



Research of New Demulsifier in Bohai Oilfield

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Abstract: The content of asphalt in an EOR oilfield of Bohai is high, reaching more than 30%, and the content of phenol and naphthenic acid is also high, resulting in high acid value of crude oil. The water content is about 85% - 95%, and it is in the later stage of mining. Because hydrophobically associating PAM is used as oil displacement agent in the platform, it is difficult to degrade and seriously affects the demulsifier. The oil-water interfacial film formed by polymer, gum and asphalt is very firm, which increases the difficulty of dehydration. There is no ideal product in the selection and application of reverse demulsifier for heavy crude oil with high content of asphalt, high water content and high acid value. In this experiment, triethanolamine was selected as the starting agent from the aspect of branching and introducing nitrogen element, and water-soluble triblock polyether was synthesized according to the ratio of PO: EO: PO=2:7:6, and then crosslinked with 3% (relative polyether mass) epichlorohydrin. In the process, the crosslinking temperature was 80°C, the reaction time was 5h, and potassium hydroxide solution was used as catalyst. At last, the demulsifier product with good effect of clear water was made, and good effect was obtained in field application.

Keywords: Triethanolamine, Demulsifier, Epichlorohydrin, Polyether, Heavy Oil

1. Introduction

Chemical demulsifier has become more and more mature after the development of three generation products. Now, it is mainly focused on the methods of head modification, tail changing, bone addition, chain expansion, grafting, cross-linking, and compound [1, 2]. The changing of the head and cross-linking occupy the main means of modification, and the effect is good. In the process of head modification, the starting agent changed from polyols, polyene polyamines to phenol (aldehyde) amine resins. The basic change was to study the targets of multi branches, large molecular weight and heteroatoms [3, 4].

2. Experiment

The average surface density of this oilfield crude oil is 0.981g/cm³, and the average surface viscosity is 1210.8 MPa · s; The average wax content is 3.8%, the average sulfur content is 0.25%, the asphalt content is 11%, the gum content is 15.2% - 37%, the acid value is 4.79mg-KOH/g, and the API value is about 10, which is a heavy heavy oil [5]. The

existence of natural emulsifier is easy to form w/o film. At the same time, the polymer AP-P4 will be degraded into short chain polyacrylic acid salt and a small amount of quaternary ammonium salt in the formation. On the one hand, the formation water is of NaHCO₃ type, which is easy to form hydrolyzed polyacrylic acid monovalent salt, and tends to form o/w emulsifier; On the other hand, quaternary ammonium salt is easy to adsorb on the anionic sandstone surface, which reduces the permeability of crude oil, even more than 60%. The existence of w/o and o/w films makes the system form a complex membrane structure such as o/w/o or w/o/w, which increases the difficulty of demulsification [6]. In view of this situation, the following modification methods were carried out: TDI crosslinking [7], star structure [8], acrylation [9], organosilicon modification [10], anion modification [11], phenol amine resin initiator [12], and the effect was not good. Because of the high content and high polarity of colloidal asphaltene in the oilfield, demulsifier with strong polarity should be used. Because amine group is easy to absorb the material with strong polarity, it should contain necessary nitrogen atoms. After analysis, a new demulsifier must be studied by selecting suitable starting agent. In this experiment, triethanolamine was used as the

starting agent to study a new demulsifier. It not only meets the requirements of introducing nitrogen atoms, but also satisfies the structure of multi branches.

2.1. Materials and Instruments

Triethanolamine, PO, EO, KOH, Epichlorohydrin (all are industrial grade);

Integrated manifold oil sample, 20-200 μ L adjustable micro pipette (planland), multiple light scattering instrument (turbiscanlab), and infrared analyzer (Bruker vertex 70).

2.2. Experiment Method

(1) Preparation of Demulsifier

Add quantitative triethanolamine and potassium hydroxide into the autoclave, deoxidize with N₂, replace for three times, and vacuum. A certain amount of PO was added at 135 \pm 5 $^{\circ}$ C, until the reaction was complete; Then control the kettle temperature at 120 \pm 5 $^{\circ}$ C, a certain amount of EO was added at 5 $^{\circ}$ C until the reaction was complete; Raise the temperature to 135 \pm 5 $^{\circ}$ C, and PO was added into the autoclave. When the reaction is complete, the polyether product is formed;

The polyether product is added into a four port glass bottle, and then a quantitative KOH solution (5mol/L) is added, which is stirred evenly at 60 $^{\circ}$ C, and then epichlorohydrin is added into the bottle. After dropping, the temperature is raised to 80 $^{\circ}$ C for 5h. After that, the final product is got, by lowering the temperature.

(2) Demulsification and water-clarifying experiment

Refer to Q/HS 2020-2004 «quality inspection method of crude oil demulsifier» and SY/T 5797-93 «performance evaluation method of oil in water emulsion demulsifier», the effect of demulsifier on SZ36-1cepk manifold oil water sample is investigated.

First, under the simulated field conditions, different types and concentrations of the comprehensive demulsifiers to be evaluated are used to treat the manifold oil and water samples. Then, the size, firmness, generation time, floc floating speed, water color and clarity of the treated flocs at the oil-water interface are observed to determine the application effect of the comprehensive demulsifier. The demulsifier that can quickly produce large floating flocs and is stable, and the water color is clear and transparent. The specific operation steps are as follows:

1) Take the oil and water sample from the manifold, and shake it evenly, then pour it into the dehydrating bottle, and heat it in a constant temperature water bath at 70 $^{\circ}$ C;

2) After heating for 10 minutes, add the reagent into the dehydrating bottle according to the predetermined concentration (stock solution), and shake it with an oscillator for 50 times to make the reagent mix evenly in the sewage;

3) Immediately observe the sewage state, once the oil and water samples are mixed. Record the test phenomena, and start timing at the same time. After 10 minutes, observe the change of oil and suspended solids [13-15].

3. Result & Discussion

3.1. Water Clarifying Effect

Table 1. Comprehensive demulsifier performance evaluation.

reagent	density (mg/L)	total (μ L)	Volume liquid (mL)	floc floating velocity	floc size	water color		
						1min	5min	10min
TEA	500	40	80	fast	mid, small	B+	A	A+
FP	500	40	80	slow	mid, small	B	A-	A-
AP	500	40	80	slow	mid, small	B	B+	B+
AE	500	40	80	slow	mid, small	B-	B	A-
SP	500	40	80	slow	mid, small	B	A-	A-



(from left to right: Tea/FP/APAE/SP)

Figure 1. Performance evaluation of comprehensive demulsifier.

It is found that the effect of triethanolamine initiator on water clarifying of platform manifold is the most obvious at the concentration of 500 mg/L. The longer the standing time is, the more obvious the flocculation effect is. Polyene polyamine, phenol amine resin and high carbon alcohol are the second, and triblock polyether is better than diblock polyether at water clearing.

3.2. Concentration Gradient Experiment

In order to ensure the authenticity of the reagent effect, the concentration gradient experiment uses the centrifugal bottle to sample directly at the manifold to confirm the effect according to the field conditions.

Table 2. Performance evaluation of comprehensive demulsifier.

sample	density mg/L	total (μ L)	liquid volume (mL)	floc floating velocity	floc size	water color		
						1min	5min	10min
T-1	200	16	80	slower	mid, small	B-	B+	A-
T-2	300	24	80	slow	mid, small	B	B+	A
T-3	400	32	80	fast	mid, small	B	A-	A
T-4	500	40	80	faster	mid, small	B+	A	A+
T-5	600	48	80	faster	mid, small	A-	A+	A+
T-6	700	56	80	soon	mid, small	A	A+	A+

From this group of experiments, it is found that triethanolamine series takes on obvious effect of water clarifying with the increase of concentration. Considering the effect and economy of the reagents, the water color is bright and the floc state is ideal at the concentration of 500mg/L.

3.3. Infra-red Analysis

The broad and strong absorption peak near 3300cm^{-1} is the stretching vibration absorption peak of hydroxyl group, and the stretching vibration absorption peak near $1000\text{-}1100\text{cm}^{-1}$ is the stretching vibration absorption peak of ether bond. The bending vibration absorption peak of methylene is near 1460cm^{-1} .

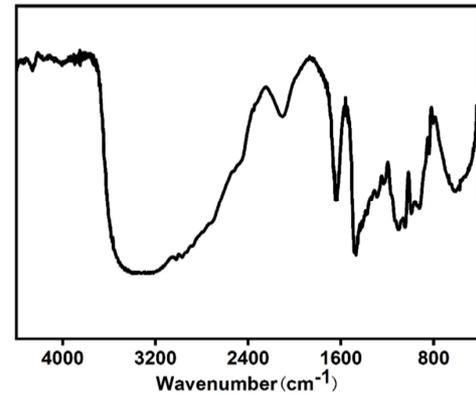


Figure 2. The analysis of infra-red.

3.4. Backscattering and Transmission Experiment

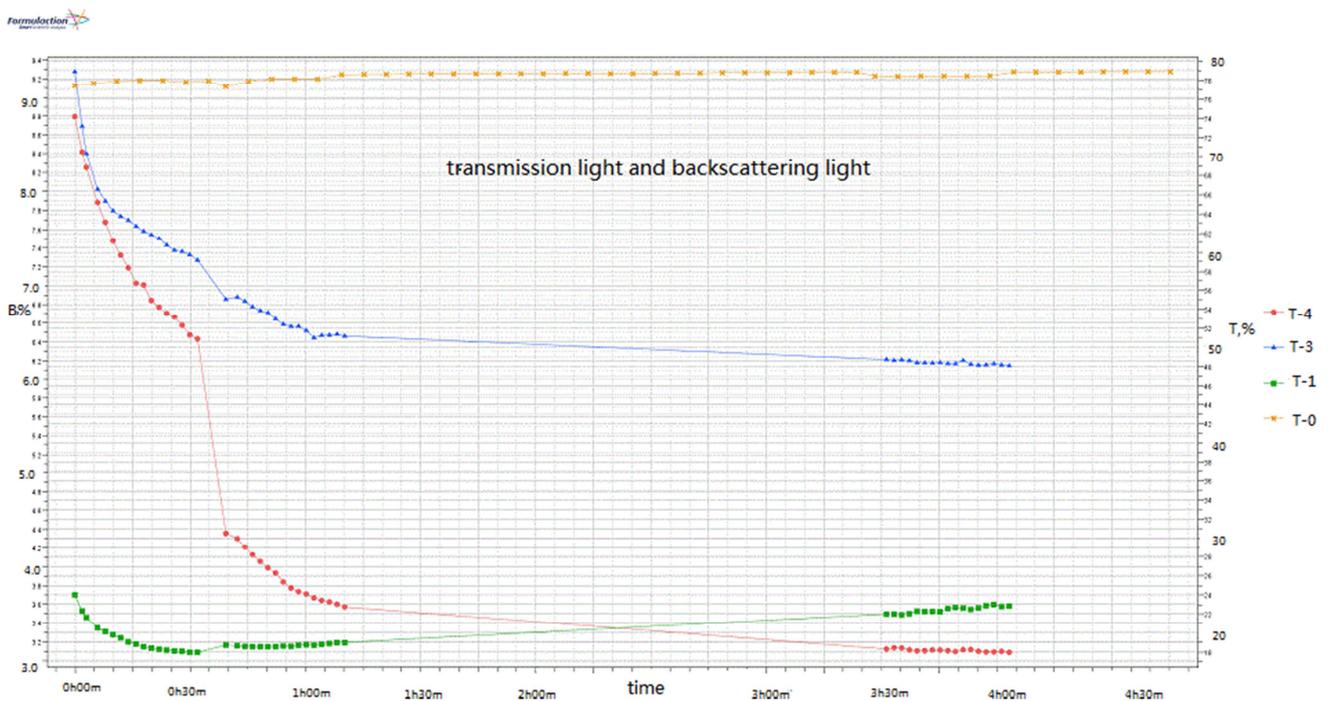


Figure 3. Transmission and backscatter images of T series.

It can be seen from the figure that the transmitted light signal of the modified polyether of triethanolamine initiator series changes greatly, and the water quality is greatly improved. The modified polyether of triethanolamine initiator series has good demulsification effect, and has obvious effect on heavy oil with high acid value.

4. Field Application

The daily volume of fluid production is about 35000m^3 , and the water content is 85%. The crude oil system and water

system are respectively divided into three-stage processing systems, in which the processing temperature of the primary separator is 75°C. The polymer content in the produced liquid is about 200mg/L, and the polymer injection effluent has a serious impact on the heaters at all levels of the crude oil system. Due to the large temperature drop range of heater, long equipment cleaning cycle and no standby equipment during cleaning, the heater is in isolation cleaning all the year round, and the water content of exported crude oil cannot be effectively guaranteed. Due to the influence of polymer flooding, most of the produced liquid of the platform is free water, which is difficult to be treated, and the oil content of the sewage is high, up to nearly 25000mg/L. The waste oil from the sewage system is simply settled by the waste oil tank, and the waste oil with water content of 40% - 50% in the upper part is exported, which increases the water content of the export.

The oil content of wastewater from inclined plate degreaser is as high as 20000mg/L, the pressure of inclined plate degreaser treatment is high, the amount of waste oil is large, and the polymer is seriously accumulated in the inclined plate degreaser, which affects the treatment effect and capacity. Moreover, the effect of air flotation treatment is not obvious, and the oil removal effect is basically not achieved.

The polymer in the water injection buffer tank is overstocked seriously, which makes it easy to put large polymer into the water injection booster pump after the liquid level is reduced, and it is easy to shut down the booster pump. The oil content in all levels of wastewater exceeds the design value, and the oil content in water injection is high.

Through the field test, the injection concentration of the demulsifier is reduced from 700mg/L to 500mg/L, the outlet water cut is reduced from 12% to 7%, the oil value of the outlet sewage is reduced to 10000mg/L, and the water cut of the exported crude oil is significantly reduced.

5. Conclusion

(1) According to the evaluation results, in the repeated verification and evaluation of the oil and water samples taken from the process manifold, the effect of comprehensive demulsifier initiated by triethanolamine in the bottle test is relatively ideal, and the longer the action time is, the better the water quality is.

(2) Triethanolamine was used as the starting agent of polyether, the ratio of PO: EO: PO was 2:7:6, then 3% (relative polyether mass) epichlorohydrin was used as the crosslinking agent, the crosslinking temperature was 80°C, the reaction time was 5h, and the hydrogen oxidant solution was used as the catalyst.

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