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HISTORY AND DEVELOPMENT OF DEEMULGATORS IN PRIMARY PROCESSING AND PREPARATION FOR OIL PROCESSING

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ANNOTATION

The article analyzes the processes of formation, production and use of chemical reagent demulsifiers for desalination and dehydration of oil emulsions, the main stages of industrial development of domestic demulsifiers. It describes the experience of the Grozny Research Institute in the development and use of demulsifiers.

Keywords: oil emulsions, demulsifiers, desalination, dehydration,

INTRODUCTION

Since the beginning of the organization of industrial production and oil refining, the problem of effective disposal of water-oil emulsions has arisen. Water and salts in oil cause the following disadvantages:

- Reduces the service life of oil fields and oil refining equipment,
- Difficult to transport and process oil.

The mechanism of destruction of fat emulsions consists of three stages: the collision of water globules, their aggregation into larger droplets, the deposition of droplets or their separation in the form of a continuous aqueous phase. To ensure the maximum possibility of collision of water globules, the speed of their movement in the oil is increased in various ways: mixing in mixers, mixers, heating, ultrasound, electric and magnetic fields, centrifugal forces and others.

With the help of effective chemical demulsifiers, it is possible to weaken the structural and mechanical strength of the layers surrounding the water globules and make them hydrophilic to achieve the fastest and most complete elimination of oil emulsions.

Analysis of the production history of demulsifiers reagents has a long production history and a longer history of the relationship between the development of the petroleum emulsion processes and the development of the chemical and chemical industries to produce petroleum refining. In the development of industry, the production of demulgators in Grozny has gone through several stages:

Establishment of the first research on chemical demulsification of petroleum emulsions and oils in the 1920s.

Introduction of the industrial method of demulsification of oil emulsions using reagent-demulsifier NPK for dehydration and desalination of Grozny oils in the 1930s.

Establishment of production of non-ionic surfactants in 1940-1950.

Research on the improvement of the NCC demulsifier in 1950-1960.

Research and application of imported demulsifiers in 1970-1980.
Forming the direction of application of non-traditional methods of preparation of Grozny oils using various demulsifiers (from 2000 to the present).
The method of chemical demulsification of oils was first developed in Russia in 1913 by L.F. Berkgan, and in the United States in 1914 by Barnickel.
One of the first, more than 100 years ago, surfactants were used as demulsifiers, which had the ability to change phase interactions at different interfaces. The hypothesis of the chemical nature of adsorption forces and the role of surfactants in oil preparation and refining processes was first proposed by L.G. Gurvich was admitted in 1912-1914.
The research of the American scientist I. Langmur played an important role in studying the effect of surfactants on oil emulsions. Soap solutions were used in the 1920s to break down oil emulsions on an industrial scale in the United States. One of the first demulsifiers was the American Tretolight, consisting of sodium oleate (83%), phenol (4%), water (1%), sodium silicate, sodium rosin soap, and paraffin.
The problem of the use of demulsifiers in the USSR became especially acute in the 1930s, when the production of heavy and emulsion oils increased significantly. Most of the local oils produced before 1930 were separated in tanks only before refining. The same emulsions still obtained in some fields quantitatively accounted for a relatively small fraction of oil production. In most cases, they had low stability and could be broken down by the simplest methods - by sedimentation and heating.
Stable emulsions fell from the tanks after sinking into open water basins, where they decompose completely or partially during prolonged drowning. The upper sedimentary oil layer is poured into the raw material reservoirs, and the lower part is a stable emulsion called puddle or reservoir mud, which resembles the production waste that enters the sewer. Often, this pool is simply burned after a large amount of “dirt” has accumulated. Such "burning of pools" was observed until 1931, especially in the new fields of Grozny.
In Zavodskoye district of Grozny, sedimentary ponds, which began to be filled with oil, oil emulsions and various oil wastes in the early 1930s, still exist today. While the pools have emulsions for months and hard to break down, over the years the oil emulsion has gradually turned into a pure oil called “lake oil”.
This oil completely eliminated gasoline fractions (at least 15%), while in the emulsion state, the oil held the lighter gasoline fractions longer. As a result of contact with air, the oil of the "lakes" turned into a resin, the specific gravity of the emulsion and the viscosity of the oil were significantly increased. The resins formed during the decomposition of the emulsions reduced the surface tension between water and oil. High specific gravity and high viscosity prevented the separation of water and oil.
All researchers have acknowledged that old, air-resistant emulsions are very difficult to break down. Given these factors, as well as the large loss of light oil fractions, sedimentation in water bodies has been recognized as an uncertain method of using oil emulsions. In the 1920s, enterprises in Grozny produced up to 150,000 tons of oil emulsion per year, which was a relatively large and least rationally used piece of oil.
The first researchers of petroleum emulsions at the Grozny Scientific Research Institute were V.A. Selskiy, I.O. Luchinskiy, S.A. Vyshetravskiy, I.N. Ackerman et al [4]. In 1923, V.A. Selsky

underwent microscopic examination of Grozny oils extracted directly from working wells. However, he found that almost 90 percent of the oils contained some or all of the emulsion.

I.O. that emulsions of Grozny oils contain minerals insoluble in water and acids. Luchinsky identified it through his own experiments. Such were the emulsions of the oils flowing from Novye Promyslovy and Salt Balka. However, although the stability of such emulsions was very high, they could be decomposed by boiling with benzene or prolonged treatment with superheated water vapor or superheated petroleum gas.

I.O. The method of disintegration of emulsions used in the Luchinsky plant, proposed and developed by - was carried out by heating at a temperature of 60-120 ° C under a pressure of up to 7 atm. Based on this method, an experimental semi-factory was built in 1923 in new deposits. 1924-1925. At the Central Software Laboratory, Grozneft S.A. Vyshetravsky studied field emulsions of Grozny oils, which aroused great practical interest in the preparation of Grozny oil for refining.

He found that oil emulsions fall into two categories: relatively easily decomposable emulsions (most) and extremely stable and difficult to decompose emulsions (minority). In the 1920s and 1930s, the presence of oil emulsions, especially the stable ones, greatly hindered the refining of oil, so it was necessary to completely or almost completely remove the oil from the emulsions in order to process it in stationary accumulators.

1924-1925. I.N. Ackerman conducted semi-factory-wide experiments on dewatering emulsions using high-voltage currents. These experiments gave positive results for the category of emulsions, which are more prone to disintegration. During this period, other methods of breaking down the emulsion were also developed: heating at different temperatures, using different chemical reagents (sulfuric acid, solvents, etc.), but they were expensive and inefficient.

The main of these methods was the Buch method, which consisted of treating the emulsion with reconstituted sulfuric acid. In Grozny Scientific Research Institute in 1928-1929. Led by S.A. Vyshetravsky continued research on the preparation of oils supplied for refining at the Grozny oil refineries. In the 1930s, A.I. Under his leadership, research was conducted mainly on the preparation of North Caucasus oils for refining.

At this time, much attention was paid to the synthesis of demulsifiers. Researchers have synthesized and tested a large number of demulsifiers, the most effective of which were based on unsaturated fatty acids. When sulfo group is added to these compounds, the efficiency of the reagents is significantly increased. Twitchell reagents (substituted sulfonic acids) and Walker reagents (alkylated aromatic sulfonic acids) began to be widely used. Later, sulfonated castor oil, as well as phenol-formaldehyde, alkyd and glyphthalic resins, were used as demulsifiers.

For many years, the basis for obtaining effective demulsifiers was oleic acid, from which alkylated or arylated amides were obtained. Sodium salts of sulfonated esters of succinic and phthalic acids, amides of sulfoaciruses (sulfoacetic, sulpropion, sulfobutyric) and others were also used.

Beginning in 1934, they began to introduce the chemical method of demulsification, which consisted of the application of deemulgator reagents and the subsequent precipitation of the oil from water and dirt. NBC (neutralized black contact), paraffin alkali wastes, as well as calcium sulfonic acid, aluminum sulfonic acid, and aluminum naphthenates were used as demulsifiers.

NCC was one of the first commercial demulsifiers widely used in the oil industry in the USSR since the 1930s.

NPA is an anionic demulsifier, which is a mixture of sulfonation products, resinous substances, sulfates and others. The demulsifying properties of NPA are mainly reflected in the salts of water-soluble sulfonaphthenic acids - anions. The chemical composition of sulfonaftenic acids in NBC varies and depends on the composition and quality of the distillates obtained for sulfonation.

NPs were obtained primarily as a by-product in the production of Petrov contact, as well as in the purification of petroleum distillates with sulfuric acid, oleum or sulfuric anhydride. As the demand of the Soviet oil industry for demulsifiers increased, special devices were built for the production of NBC by sulfonation of kerosene-gas oil fractions of oil and neutralization of the formed acid resin.

The first plant to produce NBC in the USSR was established in 1943 at the Ufa refinery, in 1952 in Grozny, and then at other plants. In the 1950s, demulsifiers such as anionic NSPs, similar SNS and SSHRD (sulfonated shale resin distillates), sulfonols (alkylaryl sulfonates), and others were developed and used in the USSR oil industry; reagents based on noionic OFAs (oxyethylated fatty acids), OFAlc (oxyethylated fatty alcohols), KS-59 (oxyethylated xylitol monoesters), oxyethylated alkylphenols (OP-10, KAUFE, UFE, OlPASFE) and propylene oxide blockers and ethylene oxides.

The main developers of the reagents were VNIINeftekhim, VNIINP, Giprovostokneft and other specialized research institutes [8]. In 1955-1960, the issue of demulsification and desalination of oils supplied to Grozny refineries became very relevant, as the crude oil of Grozny refineries, in addition to being multi-grade, in some cases with a high content was also distinguished. emulsion water and salts.

During this period, Grozny oil refineries received oils from Western Siberia, Dagestan, Stavropol-Dagestan for refining. At that time, the most polluted eastern sulfur oils of the Ozeksuatskaya, Bugulma and Zhirnovskaya types were processed at the Grozny refineries.

The processing of sufficiently desalinated oils at the Grozny oil refineries led to the breakdown of the plant equipment. In the current situation, there is a need to improve the quality of oil refining in existing dewatering plants and increase their permeability [11]. At GrozNII, samples of surfactants recommended by other institutes and plants were tested as demulsifiers. In 1957, GrozNII together with the staff of the State Oil Refinery conducted a study of electric desalination plants (ELOU) in Grozny. The first task in conducting this research was to improve the quality of the NBC-type demulsifier produced at the Novo-Groznensky plant since 1952.

In 1957 in GrozNII M.P. Bortsova, R.A. Filin and N.P. Studies by Shpichko have shown that the effect of demulsification and desalination depends not only on the properties of the demulsifier, but also on the nature of the oil emulsion.

Studies have shown that the NBC demulsifier prepared in the form of sulfo salts of sour oil fractions did not effectively break down emulsions of sour oils in all cases. For this purpose, NPK began to be used, in which the active substance is the sulfo salts of the paraffin fraction of heavy Malgobek oil, which have an effective effect on emulsions of sour oils.

In addition to the sulfonic acid salts of kerosene-gas-oil fractions, some products of petrochemical processes have also been tested as demulsifiers. Alkylarylsulfonates (synthetic detergents) obtained at the Grozny cracking plant were tested: azolate A and sulfonol NP-2.
Azolate Ozexuate is a satisfactory demulsifier for oil emulsions and is much less active than Bugulma oil emulsions. From the isolation, sulfonol NP-2, which differs mainly in the nature of the alkyl groups, has proven to be an effective demulsifier for both emulsions of Osexuate oil and for sour oils of the Bugulma type.
Demulsifiers based on petroleum fractions of fatty acids and some by-products of synthetic production of phenol at the Grozny Chemical Plant were also tested in these oils. Employees of the Grozny Oil Refinery N. Bondarenko and L.I. At the suggestion of the Kurachinsky, trinatri phosphate was tested as a demulsifier.
The results of research conducted by Grozny Scientific Research Institute on the selection of demulsifiers for various oils are published in his research reports for 1958-1963 * [13]. During this period, the preparation of oil for refining for Grozny refineries was carried out by thermochemical and electrical methods. NBC was used as a demulsifier in the first case, and sodium hydroxide in the second case, but the use of these reagents did not always lead to the desired result. For example, emulsions of Ozeksuatskaya oil, which are characterized by high stability, were not destroyed in the electric field at ELOU.
Ozeksuatskaya oil was crude oil sent to the Grozny refineries by the Stavropol Economic Council. This oil mixture was obtained by deemulgation and dehydration only in the presence of more effective demulsifiers than NBC. In this regard, the selection of more effective demulsifiers from NPK for the preparation of oils supplied to Grozny remains an urgent task.
However, given that the Grozny refineries are not equipped with these demulsifiers, it was advisable to organize the production of more efficient demulsifiers based on local raw materials than NCHK, using the existing production capacity at the Grozny refineries.
In 1960-1963, the Grozny Scientific Research Institute worked in the laboratory on the production of pyrolysis resin from the pyrolysis of petroleum hydrocarbons at the Grozny Chemical Plant, as well as demulsifiers based on local raw materials from scrubber condensate.
A scrubber condensate-based demulsifier is prepared by sulfonating the condensate with sulfuric acid obtained from the alkylation process and then neutralizing the sulfonic acids with a sodium hydroxide solution. The process of preparation of a demulsifier based on pyrolysis resin includes alkylation of resin with olefins in the fractions of thermosetting oil products of kerosene oil, distillation of alkylation products with isolation of the target fraction of alkylate at a temperature of 190-360 ° C. sulfonation of this fraction and neutralization of the sulfonic batch.

Table 1. Comparative characteristics of demulsifiers in petroleum demulsification

Indicators	Demulsifiers				
	Based on the pyrolysis resin of the Grozny Chemical Plant with a thermal cracking kerosene fraction		Sulfonol		NChK Novogrozny Zavod
			Krasnovodsk plant NP1	**NP2**	
The content of active substances, % wt.	43,2	52,7	44,2	50	18,0
Surface tension (days/cm) at surfactant concentration, wt %:					
0,125	36,4	38,6	34,5	37,7	57,3
0,250	34,6	35,9	32,7	32,7	41,9
0,500	30,9	33,2	30,0	32,4	39,4
Consumption, g/t	700	1000	250	—	2700

Industrial tests and research conducted at the Grozny Research Institute have shown that a product capable of deemulgation based on pyrolysis resin of the Grozny Chemical Plant is 5-8 times higher than the NSP produced at the Novo-Grozny Oil Refinery. (Table 1).

The suitability of a pyrolysis resin-based demulsifier as a surfactant in oil production processes has also been confirmed in the laboratory. Grozny Scientific Research Institute developed a scheme for obtaining a resin-based demulsifier for thermal cracking of paraffin oils for pyrolysis of gases and paraffin olefins.

The demulsifier was called SP. In the process of making the demulsifier, the joint venture obtained valuable fractions, which were used as fuel components. Deemulgator SP was tested in emulsions of Stavropol oil. The optimal consumption of SP demulsifier in one-stage thermochemical desalination was 700 g / t of oil. When combining thermochemical method with electric method, the consumption of demulsifier decreased to 250 g / t of oil. The use of SP demulsifier instead of NBC in thermochemical desalination of Stavropol oils gave significant economic benefits, which doubled when using the combined method of desalination.

In industrial conditions, the possibility of destroying emulsions of Osexuate oil with KAUFE14 and UFE8 nonionic surfactants obtained on the basis of ethoxylated phenols * was tested [18]. These surfactants were proposed by LenNIINeftekhim and in 1959-1960. was first industrially tested at oil refineries in the USSR.

The Grozny Scientific Research Institute also conducted industrial trials of OP-7 and OP-10 nonionic surfactants as oil demulsifiers. Reagent-demulsifier OP-7 is a non-ionic surfactant mixture of polyethylene glycol esters of mono- and dialkylphenols with a radical (alkyl residue) containing a carbon atom C8-C10. The OP-10 demulsifier belongs to the same class of chemicals as the OP-7 reagent, the only difference being in the high levels of oxyethylation. OP-7, OP-10 brand reagents are light yellow-light brown oily liquid with a moisture content not exceeding 0.5%.

The surfactant KAUFE14 was found to be the most effective demulsifier of Ozexuat oil. In order to reduce the residual content of chloride salts in the oil below 50 ml / l, thermal desalination consumed 325 g per ton of oil, and NCHK 2-3 kg.

In addition, tests have shown that Ozexuate oil can also undergo electrical desalination using KAUFE14. The amount of chloride salts in the oil was reduced to 40 mg / l, but this result was achieved by consuming KAUFE14 530 g / t. The surfactant UFE8 did not have a demulsifying effect on Osexuate oil.

In the process of demulsification and desalination of oils of the Stavropol Economic Council, as well as Zhirinovskoye oil, nonionic surfactants and alkylarylsulfonates, for example, sulfonols of the Krasnovodsk oil refinery were effective demulsifiers.

Table 2. Demulsification of oil in industrial enterprises.

Installation	Demulsifier	Demulsifier consumption, g/t	Content of chloride salts in oil, mg/l		
			original	after processing	
				the average	minimum
			Oil ozeksuatskaya		
	НЧК	2700	3900	86	66
Thermochemical					
	КАУФЭ 14	325	4000	35	28
	УФЭ$_8$	435	3930	1950	1100
	Сульфонол	220	4100	200	—
	НЧК	3000	3820	2140	—
	КАУФЭ 14	530	2330	96	39
	Sulfonol	260	3890	68	39
			oil zhirnovskoe		
	НЧК	4000	2010	450	—
ELOU					
	NaOH	350	2070	111	Absence
	Sulfonol	200	1310	29	Absence

Tests of sulfonic acid have shown that it can also be used as a demulsifier for Ozexuate oil, however, its consumption should not exceed 220-250 g per ton of oil so that the residual salt content in the oil is less than 50 ml / l.

The main results of demulsification of these oils are given in the table 2.

In the Grozny Scientific Research Institute in 1970-1980, research was conducted on the preparation of local oils for processing using demulsifiers: disolvanes RO (CH2CH2O) CH2CH2OH, diproxamines. H (C3H6O) n1 (C2H4O) m1-N-CH2-CH2-N- (C2H2O) m2 (C3H6O) n2, OZHK - SnH2n + 1COO (C2H4O) mH, etc.).

Disolvanes 4411, 4422, 4490 were often used in oil field preparation. Thus, the use of disolvan 4411 allowed to reduce the water content of commercial oil by 0.5-1% with the specific consumption of 68 g / t of refined oil from the Samgori field.

In the 2000s, the Grozny State Petroleum Institute conducted research on the preparation of oils for refining, and now the Grozny State University of Petroleum Technology (GGNTU) in collaboration with the Astrakhan State Technical University. The study of the effectiveness of

dehydration and desalination of Grozny oils was carried out using non-ionic and oil-soluble demulsifiers: Progalit NM 20/40, Kemelix 3307 X, Hercules 1603.

Progalite NM 20/40 belongs to the class of nonionic surfactants such as block copolymers of ethylene and propylene oxides. The Hercules demulsifier is a mixture of oxyalkylated resins, polyoxyalkylene glycols and other surfactant components and is effective at temperatures around 30 ° C.

Imported demulsifier Kemelix 3307X (UK) is an oil-soluble demulsifier containing ethoxylated phenol-formaldehyde resins mixed with ethoxylated polyglycols or ethoxylated amines. Studies by the authors have shown that selected samples of demulsifiers are effective in the destruction of petroleum emulsions of Grozny oils: improvement of the desalination process with increasing concentration was noted, Hercules demulsifier showed the highest activity, followed by Kemelix. The smallest result of desalination was achieved in the Progalit demulsifier.

Desalination was more difficult for Grozny Chernaya oil, which also studied the effect of magnetic treatment of the Hercules demulsifier on its desalination process. Currently, the requirements for the composition of undesirable components in the oil are increasing, as their presence leads to corrosion of the equipment, significantly reduces the quality characteristics of the resulting oil products and the service life of expensive catalysts.

In this regard, there is the issue of improving the existing processes of desalination and dehydration of oil using non-traditional methods, recently interest has increased significantly. These methods include exposure to various fields, ultrasound, magnetic processing, and more.

The use of these methods in the processing of hydrocarbons allows to increase the yield of light distillates and oil refining. The use of a magnetic field in the desalination, dewatering and primary refining of oil allows to increase the depth of dewatering and desalination and increase the yield of light distillates by 1.1-1.5 times, depending on the raw materials used in the process. Magnetic treatment of hydrocarbon emulsions in some cases improves their stratification. The separation rate of emulsions and their degree of dehydration depend on a number of parameters, among which magnetic induction and flow rate have the greatest effect. The method of magnetic treatment of emulsions can be combined with thermal and chemical methods.

When combining the magnetic treatment of oil with a chemical method, both the mixture of the initial emulsion with the deemulgator solution and the deemulgator solution were magnetically treated, followed by mixing it with emulsions. The study of the effect of magnetic treatment of deemulgator solutions (Kemeliks, Hercules, Progalit) on the desalination efficiency of black oil compared with Moscow and Grape Grozny oils was carried out in a flow magnetic device.

The greatest desalination depth for Chernaya oil from the studied Grozny oils was achieved at all concentrations of demulsifiers included in the oil. Analysis of the magnetic processing factors of Grozny oils shows that the increase in magnetic field induction and the addition of a demulsifier lead to an increase in the degree of emulsion separation. An increase in the flow rate through the core in the studied range reduces the emulsion separation efficiency. A similar but less obvious effect of desalination of paraffin oil is achieved by magnetic treatment of the demulsifier solution added to the oil.

Currently, GGNTU continues research to improve the process of preparing oil for primary refining using non-traditional methods of activation of crude oil under the influence of various types of deposits (electric, acoustic, magnetic).

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