard GOST 9.506-87 (Table 2). The tests were conducted in a U-shaped tube equipped with a mechanical stirrer, operating at 500 cycles per minute for a period of 6 hours.

The corrosion rate was calculated using the following formula:

$$V_k = \frac{m_1 - m_2}{S \cdot \tau},$$

where $V_k$ is the corrosion rate ($g/m^2 \cdot h$); $m_1$ is the weight of the sample before the test (g); $m_2$ is the weight of the sample after the test (g); S is the surface area of the sample ($m^2$); and $\tau$ is the test duration (h).

If an inhibitor is used, the protection effect of the reagent against hydrogen sulfide corrosion (Z) is calculated based on the following formula:

$$Z = \frac{(V_{k_0} - V_{k_1})}{V_{k_0}} \cdot 100\%,$$

where $V_{k0}$ is the corrosion rate in the uninhibited medium ($g \cdot m^{-2} \cdot s^{-1}$); and $V_{k1}$ is the corrosion rate in the inhibited medium ($g \cdot m^{-2} \cdot s^{-1}$).

The microbiological analysis of the reservoir water samples was performed by culturing the samples on selective media suitable for each microbial group. The amount of sulfate-reducing bacteria (SRB) was determined according to the NACE TMO194-2014 standard («Field Monitoring of Bacterial Growth in Oil and Gas Systems»). This standard defines the procedures for water sample collection, initial bacterial count determination, and monitoring the bacterial population after biocide application. The selective medium used for SRB analysis consisted of the following components: Postgate B (g/l): 1.0 $NH_4Cl$; 0.5 $K_2HPO_4$; 2.0 $MgSO_4 \cdot 7H_2O$; 1.0 $CaSO_4$; 0.5 $FeSO_4 \cdot 7H_2O$; 25 NaCl; 1.0 yeast extract; 3.5 ml Na lactate (60%); 0.1 g ascorbic acid; and 0.1 g thioglycolic acid.

To determine the presence of SRB, 1 ml of the water sample was placed in a sterile glass container

Table 1

**Physicochemical properties of the «NS-41A» inhibitor-biocid**

| Property | Value | Test method |
|---|---|---|
| external appearance | dark brown liquid | visually |
| density at $20^0C$, $g/cm^3$ | 0.924–0.963 | state standard GOST 3900-85 |
| freezing temperature, $^0C$ | <–20 | state standard GOST 20287-91 |
| kinematics viscosity at $20^0C$, $mm^2/s$ (sSt) | 36 | state standard GOST 33-2000 |
| pH, diluted solution | 9–10, 3% $H_2O$ | potentiometry |
| ignition temperature, $^0C$ | <65 | state standard GOST 6356-75 |

and mixed with 9 ml of Postgate medium. After five minutes of mixing, the first dilution was obtained. The sample was further diluted using sterile pipettes in a series of dilutions (1:100; 1:10,000, etc.), and each dilution was plated on nutrient media. After the inoculation process, all samples were incubated at $32^0$C for 15 days. The presence of bacteria was determined by observing the growth on the nutrient media. The presence of sulfate-reducing bacteria was confirmed by the observation of iron-sulfide precipitates.

The number of bacterial cells (cells/ml) was calculated using the following formula:

$$M = \frac{10^{n-1}}{V},$$

where n is the bacterial growth noted in the last dilution tube; and V is the volume of the water sample taken for inoculation (ml).

Iron bacteria (FeB) and hydrocarbon-oxidizing bacteria (HOB) were cultured in Volf and Raymond media, respectively. The results obtained are presented in Table 2.

The chemical analysis of the water samples was conducted in accordance with MS 1669347-05-04 standard. Parameters including pH, density, and the concentration of $Cl^-$, $SO_4^{2-}$, $CO_3^{2-}$, $HCO_3^-$, $Mg^{2+}$, $Ca^{2+}$, $Na^+$, and $K^+$ ions were determined. Based on the Palmer and Sulin classification system, the type of reservoir water was identified (Table 3).

As seen from the analysis of Tables 2 and 3, the reservoir water sample taken from well No. 2425 of OGPU No. 1 is more aggressive compared to the other well samples. Specifically, the bacterial count in the reservoir water of this well is $10^5$—$10^6$ cells/ml, the corrosion rate is K=1.2870 g/m²·h or 1.4414 mm/year, the total mineralization is 54398.61 mg/l, the content of $H_2S$ is 91.56 mg/dm³, and the pH of the water is more acidic (pH 5.5) compared to the other samples. Taking all these factors into account, the bactericidal inhibitor effect of the prepared compositions was studied at concentrations ranging from 25—250 mg/l in the water sample taken from well No. 2425 (Table 4).

As shown in Table 4, the corrosion rate in an uninhibited environment was 1.2870 g/m²·h, with the bacterial count ranging between $10^5$—$10^6$ cells/ml. When various concentrations of inhibitor were added to the system, a decrease in the corrosion rate of the metal was observed. Specifically, after adding the inhibitor at a concentration of 25 mg/l, the corrosion rate decreased by 2.63 times. At this concentration, the SRB count was $10^5$ cells/ml, the HOB count was $10^5$ cells/ml, and the FeB count was $10^5$ cells/ml.

At the higher concentration range (200—250 mg/l), the inhibitor demonstrated high effectiveness against both hydrogen sulfide and microbiological corrosion. Therefore, a concentration of 200 mg/l was selected as the optimal dosage. At this concentration, the «NS-41A» bactericidal inhibitor reduced the hydrogen sulfide corrosion rate by 64.38 times, with a metal loss of 0.0003 g, and the protection efficiency reached 96% (Fig. 1). At the same concentration of that bactericidal inhibitor, all bacteria causing microbiological corrosion (SRB, HOB, and FeB) were destroyed (Fig. 2).

It can be suggested that the high efficiency of NS-41A arises from a combined surface†protective and antimicrobial action. In our view, the sulfonate component likely adsorbs onto the steel, forming a thin, hydrophobic layer that impedes direct contact with corrosive agents, while the aminoethylethanolamine fraction may help moderate localized acidity where $H_2S$ is present. At the same time, we assume that the amine functionality interferes

Table 2

**Results of the microbiological analysis of the water sample of NQCS No. 1**

| Well number | Microorganisms, cells/ml | | | Content of $H_2S$, mg/dm³ | Corrosion rate, g/m²·h, (mm/year) |
|---|---|---|---|---|---|
| | SRB | FeB | HOB | | |
| 2167 | $10^4$ | $10^5$ | $10^7$ | 20.45 | K=0.5382, (0.6027) |
| 2416 | $10^2$ | $10^6$ | $10^6$ | 22.15 | K=0.5656, (0.6334) |
| 2568 | $10^3$ | $10^5$ | $10^7$ | 27.26 | K=0.8686, (0.9728) |
| 819 | $10^5$ | $10^6$ | $10^5$ | 25.26 | K=0.9222, (1.032) |
| 2417 | $10^3$ | $10^6$ | $10^7$ | 20.44 | K=0.6727, (0.7553) |
| 966 | $10^2$ | $10^5$ | $10^6$ | 8.52 | K=0.6061, (0.6788) |
| 2425 | $10^6$ | $10^5$ | $10^6$ | 91.56 | K=1.2870, (1.4414) |

Table 3

**Results of chemical analysis of water samples of NQCS No. 1**

| Well number | pH | Density | Total mineral. | $Cl^-$ | $SO_4^{2-}$ | $CO_3^{2-}$ | $HCO_3^-$ | $Na^++K^+$ | $Ca^{2+}$ | $Mg^{2+}$ | $Fe^{3+}$ | Type of water |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | Concentration of ions, mg/dm$^3$ | | | | | | | | |
| 2167 | 8.0 | 1.014 | 22591.77 | 9926.00 | 4.94 | 570.00 | 3599.00 | 8354.46 | 40.08 | 97.28 | 179.03 | II |
| 2416 | 7.0 | 1.010 | 20475.83 | 9571.50 | 4.11 | 480.00 | 2562.00 | 7778.05 | 80.16 | 0.00 | 281.77 | II |
| 2568 | 7.8 | 1.009 | 17622.86 | 7799.00 | 146.49 | 420.00 | 2623.00 | 6481.24 | 80.16 | 72.96 | 1152.69 | II |
| 819 | 7.0 | 1.030 | 47666.15 | 25524.00 | 60.90 | 30.00 | 3538.00 | 18198.45 | 120.24 | 194.56 | 794.08 | II |
| 2417 | 7.4 | 1.007 | 13396.60 | 5672.00 | 15.64 | 300.00 | 2440.00 | 4855.81 | 40.08 | 72.96 | 307.36 | II |
| 966 | 7.7 | 1.016 | 25791.55 | 11698.50 | 16.46 | 120.00 | 4331.00 | 9488.23 | 40.08 | 97.27 | 1152.69 | II |
| 2425 | 5.5 | 1.037 | 54398.61 | 31550.50 | 13.99 | 180.00 | 1098.00 | 21030.99 | 160.32 | 364.80 | 320.17 | III |

with the metabolic activity of sulfate reducing, iron oxidizing, and hydrocarbon oxidizing bacteria, either by disrupting membrane integrity or by inhibiting key enzymatic processes, thus reducing biofilm formation and microbial induced corrosion. Together, these effects would explain the markedly lower corrosion rates and the apparent elimination of microbial colonies at the optimal dosage of 200 mg/L.

***Conclusions***

1. The water samples taken from the flooded operational wells of the «Neft Daslari» OGPU No. 1 were subjected to chemical and microbiological analysis under laboratory conditions in accordance with the existing regulatory documents. The corrosion aggressiveness was determined, and the most aggressive water sample was selected to study the protective effect of a newly developed inhibitor-bactericide.

2. The «NS-41A» bactericide-inhibitor demonstrated a high protective effect against hydrogen sulfide corrosion in pipelines operated in the mines. Specifically, at a concentration of 200 mg/l, the protection efficiency against $H_2S$ corrosion reached 96.4%.

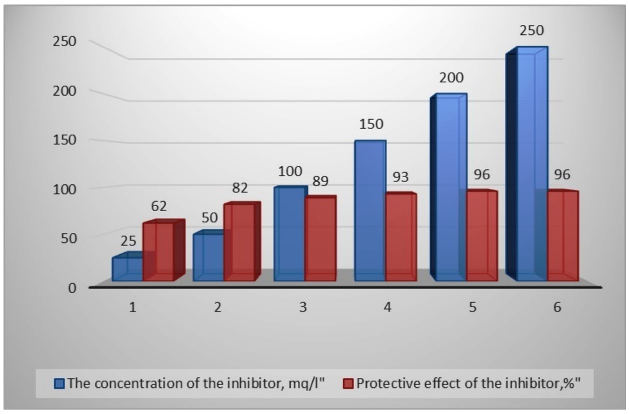



Fig. 1. Protective effect of the «NS-41A» reagent against hydrogen sulfide corrosion

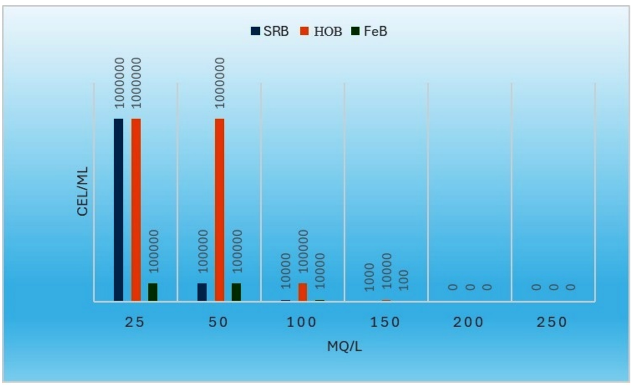



Fig. 2. Protective effect of the «NS-41A» reagent against various types of bacteria

3. The «NS-41A» bactericide-inhibitor exhibited a strong biocidal effect against iron bacteria, hydrocarbon-oxidizing bacteria, and sulfate-reducing bacteria, which are responsible for microbiologically induced corrosion. At a concentration of 200 mg/l, the reagent showed a 100% protective effect against the aforementioned bacteria. This inhibitor-bactericide is considered suitable for future use in preventing internal corrosion in pipeline systems within the mines.

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**ДОСЛІДЖЕННЯ АНТИКОРОЗІЙНОЇ ДІЇ ІНГІБІТОРА-БАКТЕРИЦИДУ НА ОСНОВІ СУЛЬФОНАТІВ І АМІНІВ У ПОПУТНИХ ВОДАХ**

*Е.Ф. Султанов, А.Н. Курбанов*

Корозія не лише підвищує витрати на обслуговування, але й становить загрозу для довкілля та безпеки. Використання інгібіторів на основі сульфонатів і амінів для захисту нафтовидобувної інфраструктури від корозії є важливим досягненням у нафтогазовій промисловості. У даній роботі досліджено розробку та ефективність нового бактерицидного інгібітора NS-41A для зменшення корозії, спричиненої сірководнем, а також мікробіологічно індукованої корозії у пластових водах. Було проведено хімічний та мікробіологічний аналіз проб води з видобувних свердловин на нафтогазовому промислі «Нафтові Камені». Свердловина № 2425 була визначена як найбільш агресивна: корозійна швидкість становила 1,2870 г/м$^2$·год, вміст сірководню – 91,56 мг/дм$^3$, а кількість бактерій – $10^5$–$10^6$ клітин/мл. Ефективність NS-41A оцінювалася в концентраційному діапазоні 25–250 мг/л. За оптимально-

Table 4

**Protective effect of «NS-41A» inhibitor-bactericide**

| Concentration of NS-41A reagent, mg/l | Metal loss, g | Corrosion rate, g/m$^2$·h | Retardation factor | Protection effect, % | SRB, cell/ml | HOB, cell/ml | FeB, cell/ml |
|---|---|---|---|---|---|---|---|
| – (without inhibitor) | 0.01200 | 1.2870 | – | – | $10^6$ | $10^6$ | $10^5$ |
| 25 | 0.0040 | 0.490 | 2.63 | 62 | $10^5$ | $10^5$ | $10^5$ |
| 50 | 0.0022 | 0.240 | 5.85 | 82 | $10^4$ | $10^5$ | $10^4$ |
| 100 | 0.0010 | 0.140 | 9.90 | 89 | $10^3$ | $10^4$ | $10^3$ |
| 150 | 0.0006 | 0.090 | 14.30 | 93 | $10^2$ | $10^3$ | $10^1$ |
| 200 | 0.0003 | 0.050 | 25.74 | 96 | 0 | 0 | 0 |
| 250 | 0.0003 | 0.051 | 25.72 | 96 | 0 | 0 | 0 |

го дозування 200 мг/л корозійна швидкість зменшилась у 64,38 рази, досягнувши 96,4% ефективності захисту, при цьому сульфатвідновлювальні бактерії, залізобактерії та вуглеводнеокиснювальні бактерії були повністю знищені. Інгібітор синтезували у два етапи з використанням важкого газойлю, натрієвого сульфонату та аміноетилетаноламіну. Лабораторні експерименти показали, що співвідношення натрієвого сульфонату до аміноетилетаноламіну 4:1 (NS-41A) забезпечує значну інгібіторну та біоцидну активність. Це дослідження підкреслює потенціал NS-41A як економічно вигідного та ефективного інгібітора для промислового застосування. Воно також створює цінну основу для подальших інновацій у галузі антикорозійного захисту з можливістю адаптації до інших галузей промисловості.

**Ключові слова**: натрієвий сульфонат; аміноетилетаноламін; інгібітор-бактерицид; швидкість корозії; залізобактерії; вуглеводнеокиснювальні бактерії; сульфатвідновлювальні бактерії; ізопропіловий спирт.

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