



New research progress of the demulsification of produced liquid by polymer flooding

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ABSTRACT

Polymer relies on its special properties, which is an effective means to enhance oil recovery. But the composition of its produced liquid is very complex, especially emulsifying phenomenon severely constrains the process oil-water separation at a later stage. At present technical means of demulsification taken by both home and abroad oilfield mainly include physics, chemistry and other methods. Currently there have been developed several new types of demulsifier including non-polyether polymer demulsifiers, amphoteric demulsifier, demulsifier plus chain extender, excluding epoxides demulsifier, complex type demulsifier, for the O / W emulsion breaker. Research on demulsifier mainly based nonionic polyoxyethylenepolyoxypropylene block polymer, the modification on the basis of the traditional demulsifier, its main research methods are: "changing the head, exchanging the tail, adding bone, and extending the chain, grafting, crosslinking, complex compound "and so on.

Key words: Polymer flooding; Produced fluids; Demulsifiers; New progress

INTRODUCTION

Currently, to some oilfield into the middle of water flooding development , the application of HPAM flooding by increasing the viscosity of the injecting water , to make it closer to the viscosity of oil - water mixtures as far as possible, so that reach the control of oil - water flow ratio, making the reservoir plane promoted more uniform, and increase the sweep efficiency. In addition, through the strengthening of Water Injection Profile, and to expand the volume of flood out. Solving the inconsistency of water propulsion of high permeability zone and low permeability zone, water and oil viscosity is not the same, it will exacerbate advance inconsistent. The appearance of low permeability zone, which makes crude oil cannot achieve the recovery results. When the high permeability layer increases the resistance, reduces water absorption index, water absorption low permeability layer to improve the level of spread range then get increases. Increase water pressure, so that the different permeability layers have more water into the low permeability reservoir, increased vertical and horizontal spread area relative to the ultimate goal of improving water absorption profile. These have been recognized by the majority of scholars, but high concentrations of polymer flooding produced water polymer concentration of high viscosity , high degree of emulsification , the small size of oil droplets and more, eventually leading to treatment more difficult, how to effectively breaking placed in front of scholars important issue.

POLYMER FLOODING FLUID CHARACTERISTICS

Formation conditions and mechanism of polymer flooding oil emulsion includes the formation conditions and mechanisms of conventional crude oil emulsion, but it also has its own characteristics [1-6]. Currently polymers flooding commonly used polymers are partially hydrolyzed polyacrylamide and hydrophobically modified product. Higher viscosity of the polymer solution, causing a large viscosity of oil emulsion liquid phase, the viscosity of the

liquid phase increased, resulting in a stable oil emulsion; On the other hand due to the partially hydrolyzed polyacrylamide contains a lot of $-\text{COO}^- \text{Na}^+$ group, it is strongly hydrophilic groups, A large number of strongly hydrophilic groups adsorbed on the oil-water interface, it will increase the thickness and strength of the oil-water interface. Meanwhile, hydrophobically modified polymer owing to its amphiphilic structure, easily adsorbed on the oil-water interface, reduces the oil-water interfacial tension, and further improves the stability of the emulsion. For oily wastewater, since the presence of sodium in the polymer group bobbin in O / W type emulsion, sodium carboxy extends partially ionized water phase, an oil-water interface in an adsorption COO water film is negatively charged, lead ion distribution in the electric double layer formed around the diffusion, so that the potential of the emulsion ZeTa increased, increasing the resistance of the emulsion droplets collide with each other, increasing the stability of oil-containing wastewater. A combination of factors led to the polymer flooding to increase the difficulty of liquid chemical demulsification.

For more breaking problems, has developed a suitable polymer flooding oil recovery demulsifier solution, which breaking mechanism comprising: a polymer flooding Demulsifier higher surface activity than conventional demulsifiers, as the demulsifier itself contains positively charged, so that the demulsifier can quickly dispersed into the oil - water interface, will supplant emulsifiers, demulsifiers itself constitutes a new and easy interface membrane rupture. This membrane under the action of gravity sedimentation and electric power, oil and water separation makes it easier broken into layers; polymer flooding Demulsifier chemical reaction can occur with crude oil output liquid polymer, reducing the viscosity of crude oil emulsion; polymer emulsified oil demulsifier drive a strong ability to dissolve the membrane, by rupture or dissolution of the emulsion; also be in charge of the membrane and the oil-water interface, the interface membrane damage by charge conservation.

POLYMER FLOODING OIL EMULSION BREAKING MECHANISM

Liquid polymer flooding is a very complex emulsifying system. Polymer Flooding was the main problem is the oil-water separation technology research which produced fluid stability of thermodynamically unstable system. Crude natural surfactant on emulsion stability play a significant role in adding demulsifiers cause natural surfactant and demulsifier adsorption of oil-water interface in the competition. Demulsifier performance quality evaluation, depending on whether it can effectively destroy the mask emulsion sector capacity in three specific areas: diffusion demulsifier adsorption, flocculation and aggregation nodal wetting film formation. So far, many scholars have done a lot of work on emulsion stability and emulsion breaking, but a lot of work is done on the viscosity and interfacial tension on.

Stable interfacial film

By a large number of studies shows: W/O type emulsion more stable crude oil, breaking it more difficult, because it has a lot of film strength, which increased the crude oil droplets collide and burst through the difficulty, thus breaking the key is to destroy milk interfacial film. For the W / O type emulsion, the active ingredient adsorbed to the interface, such as plastics, asphalt, etc., so that the oil-water interfacial tension is reduced; viscoelastic film occurs steric stabilizing effect, prevent the formation of poly- dispersed droplets and barrier.

Li Mingyuan lot of research [7-8], who found through: the breaking process, the interaction between the demulsifier and crude oil emulsion interfacial film should be taken seriously enough, because demulsifier mixed reaction occurs at the interface film generated charges, destroyed the original monolayers reached breaking purposes. Sjoblom et al [9] through a lot of study, axisymmetric equilibrium model for the role of demulsifier launched a new description. Wasan et al [10] The study confirmed that the effect of demulsifier its interfacial adsorption force has a very close relationship; demulsification its interface is directly related to the activity, in order to achieve the effect of surfactant required breaking over interfacial tension gradient, However, the efficiency and reduce the interfacial viscosity breaking no correspondence. Hunsel et al [11] found that some of the lower molecular weight polymer in the oil-water interface exhibits strong affinity to adsorption at the interface, this process is irreversible, the occurrence of displacement film formation.

Electric pairs of layers stable

Some O / W type emulsion containing HPMA, charged droplets at the interface forming an electric double layer, adjacent to each other so that electrostatic repulsion of droplets, so as to increase the viscosity of the aqueous phase, thereby obstructing the droplet coalescence. Gravity exists between dispersed droplets, there is also an electric double layer repulsion, and is its decisive role of these two opposing forces on the stability of the emulsion.

In order to study the liquid polymer flooding, the following from a W / O emulsion and O / W type emulsion comprehensive deal with two aspects to discuss breaking mechanism.

Breaking mechanism W / O emulsion of crude oil

In the polymer flooding liquid emulsion system, the effect of a stable interfacial film based W / O emulsion breaking the key factor is stable interfacial film, which can be interpreted as breaking process: demulsifier molecules attached to the emulsion molecule drop interface, diffusion and penetration absorption, instead of natural emulsifier, emulsion hinder migration to the interface of the active material, thereby forming the tension gradient is positive, the lower water interfacial film is formed compared to the stability of the mixed film poor[12].

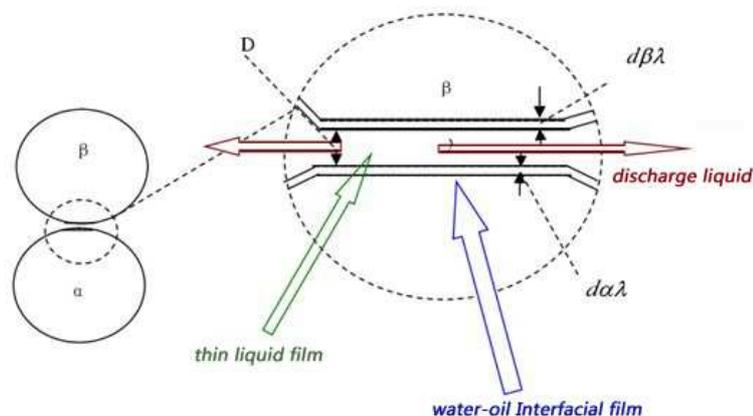


Fig1 Between the two drops of liquid thin film the liquid discharge diagram

Brownian motion induced in the fine droplets of gravity and flocculation of the dispersed phase droplets collected into loose flocs" within the flocs of fine droplets remain independent existence, this process is reversible flocculation" and during the subsequent polymerization of these loose flocs formed in the thin film adjacent droplet discharge until thin membrane rupture, the water contained in the release film, a diversity synthesis irreversibly large droplets resulting emulsion reduce the number of droplets. When the droplet grows to a certain diameter, the density difference due to water, the oil and water to be separated to achieve demulsification, shown in Figure 1.

O / W emulsion of crude oil emulsion breaking mechanism

In the solution of crude polymer flooding, some O / W emulsions are stable electrical double layer, the emulsion is greater than gravity when the system Vanderwaals electrostatic repulsion, the emulsion instability dominates the O / W emulsion. Studies have shown that: stability of the emulsion that has the potential to double, double flocculation process is to eliminate the repulsion potential curves droplet flocculation occurs, there is a potential "second small", and in this small flocculation of the contemplated coalescence will gradually here, and thus undermine the stability of O / W emulsion.

RESEARCH AND DEVELOPMENT STATUS OF THREE DEMULSIFIER DIRECTION**Demulsifier Research Status**

Since the late 1980s, foreign (mainly U.S.) research and development Demulsifier rapidly. According to recent years, foreign patent search on demulsifier, will have a representative summarized as follows:

(1) The alkoxyated alkyl phenol polymer and a modified product

Patents on such reports more demulsifier, demulsifier for primarily W / O type emulsion. Oxyalkylatedalkylphenol aromatic aldehyde polymer [13-15] The structure in FIG 2, R7, R11 represents a C1 to C18 alkyl chain one, R8 represents H, methyl or ethyl represents R9, R12 H, C1 a C18 alkyl chains, C5-C10 aryl group, a hydroxyl group, an epoxy group or a halogen atom. The patent also reports an alkoxyated alkyl phenol resins, polyethylene glycol, or mixtures with other phosphorus-containing compounds for the novel demulsifiers esterification W / O emulsion [16].

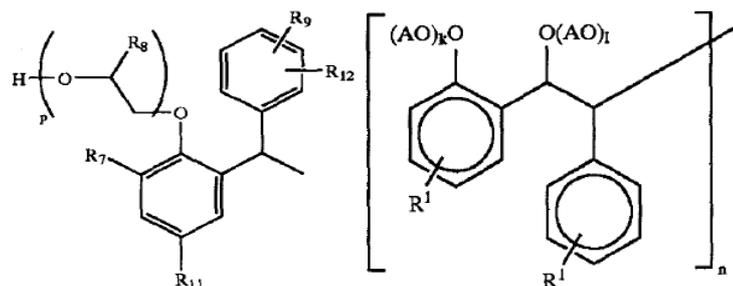


Fig.2 the structure of alkyl phenol aldehyde polymer Fig. 3 The structure of alkyl phenol formaldehyde biformyl

Alkoxyatedalkylphenols addition both for W / O emulsion and suitable O / W emulsion glyoxal resin [17], the structure shown in Figure 3, AO representative of ethylene oxide, propylene oxide or butylene oxide.

(2) Analkoxyatedalkylphenol amine polymer

Alkylphenols such demulsifier the polymerization and then the amine group of the obtained product is alkoxy, for W / O type emulsion is very effective dewatering and desalting [18]. The structural formula shown in Figure 4, R1 representative of C1-C8 alkyl chain, R2, R5, R6, R7, R8 represents H or methyl, R3, R4 representative of H, C1-C3 alkyl group, an aryl group, a group of light, alkoxy group or a halogen atom.

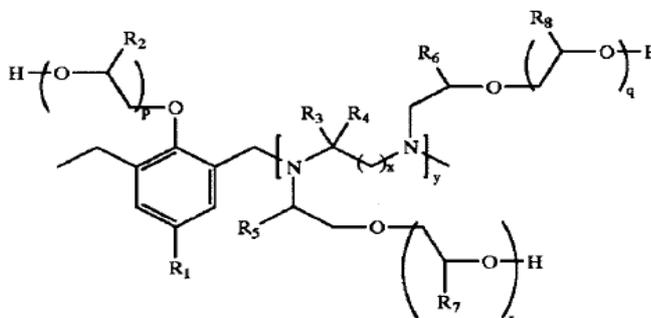


Fig. 4 the structure of alkyl phenol amine polymer

(3) A high molecular weight demulsifier

After such a demulsifier epoxidized monohydric alcohols esterified with a radical polymerizable monomer obtained by homopolymerization or copolymerization of novel high molecular weight demulsifier [19]. Its molecular weight ranging from 10,000 a 500000. Alcohol is generally a linear or branched chain monohydric alcohols of 6-30 carbon-containing radical polymerizable vinyl aromatic monomer is generally based, acrylic or methacrylic acid, epoxide typically ethylene oxide, propylene oxide, or butylene oxide. The demulsifier of an API gravity of 28 or 8 25 °C a viscosity in the range of 3 to 10000 very efficient demulsification of crude oil.

(4) Alkyl aryl sulfonic acid demulsifier

This class is a non- polyether demulsifier alkyl aryl sulfonic acid and the demulsifier additive composition for a variety of [20] the structure is simple as follows: R a Ar a SO₃H, R represents an at least 16 C atoms and at least one alkyl group, Ar represents a branched containing at least two six -membered aromatic ring aryl. Additives are: two propylene mono-butyl ether, iso- paraffinic solvent, naphthenic solvent, diethylene glycol monobutyl ether, benzyl alcohol and the like.

(5) Some demulsifier for O / W type emulsion

Overseas studies on the O / W emulsion breaker is greater. Alkoxyatedpolyglyceroldemulsifier [21] It is an O / W emulsion breaker, the structure shown in Figure 5. The alkylphenol resin and two acid derivative [22] is also effective in O / W type demulsifier structure shown in Figure 6, AO representative of ethylene oxide, propylene oxide or butylene oxide

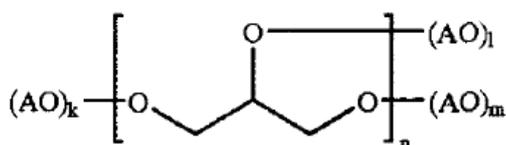


Fig. 5 polyglycerol structure of Demulsifier

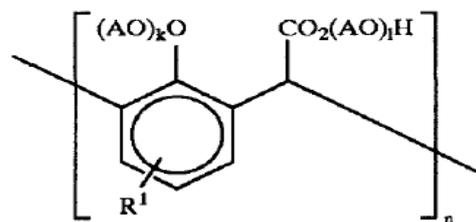


Fig. 6 the structure of two acetic acid derivatives

Demulsifier developed over several typical results show that: ① non- polyether polymer demulsifier is the rapid development of a class of demulsifier, not only dehydrated quickly, aqua clear, with less, but also especially suitable for heavy broken milk; ② gender demulsifier appear as crude oil emulsion breaking added new vitality, because not only has a good gender demulsifier desalination effect of dehydration, but also for H₂S, HCl, CO₂ and salt corrosion has excellent corrosion inhibition; ③ relative molecular mass continues to increase, the performance of various chain extenders such trend. Currently used abroad more chain extenders include aldehydes, dicarboxylic or polycarboxylic acid, a polyisocyanate and epoxy derivatives cool [23]; ④ epoxide alternatives appears. Due to the toxicity of epoxides, danger and difficulty with crude oil emulsion breaking increase in non-polyetherdemulsifierdemulsifier represents the trend of development. Other foreign substances have been

reported substitution of ethylene oxide, also contain epoxide demulsifier most patents appear ; ⑤ complex demulsifier . Specificity due to strong demulsifier A demulsifier is only suitable for certain formations , breaking some of the region 's crude oil emulsion , demulsifier complex to solve specific problems ; ⑥ there were many broken for the O / W emulsions.

Demulsifier development direction

Currently , chemical demulsifier type from domestic and foreign research point of view, mainly non-ionic polyoxyethylene -polyoxypropylene block polymer -based, modified on the basis of traditional demulsifier , which are mainly studied : " to change the head , for the tail , and bone , chain , grafting , crosslinking, complex " and so on [24-26].

(1) Change the head

First selection means is changed, the design and synthesis of an active hydrogen initiator. Initiators are usually phenols, alcohols, fatty acids, fatty amines. Now, with the deepening of the study, a simple, single- initiator of people employed increased from turning into a complex diversity.

① phenolic initiator . Phenolic initiators used in the past, mainly nonylphenol, octyl phenol, butyl phenol , its structure is composed of simple , now people began to use different branched structure of various types of phenolic resins and various alkylphenols with bisphenol a complex as the initiator , such demulsifier for crude oil emulsion breaking effect .

② amines , alcohols initiator . Currently used amines , alcohols initiator functional groups gradually increased , there has been triethylenetetramine , tetraethylenepentamine , pentaethylenhexamine functional groups , such as six , seven functional groups , eight functional initiators . Now with an alcohol amine was also combine the characteristics of synthetic amino alcohol as a starting agent, synthetic polyoxyethylenepolyoxypropylene block polymer demulsifier breaking effect.

③ carbohydrate initiator . In addition to simple sugars pentoses, hexoses, etc., the derivatives thereof are gradually used as the initiator compound and oligosaccharides.

④ send winded class initiator . Tut system or a derivative thereof to the initiator, with ethylene oxide, propylene oxide or butylene oxide or mixtures thereof are polymerized to obtain a good demulsificationdemulsifier. In addition, you can send voice quaternary amine, generated demulsifier also has bactericidal, antiseptic, flocculation and other effects.

⑤ microphone wow Lynn class initiator . M is an imidazole Lin 41T demulsifier as the initiator and sodium hydroxide as catalyst for the synthesis of the different blocks in the order of different scales , a series of different molecular weight demulsifier , and then chain extended with different chain extenders , and finally with toluene diluting . The agent is the role of heavy oil significantly.

⑥ phthalocyanine multi amine initiator . Acid and using a binary shuttle polyamine, polyamine amine initiator obtained phthalocyanine then with ethylene oxide, propylene oxide, and butylene oxide block polymerizable reaction resulting water-in- oil demulsifier and oil in water emulsion breaking effects are very good.

⑦ dendritic initiator. Using two polyfunctional compounds A and B to afford the product C for the next reaction as the initiator , and then C then A, B of the reaction product of a more complex structure D, the next step can be used as the starting agents, and so forth, can be obtained complex structure, molecular weight demulsifiers . This class demulsifier with less, good breaking effect.

(2) Exchanging the tail

For the end use of the new chemical demulsifier polymer end groups of the same or different classes obtained by esterifying, this method is an effective method for increasing the molecular weight. Such as sealed with rosin acid, sulfuric acid and other agents on the tail esterified polyether demulsifier or modified using acetic anhydride, benzoyl chloride and phthalocyanine series of polyether carboxylic acids esterified demulsifier, improved breaking effect on significant role. Also useful reaction of maleic anhydride and an amine polymer with maleic anhydride or esterified polyether modified, resulting demulsifier for water-in -oil (W / O) crude oil emulsion breaking good results.

(3) Adding bone

Add a new bone is added demulsifier molecule skeleton generate a new demulsifier. For example n-butanol as the

initiator, in the alkali-catalyzed PO, EO synthesis polyoxyethylenepolyoxypropylene, then reacted with the ethoxylated polysilane, demulsifiers obtained both demulsification effect, also has anti-wax effect.

(4) A extender chain

Chain using an appropriate chemical method, the bifunctional active hydrogen compound as a chain extender, a low molecular weight polymer is attached to form a linear molecule, the molecular weight increases exponentially or several times to enhance the demulsification. When a prepolymer having three or more reactive functional groups, the crosslinking may occur, demulsifiers mesh generation. Some use of dicarboxylic acid or dimer fatty acid as the chain extender, of polyoxyalkylene chain aliphatic primary amine to obtain a primary amine, polyoxyalkylene ester, water in oil emulsion having good demulsification. Also useful 2-fumaric acid, phthalic acid as a chain extender, as well as with four acrylic succinic anhydride as a chain extender, have made a good breaking results.

(5) Grafting

Graft reaction using specific chemical that certain functional groups on the polymer chain, the amount of reaction with other compounds, thereby introducing a molecular weight molecule having a specific functional group or a branched chain, increasing the molecular weight or molecular structure of a minor change, breaking the molecule effect is enhanced.

(6) Crosslinking

Crosslinked using crosslinking agents, crosslinking the polymer to form much larger molecular weight of ultra-high molecular weight. Agents or as the crosslinking agent is at least one prepolymer has three or more functional groups. Using sorbitol, glycerin or polyethylene polyamine synthesis as initiator polyoxyethylenepolyoxypropylene compound, then polyols or bicyclic compounds as crosslinking agents, synthetic demulsifier with simple preparation, good breaking effects advantages. Polyoxyalkylene compound and a phenolic resin with a minor cross-linking has a good demulsifier for crude oil demulsification. However, due to the crosslinked product was difficult to dissolve, the present application is also very small.

(7) Complex compound

Complex is the use of the synergies of various surfactants, various demulsifiers have different effects mixed in certain proportions, so demulsifier has wide adaptability, while also providing a wider choice of demulsifier; the demulsifier or different organic or inorganic additives are mixed to obtain both a demulsifier breaking effect, but also has other effects, such as dewaxing, viscosity and other effects.

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