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Synthesis and Study of Demulsifiers Based on hydrolyzed Polyacrylonitrile and Ethylene Oxide

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ABSTRACT: The article shows the demand for demulsifiers in oil production. The demulsifier DE-2 based on polycarboxylates and ethylene oxide was obtained. The optimal ratio of hydrolyzed polyacrylonitrile and ethylene oxide was determined. The forming chemical bonds with IR spectroscopy are shown, and the results of a study on desalting and dehydrating oil with the addition of a synthesized demulsifier

KEY WORDS: demulsifiers, ethylene oxide, hydrolyzed polyacrylonitrile, IR spectroscopy, desalting, dehydrating.

I. INTRODUCTION

Water-oil emulsions are a wide area, and several books have been written on this subject, in particular. As a result of the downhole penetration of the underlying water or the water that is pumped into the formation to maintain pressure, water appears in the oil. During the movement of oil and produced water through pipelines and the wellbore and their mutual mixing, crushing occurs (this process is called dispersion), as a result of which water-oil emulsions are formed. An emulsion is a mixture of two mutually insoluble liquids, one of which is dispersed into the other in the form of small droplets (globules). The dispersed liquid is the dispersed phase (internal), and the liquid in which it is located is the dispersion medium (external).

II. SIGNIFICANCE OF THE SYSTEM

The paper mainly focuses on how to get effective demulsifiers for the destruction of water-oil emulsion and their application. The study of literature survey is presented in section III, Methodology is explained in section IV, section V covers the experimental results of the study, and section VI discusses the future study and Conclusion.

III. LITERATURE SURVEY

Oil emulsions are divided into the following three groups [3, 6]: Group I - water in oil (reverse type emulsion), in which the water content (dispersed phase) in oil (dispersion medium) ranges from traces to 90 -95% vol. Group II - oil in water (emulsions of direct type), which are formed in the processes of oil demulsification, i.e. at destruction of the return water-oil emulsions. Group III is a multiple emulsion, which are distinguished by a high content of mechanical impurities.

Studies show that multiple emulsions, in contrast to the inverse and direct emulsions, contain a large amount of mechanical impurities. The dispersed phase (water) of such emulsions is itself an emulsion, which contains particles of another phase (oil particles).

Multiple emulsions mainly refer to the so-called "trap" oil-water emulsions, which are formed during the preparation of oil in the fields

Demulsification is the destruction of the emulsion in the oil and water phases. From a technological point of view, oil producers are interested in two aspects of de-emulsification: the speed at which destruction occurs and the amount of water remaining in the crude oil after preparation. Extracted oil should usually comply with the specifications of the company and pipeline transport; therefore, the oil is desalted and dehydrated beforehand in the oil fields. A low content of water and chlorides in the oil is required to reduce the corrosive effects and salt deposits. At refineries, the main task is to remove inorganic salts (mainly chloride) from crude oil before they cause corrosion or other harmful effects on refining equipment.

Extracted oil emulsions have a degree of kinetic stability due to the formation of interfacial films surrounding water droplets. In order to separate the emulsion into oil and water, the interfacial film must be destroyed, resulting in coalescence of the droplets and separation of the aqueous phase. Therefore, the destabilization of emulsions is very closely related to the destruction of this interfacial film. Factors affecting the phase boundary and, consequently, the stability of emulsions were discussed earlier (the dispersive properties of formation water and oil, water content, natural emulsifiers, particulate matter, etc.)[1-6].

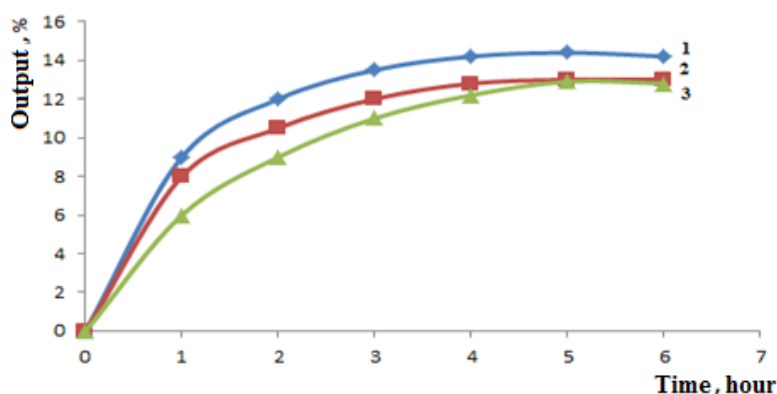
IV. METHODOLOGY

For the synthesis of the demulsifier used hydrolyzed polyacrylonitrile. Unlike the previous hydrolyzed polyacrylonitrile, polyacrylonitrile was hydrolyzed completely, before the formation of COONa groups, but in the structure obtained there is present - CONH₂. Then the obtained hydrolyzed polyacrylonitrile was neutralized to pH 8-9 with hydrochloric acid. This forms -COOH groups that react easily with ethylene oxide.

In the production of chemical products plays an important role and the time of the reaction. For this case, four ratios of initial products were also chosen. The figure below shows the dependence of the demulsifier yield on the reaction time at a temperature of 80 ° C.

V. EXPERIMENTAL RESULTS

As can be seen in Figure 1, 14.4% yield of demulsifier is obtained by carrying out the reaction under optimal conditions for 5 hours. Further continuation of the reaction under these conditions leads to a decrease in yield. This is due to the enhancement of parallel reactions (such as crosslinking, decomposition, intermolecular interaction, etc.), which lead to a decrease in the demulsifying effect of oligomeric demulsifiers.

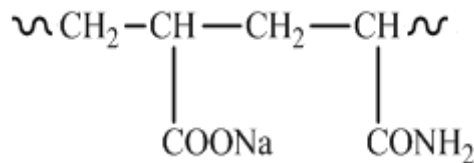


The ratio of hydrolyzed polyacrylonitrile and ethylene oxide; 1-1: 8; 2-1: 5; 3-1: 2.

Fig 1. Dependence of the output of demulsifier from time.

Thus, the optimal conditions for obtaining demulsifier, is to conduct the reaction at a temperature of 80 ° C for 5 hours at a ratio of initial products of 1: 8. The product obtained under these conditions has a very good demulsifying effect. Further investigation of the effect of demulsifier on the properties of the oil emulsion is carried out by the product obtained under the above conditions. As can be seen on the infrared spectrum of hydrolyzed polyacrylonitrile, the absorption bands, which manifest themselves in the region of 1550–1610 cm⁻¹, are characteristic of asymmetric

stretching vibrations of functional groups — COONa. The functional group - COONa has absorption bands characteristic of symmetric stretching vibrations in the region of 1400 cm^{-1} . In addition, the manifested absorption bands in the region of $3000\text{--}3200\text{ cm}^{-1}$ show that the structure of the raw material contains functional groups --CONH_2 . Based on the infrared spectrum of hydrolyzed polyacrylonitrile, it can be said that the structure of the raw material contains mainly the following functional groups.



As can be seen in Figure 2, the absorption bands, which manifest themselves in the region of $1550\text{--}1610\text{ cm}^{-1}$, are characteristic of asymmetric stretching vibrations of functional groups — COONa. These functional groups do not react with ethylene oxide.

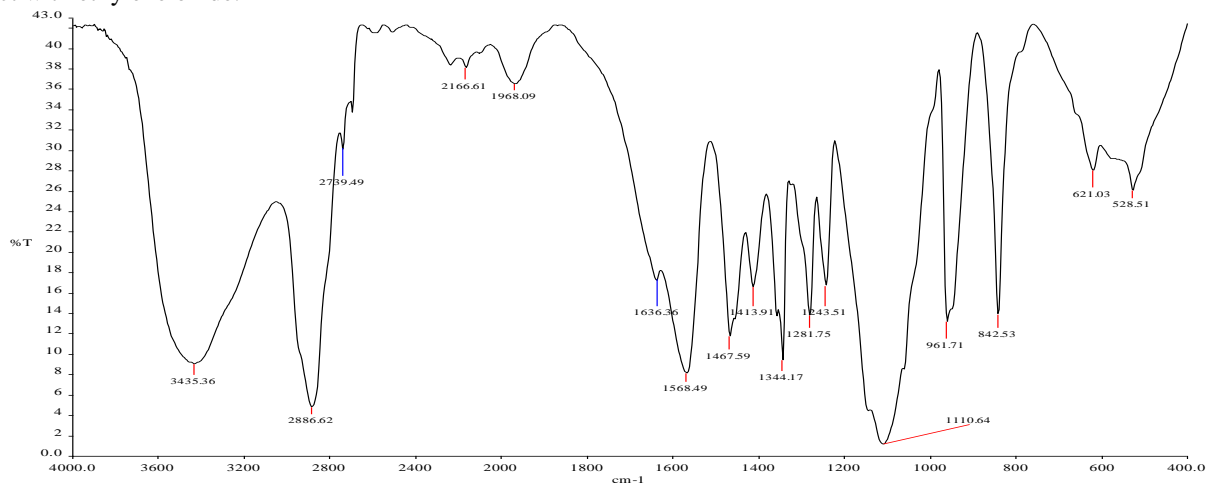


Fig 2. IR spectrum of the obtained demulsifier

The absorption bands in the region of $1300\text{--}1200$ and 1413 cm^{-1} are characteristic of functional groups — COOH. These functional groups react with ethylene oxide, but not completely. Absorption bands in the region of 1243 cm^{-1} are characteristic of ester groups that were formed during the interaction of functional groups — COOH with ethylene oxide. The absorption bands in the region of $1150\text{--}1070\text{ cm}^{-1}$ are characteristic of ether linkages, which formed between themselves two molecules of ethylene oxide.

The results of studies, placed in table 1, show that good results on desalting and dehydration of typical oil can be using obtained demulsifier in an amount of $30\text{--}40\text{ g / t}$. The degree of desalting and dehydration depends, first of all, on the initial content of salts and water in the oil. Thus, with the salt content of 505 mg / l of oil, it is possible to desalt the oil by 91.1% , with the salt content of 775 and 1438 mg/l , only by 57.7 and 69.3% . An increase in the consumption of the demulsifier above 40 g / t does not significantly reduce the residual salt content, leaving it sufficiently high ($35\text{--}51\text{ mg / l}$). The use of a demulsifier allows to obtain oil with a salt content of 14 mg / l with a consumption of demulsifier in the amount of 20 g / t and 10% of wash water.

Table 1. Results of desalting and dehydration of oil

№	Crude oil		Demulsifier	The amount of demulsifier, g / t	Content after desalting		Removed	
	salt, mg / l	Water %			salts, mg / l	water, %	salts, %	water, % of the original
Thermo chemical desalination at 60 ° C								
1	505	3,26	Obtained demulsifier	20	45,0	0,25	91,1	92,4
2	1438	5,20	Obtained demulsifier	20	441,0	1,90	69,3	63,2
3	775	4,00	Obtained demulsifier	20	327,9	1,85	57,7	53,8
4	505	3,26	Obtained demulsifier	30	5,6	0,54	98,9	83,4
5	1438	5,20	Obtained demulsifier	30	441,0	1,95	69,4	62,5
6	775	4,00	Obtained demulsifier	30	170,5	1,00	78,0	75,0
7	775	4,00	Obtained demulsifier	40	59,6	0,42	92,3	89,5
8	775	4,00	Obtained demulsifier	50	51,6	0,42	93,5	89,5
9	505	3,26	Obtained demulsifier	0	147,0	1,19	70,9	63,5
10	1108	4,60	Obtained demulsifier	30	1066,0	4,00	4,0	12,8
11	775	4,00	Obtained demulsifier	30	95,7	0,60	87,8	85,0

The resulting demulsifier turned out to be more efficient than the other demulsifiers. Obtained demulsifier can be used for oil desalting. With the consumption of DE-2 30–40 g / g and water — 10% by weight, desalination in one step allows preparing oil to a salt content of 14–15 mg / l.

As a result of the conducted experiments, it was established that at the first stage of thermo chemical processing, oil was obtained corresponding to the first group of prepared oil. After repeated thermo chemical treatment under the same conditions, oil was obtained, ready for further processing at the refinery. In tab. 2 also shows the conditions for the treatment of oil-water emulsions and the properties of the treated oils using demulsifiers developed by us. Are given in table. 2 data show that the degree of preparation of all types of oil using the developed demulsifier is higher than the known one.

Table 2.the effectiveness of the action of demulsifiers

Indicators	Oil							
	Prepared oil West To shli		Crude oil from EAST To shli		Water-oil emulsion of the North. Pamuk		Prepared oil field Northshurtan	
Temperature, ° C	80	80	80	80	60	60	80	80
Pressure, atm	1	1	1	1	1	1	1	1
Expenditure rate, g / t	10	5	30	30	30	30	14	10
The degree of dehydration,%	93	95,5	86	96	93,4	98	92	95
Residual salt content in dry oil, mg / dm ³	<2	<2	67	51	39	20	<2	<2
The time of separation of the emulsion, min	60	60	60	60	180	180	120	120

The demulsifiers intended for introduction at the sites of production, collection, preparation and transportation of hydrocarbon raw materials of the field were tested in laboratory conditions. Demulsifiers are multi-type, suitable for the destruction of various types of water-oil emulsions. They are composite compositions based on surfactants dissolved in organic solvents. The tested demulsifier is a composition based on block copolymers of ethylene oxide and is designed for dehydration and desalting of oil emulsions in the process of collecting and preparing oil in the fields.

VI. CONCLUSION AND FUTURE WORK

Thus, a technology for the production of a demulsifier based on local raw materials has been developed. As a result of the study of the synthesis of demulsifiers, the optimal production modes were chosen. According to technical indicators, demulsifiers meet all the requirements of GOST.

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