UDC 665.622.43

RESEARCH OF PROPERTIES OF KNOWN (RS-N) AND DEVELOPED DEMULSIFIERS FOR DEWATERING AND DESALTING OF OIL-WATER EMULSIONS

Yasakov E.A
Ufa State Petroleum Technological University
email: Kavich@bk.ru

M.L. Pavlov, R.A. Basimova
Scientific and Technical Centre ,,Salavatnefteorgsintez"

New compositions of demulsifiers have been developed for breaking of oil-water emulsions. Demulsifying ability has been researched for known (RS-N) and developed demulsifiers at breaking emulsions of three different types of crude oils. Optimal concentrations of demulsifiers have been selected.

Keywords: *preparation of oil, efficiency of separation, breaking of oil-water emulsions, development of compositions of demulsifier, demulsifying ability of demulsifier*

INTRODUCTION

The initial stage of oil fields development is characterized by water-free recovery of oil from flowing wells. However the water content in oil will increase during exploitation of wells. This fact leads to increasing in price of its transportation and refining. The salts dissolved in water and also mechanical impurities, containing in oil, cause corrosion and erosion of equipment. The presence of emulsifiers in oil (surfactants) such as resins, asphaltenes, and high-melting paraffins promotes formation of high-stable oil-water emulsions [1-3].

The crude oil previously dewatered on oil fields arrives to refinery where undergoes a stage of the further preparation to refining at electric desalting unit. Thus the deep removal of salts is occurred by the use of wash water under influence of electric field. The various oil-water emulsions are formed at all stages of oil preparation by washing with water. Breaking of these emulsions is carried out by using synthetic surfactants (demulsifiers) which are added to oil emulsion. Role of demulsifier consists in demulsification and prevention of its repeated formation due to decrease of mechanical strength of the protective shells which are formed on surface of water drops. The reagent is injected into emulsion and mixed with it. After that water is removed from oil

by sedimentation. Modern demulsifiers must provide full removal of water and salts, must be cheap, accessible, non-toxic and have the small consumption per ton of oil.

At JSC „Salavatnefteorgsintez" the oil preparation process is carried out at three units of refinery. The demulsifiers RS-N and RS which are developed by „Salavat-nefteorgsintez" and protected by patents of the Russian Federation are used as demulsifiers. [4-5]. They are effective enough, but the goal of selection and development of new, more effective demulsifiers always remains actual. It is so, because the solution of this object can considerably improve process of oil preparation. As a result ecology of environment will be improved and additional profit for enterprise will be generated.

OBJECTS AND METHODS OF RESEARCH

Object of research is development of new compositions of demulsifier for breaking of oil-water emulsions and selection of conditions for its application in comparison with known demulsifier (RS-N) at treatment of three different types of oil.

The following oils have been used at studying of properties and methods for demulsifiers application. It was West-Siberian oil, a crude oil of Salavat and Orenburg fields. Base properties of oil are represented in table 1.

Table 1

Properties of oil

Parameters	Oil		
	West-Siberian	Orenburg	Salavat
Density at 20 ºC, g/cm^3	0,882	1,071	0,884
Volume content of water, %	traces	61	1
Mass concentration of chlorides, mg/dm^3	10	635	540

The process of dewatering and desalting of oil has been studied in following conditions:

Quantity of demulsifier, g/t of oil	3, 5 , 10, 14, 20, 30
Pressure, atm	1
Temperature, ºC	60; 80
Time of experiment, min.	60 - 180
Temperature of wash water, ºC	70 - 80

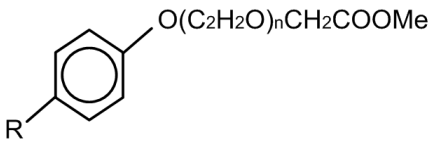
Methodology of demulsifying ability determination for demulsifiers is represented below. For preparation of stable oil-water emulsion 200 cm^3 of the oil, required quantity of demulsifier (by means of the microdispenser), 2 % aqueous solution of alkali (NaOH) in amount of 0,4 cm^3 and 50 cm^3 of distilled water at temperature 70-80 ºC have been filled into a separatory funnel. After that a mixture has been mixed during 7 minutes. The speed of rotation of the mixer is 600 rpm. The obtained oil-water emulsion has been put into the thermostat at temperature 60 or 80 ºC. After that the volume of separated water has been measured through every 15 minutes. Simultaneously the intensity of colouring of aqueous layer (presence of dissolved hydrocarbons) and clearness of interphase boundary have been evaluated visually.

Water content in crude oil has been determined by method of Dyne-Stark [6]. The content of chloride salts has been determined by titrometric analysis [7].

DEVELOPMENT OF NEW COMPOSITIONS OF DEMULSIFIER

New compositions of demulsifier have been obtained by simple mixing of components (synthetic surfactant, modifying additives and methanol-aldehydic fraction) at ambient temperature (20 - 25 ºC) in certain ratio up to getting of homogeneous solution (without visible suspended particles, cloud and sediment).

The sodium, potassium or sodium-potassium salt of carboxymethylate of oxyethylated isononylphenol (Sinterol of Technical Requirements 2484-088-05766575-2000) has been used as surfactant (anionic surfactant). It has the following structural formula:



,

where: R – C_9H_{19};

n – number of oxyethylated groups: 4, 6, 10, 12.

The nitrogen components (amides of acids) and polar electrolytes have been used as modifying additives. The amides of acids are formamide (Technical Requirements 6-09-11-2152-94), dimethylacetamide (Technical Requirements 2636-113-44493179-08) and carbamide (State Standard 2081-92). The polar electrolytes are

threesodiumphosphate (State Standard 201-76), soda ash and caustic soda (State Standard 5100-85 and State Standard 4328-77).

The methanol-aldehydic fraction has been used as a solvent. The methanol-aldehydic fraction is a waste product of butyl alcohols production (Technical Requirements 2421-111-05766575-2003).

Compositions of new demulsifier include 25 - 48 % wt. of surfactant, 3 - 8 % wt. of modifying additives (including amides of acids in range 1 - 6 % wt. and polar electrolytes in range 1 - 4 % wt.), 1 - 72 % wt. of methanol-aldehydic fraction and 0 - 43 % wt. of water.

RESULTS AND DISCUSSION

Research of demulsifying ability of demulsifiers by example of the prepared West-Siberian oil

Efficiency of separation versus time of emulsion separation at different concentrations of known (RS-N) and developed demulsifiers is represented on fig. 1 and 2.

The data on fig. 1 and 2 show that demulsifier of known composition has high enough demulsifying ability at oil-water emulsion breaking at concentrations equal 10 and 14 g/t. The developed demulsifier has high enough demulsifying ability at oil-water emulsion breaking at concentrations equal 5 and 10 g/t. It is necessary to note that at concentrations equal 10 and 14 g/t, demulsifier RS-N shows very close results, but optimal concentration is 10 g/t because more effective dewatering and desalting of oil occurs (efficiency of separation equal 93 %) at this concentration. The concentration equal 14 g/t is economically unattractive. The optimal concentration for developed demulsifier is 5 g/t because increase of concentration twice as much increases the efficiency of separation only by 0,5 % and efficiency of separation is 95,5 %.

It has been also shown that the time of oil emulsion separation for the developed demulsifier is reduced almost twice at the equal concentration of demulsifiers. The residual content of chlorides in oil did not exceed 2 mg/dm^3 in all experiments.

Thus the recommended concentration of demulsifier RS-N is 10 g/t. The recommended concentration of developed demulsifier is 5 g/t of processed oil.

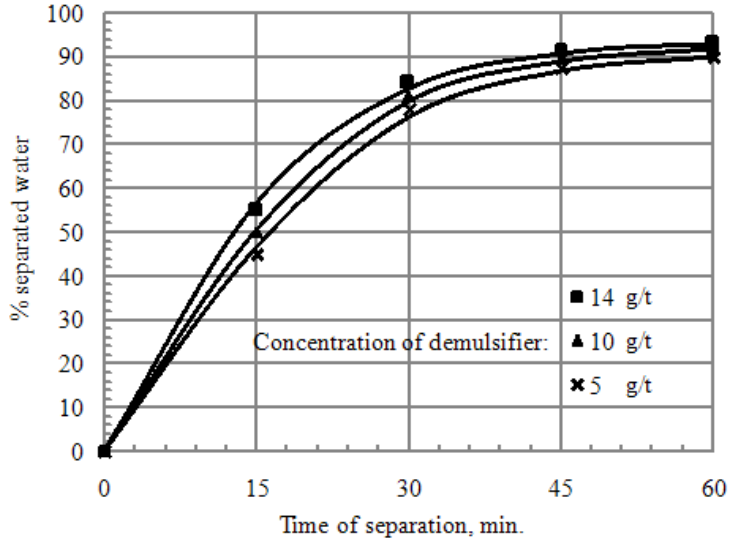


Figure 1. Efficiency of separation versus
time of emulsion separation for known demulsifier (RS-N)

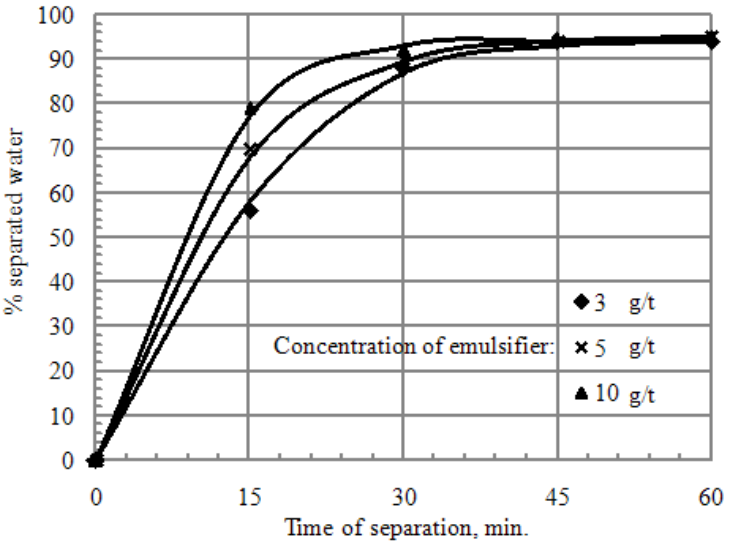


Figure 2. Efficiency of separation
versus time of emulsion separation for developed demulsifier

Research of demulsifying ability of demulsifiers by example of the Salavat field crude oil

Efficiency of separation versus time of emulsion separation at different concentrations of known (RS-N) and developed demulsifiers is represented on fig. 3 and 4.

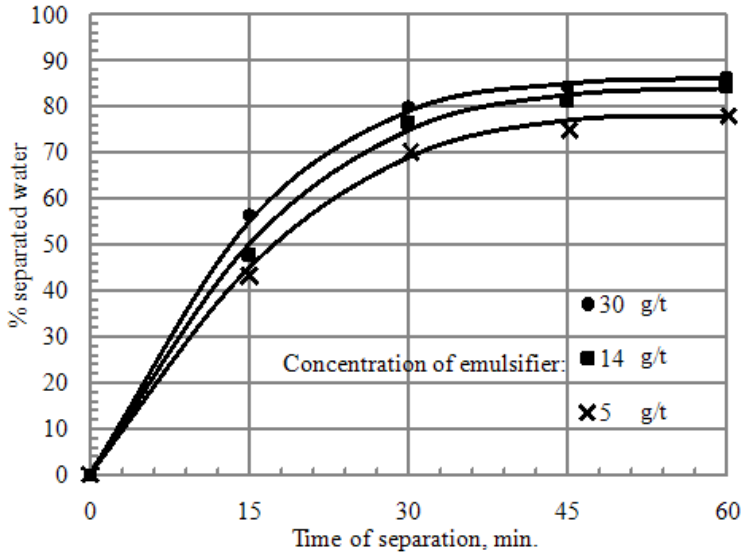


Figure 3. Efficiency of separation
versus time of emulsion separation for known demulsifier (RS-N)

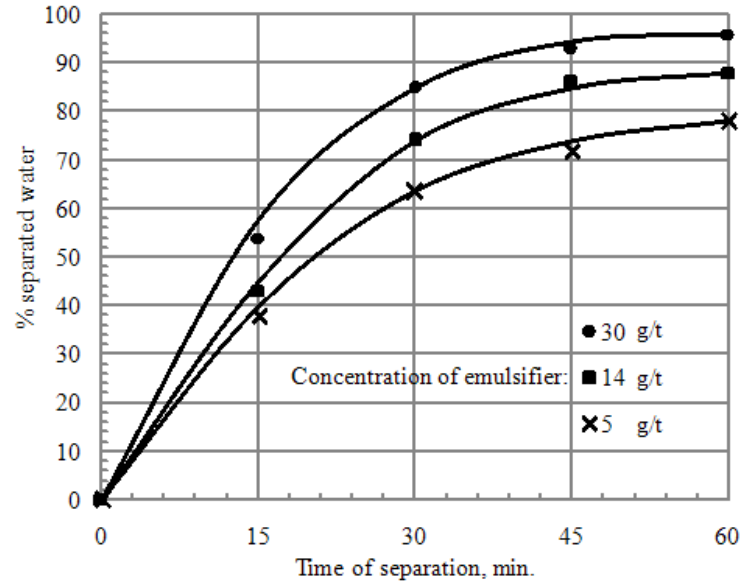


Figure 4. Efficiency of separation
versus time of emulsion separation for developed demulsifier

The demulsifier of known composition has high enough demulsifying ability at oil-water emulsion breaking at concentrations equal 14 and 30 g/t (efficiency of separation equal 84 % and 86 %). The developed demulsifier at the same concentrations achieve efficiency of separation equal 88 % and 96 %, accordingly. It is necessary to note that at concentrations equal 14 and 30 g/t, demulsifier RS-N shows very close results, but optimal concentration is 30 g/t because more effective dewatering and desalting

of oil occurs at this concentration. The optimal concentration for developed demulsifier is 30 g/t because decrease of concentration twice as much decreases the efficiency of separation at 8 % and efficiency of separation is 88 %. The residual content of chlorides in dewatered oil is 72 mg/dm^3 against 51 mg/dm^3 at concentration equal 30 g/t.

The residual content of chlorides in oil was in the range of 51-84 mg/dm^3 in all experiments. The recommended concentration of demulsifier RS-N and developed demulsifier is 30 g/t for both of them.

As a result of the made experiments it has been determined that the Salavat field crude oil (the well № 6) confirms to the first group of the prepared oil after using of RS-N and developed demulsifiers [8].

Research of demulsifying ability of demulsifiers by example of Orenburg field crude oil

The oil-water emulsion in experiments has been undergone by two thermochemical stages. Thereby the stages of oil pretreatment at the oil field and complete treatment at refinery have been simulated. Efficiency of separation versus time of emulsion separation at different concentrations of known (RS-N) and developed demulsifiers is represented on fig. 5 and 6.

The data on fig. 5 and 6 show that demulsifier of known composition has high enough demulsifying ability at oil-water emulsion breaking at concentrations equal 20 and 30 g/t (efficiency of separation equal 84,4 % and 93,4 %). The developed demulsifier at the same concentrations achieve efficiency of separation equal 88,5 % and 98 %, accordingly. It should be noted that the optimal concentration for known (RS-N) demulsifier is 30 g/t because more effective dewatering and desalting of oil occurs at this concentration. The optimal concentration for developed demulsifier is 30 g/t also (efficiency of separation equal 98 %, the content of chlorides in oil equal 20 mg/dm^3) because decrease of concentration one and a half time as much decreases the efficiency of separation at 9,5 %, and the content of chlorides is 34 mg/dm^3.

The residual content of chlorides in oil was in the range of 20-65 mg/dm^3 in all experiments. The recommended concentration of demulsifier RS-N and developed demulsifier is 30 g/t for both of them.

After the first stage of thermochemical processing the oil has been undergone by the second stages of thermochemical processing in order to get the oil which is ready for further processing at refinery. The second stage has been occurred at temperature 80 ºC.

Efficiency of separation versus time of emulsion separation at different concentrations of known (RS-N) and developed demulsifiers is represented on fig. 7 and 8.

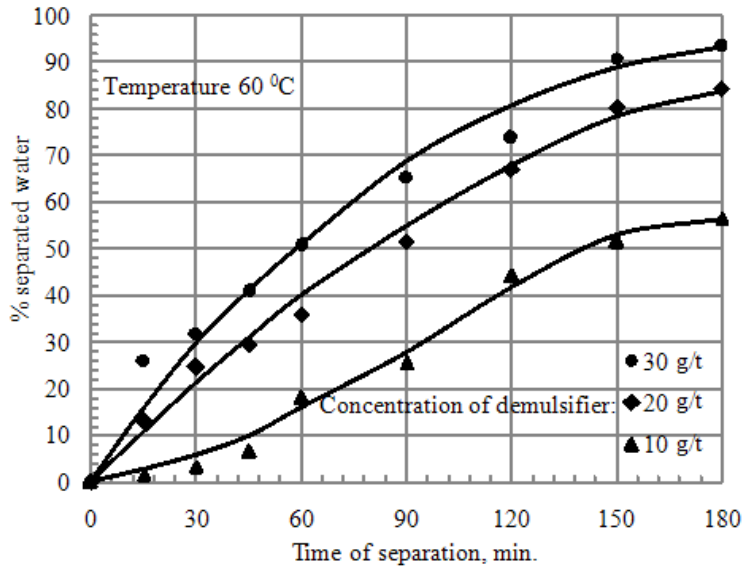


Figure 5. Efficiency of separation versus
time of emulsion separation for known demulsifier (RS-N)

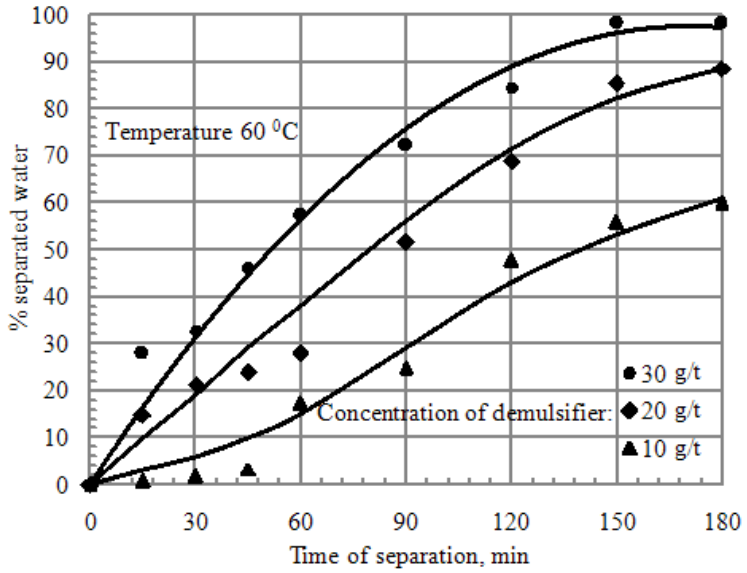


Figure 6. Efficiency of separation versus time
of emulsion separation for developed demulsifier

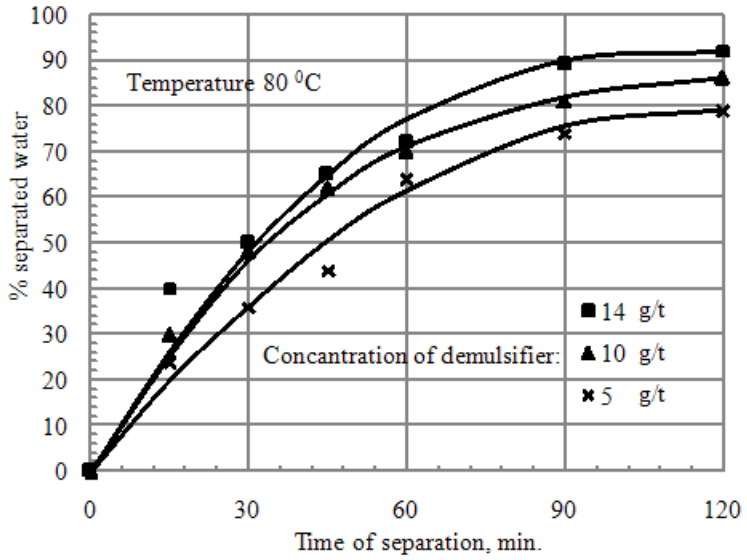


Figure 7. Efficiency of separation versus time of emulsion separation for known demulsifier (RS-N)

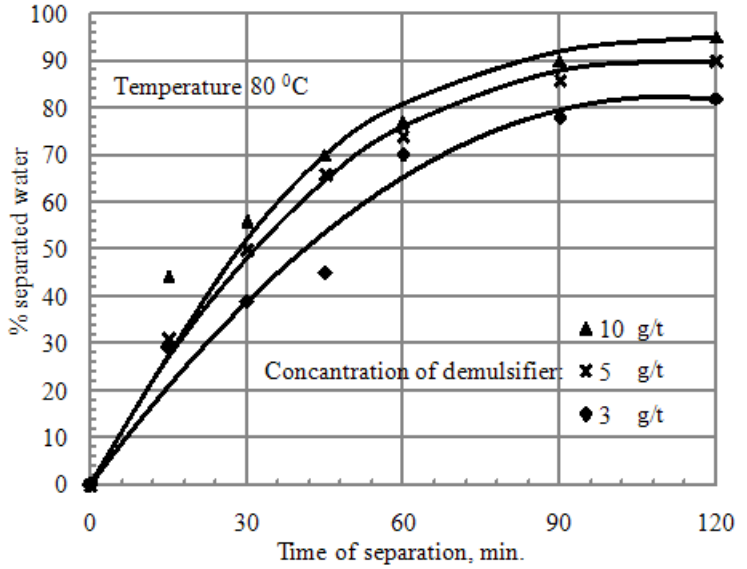


Figure 8. Efficiency of separation versus time of emulsion separation for developed demulsifier

The data on fig. 7 and 8 show that demulsifier of known composition has high enough demulsifying ability at oil-water emulsion breaking at concentrations equal 10 and 14 g/t. The developed demulsifier has demulsifying ability at oil-water emulsion breaking at concentrations equal 5 and 10 g/t. It is necessary to note that at concentrations equal 10 and 14 g/t, demulsifier RS-N shows very close results, but optimal concentration is 14 g/t because more effective dewatering and desalting of oil occurs (efficiency of separation equal 92 %) at this concentration. The optimal concentration for

developed demulsifier is 10 g/t because decrease of concentration twice as much decreases the efficiency of separation by 5 % and efficiency of separation is 90 %. The residual content of chlorides in oil did not exceed 2 mg/dm^3 in all experiments.

Thus the recommended concentration of demulsifier RS-N is 14 g/t. The recommended concentration of developed demulsifier is 10 g/t of processed oil.

As a result of the made experiments it has been determined that after the first stage of thermochemical preparation the produced oil confirms to the first group of the prepared oil [8]. After the second thermochemical preparation at the same conditions the oil which is ready for further processing at refinery has been obtained.

The achieved efficiency of separation for all observed types of oils at optimal concentrations for known and developed demulsifier has been compared by us (fig. 9).

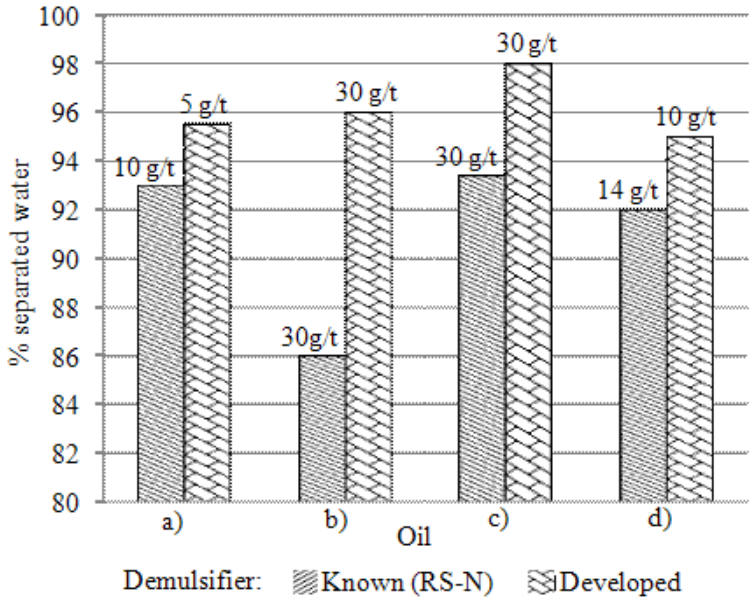


Figure 9. Comparison of efficiency of separation of oil at optimal concentrations of demulsifiers:
a) prepared West-Siberian oil;
b) crude oil of Salavat field;
c) oil-water emulsion of Orenburg field;
d) prepared oil of Orenburg field.

The conditions of oil-water emulsion processing and properties of prepared oils at using known (RS-N) and developed demulsifiers are represented in table 2.

Table 2

Comparison of effectiveness of demulsifiers

Parameters	Oil							
	Prepared West-Siberian oil		Crude oil of Salavat field		Oil-water emulsion of Orenburg field		Prepared oil of Orenburg field	
Demulsifier	RS-N	Deve-loped	RS-N	Deve-loped	RS-N	Deve-loped	RS-N	Deve-loped
Temperature, °C	80	80	80	80	60	60	80	80
Pressure, atm	1	1	1	1	1	1	1	1
Concentration of demulsifier, g/t	10	5	30	30	30	30	14	10
Efficiency of separation, %	93	95,5	86	96	93,4	98	92	95
Residual content of salt in dewatered oil, mg/dm^3	<2	<2	67	51	39	20	<2	<2
Time of emulsion separation, min	60	60	60	60	180	180	120	120

The data in table 2 show that efficiency of separation for all types of oils is higher at using of developed demulsifier in comparison with known one.

CONCLUSIONS

1. New compositions of demulsifier for breaking of oil-water emulsions are developed. They contain anionic surfactant (Sinterol) in range of 25 - 48 % wt., modifying additives (3 - 8 % wt.) and solvent (methanol-aldehydic fraction and water) in range of 1 - 72 % wt. and 0 - 43 % wt., accordingly.

2. Laboratory comparative researches of known (RS-N) and developed demulsifiers have been made on three different types of oils (West-Siberian, Salavat, Orenburg). It has been shown that the efficiency of separation of West-Siberian and Salavat oil achieves 95,5 and 96 % while using developed demulsifier. The efficiency of separation achieves 93 and 86 %, accordingly while using known demulsifier. At the first stage of Orenburg oil preparation the efficiency of separation for developed and known demulsifiers is 98 and 93,4 %. At the second stage the efficiency of separation for developed and known demulsifiers is 95 and 93 %, accordingly.

3. It has been determined that at preparation of the West-Siberian and Orenburg oils the concentration of developed demulsifier 2 - 1,5 times less, than for known one. The concentrations of demulsifier are 5 and 10 g/t of oil, accordingly. It has been noted that the velocity of separation of oil-water emulsion is higher while using developed demulsifier.

4. It has been shown that the developed demulsifier is more effective, than known one. Experimental-industrial batches of new demulsifier can be produced in scientific and technological centre of JSC ,,Salavatnefteorgsintez" according to existing technological scheme which is used for production of demulsifier RS-N currently.

REFERENCES

1. Ахметов С.А. Технология глубокой переработки нефти и газа. – Уфа: Издательство "Гилем", 2000. – 672 с.

2. Левченко Д.Н., Бергштейн Н.В., Худякова А.Д. и др. Эмульсии нефти с водой и методы их разрушения. – М.: Химия, 1967. – 200 с.

3. Мовсумзаде Э.М., Мастобаев Б.Н., Зорина С., Дмитриева Т.В. Некоторые химические препараты для подготовки нефти к переработке и транспорту // Нефтепереработка и нефтехимия. – 2000. – № 12 – С. 38-43.

4. Patent of the Russian Federation № 2278145. Composition for dewatering and desalting of oil emulsions / R.A. Basimova, A.A. Galyutdinov, H.H. Rakhimov, V.L. Kadnikov, G.N. Melnikov.

5. Patent of the Russian Federation № 2244733. A method of dewatering and desalting of oil / R.A. Basimova, A.A. Galyutdinov, V.N. Greshnov, M.R. Zidihanov, M.H. Ishmijarov, H.H. Rakhimov, M.N. Rogov.

6. State Standard 14870-77. Products chemical. Methods of definition of water. - M: Publishing house of standards, 1977. - 14 p.

7 State Standard 21534-76. Methods of definition of the content of chloride salts. - M: Publishing house of standards, 1976. - 17 p.

8. State Standard 51858-2002. Crude petroleum. General specifications. - M: Publishing house of standards, 2002. - 12 p.