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Application and Development of Emulsion Breaker for Crude Oil

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Abstract

With the continuous improvement of crude oil extraction and refining technology, the composition and properties of produced liquid are greatly different from those produced by traditional production methods. Therefore, the requirements for demulsifier performance are constantly changing and improving. At present, the function and efficiency of some crude oil emulsion breakers are difficult to meet the engineering requirements. Based on this, this paper first analyses the types and structure of crude oil emulsion breakers, then studies the research and development status and application status of crude oil emulsion breakers, and finally gives the research and development history, evaluation methods and future development direction of crude oil emulsion breakers.

Keywords: *Emulsion Breaker, Crude Oil, Application and Development;*

1. Introduction

With the rapid development of social economy, the consumption of energy in all walks of life is increasing; especially the consumption of fossil energy is increasing, which puts forward new requirements for the exploitation and refining of crude oil. However, the current crude oil extraction will significantly increase the water content of the crude oil emulsion, and increase the stability of the emulsion. The stability of the crude oil emulsion will increase the difficulty of the treatment of the produced liquid, and the difficulty of the treatment of the polymer containing wastewater will also be greatly improved due to the increase of the water content of the crude oil. It can be seen that these changes in crude oil emulsion make it more difficult to store, transport and refine, and need further treatment to meet the requirements of transportation, storage and refining.

At present, there are many kinds of emulsion breakers for crude oil, such as conventional direct alkyl polyether emulsion breakers. However, this type of emulsion breaker needs a long processing time and is difficult to meet the production requirements of rapid processing. In addition, there are also types of crude oil biological emulsion breakers. These types of emulsion breakers mainly use the high activity of biological molecules to achieve crude oil dehydration. Crude oil biological emulsion breakers benefit from the characteristics of being easily degraded by microorganisms, so they have less impact on the external environment in the process of treatment, so they are gradually popularized and applied in the oil industry. The current crude oil emulsion breaker gradually develops to the characteristics shown in Figure 1, so as to continuously meet the production and processing needs of the crude oil industry.

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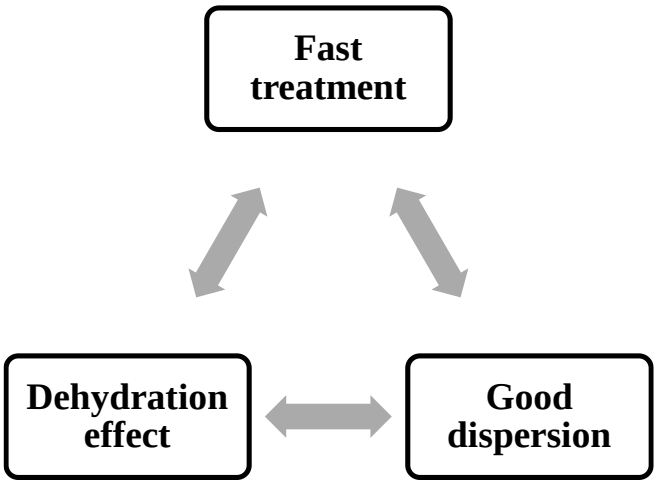

Figure 1. The development trend of emulsion breaker performance in crude oil.

The working principle of crude oil emulsion breaker is as follows in Table 1, mainly based on the mechanism of phase inversion and the mechanism of collision breaking, so as to form emulsion type surfactant with opposite phase. Secondly, the emulsion breaker and the emulsifier react to make the emulsifier lose the emulsifying property and form complex. In addition, adsorption on the interface membrane reduces its stability, resulting in flocculation, coalescence and demulsification.

Table 1. The working principle of crude oil emulsion breaker.

Principle	Effects
Phase transfer reverse deformation	Surfactant realizes phase transition
Collision breaking mask	Reduce stability, resulting in flocculation and coalescence
Complex compound	The emulsifier lost its emulsifying property

Based on the relevant research data, there is still a big gap in the research and technical conditions of crude oil emulsion breakers between China and developed countries. And with the continuous improvement of crude oil extraction and refining technology, the composition and properties of produced liquid are greatly different from those produced by traditional production methods. Therefore, the requirements for emulsion breaker performance are constantly changing and improving. In the current situation of heavy crude oil and low-quality crude oil, the demand of crude oil processing and refining industry for crude oil emulsion breakers with good interfacial activity, strong flocculation rejection ability and good wetting permeability is also increasing[1].

In this context, the performance of crude oil emulsion breaker needs to be further optimized and improved. At present, the performance improvement of crude oil emulsion breaker is mainly based on the development direction as shown in Figure 2 below, and continuous adjustment based on the nature of the oilfield. Therefore, it has important practical value to study the application of crude oil emulsion breaker.

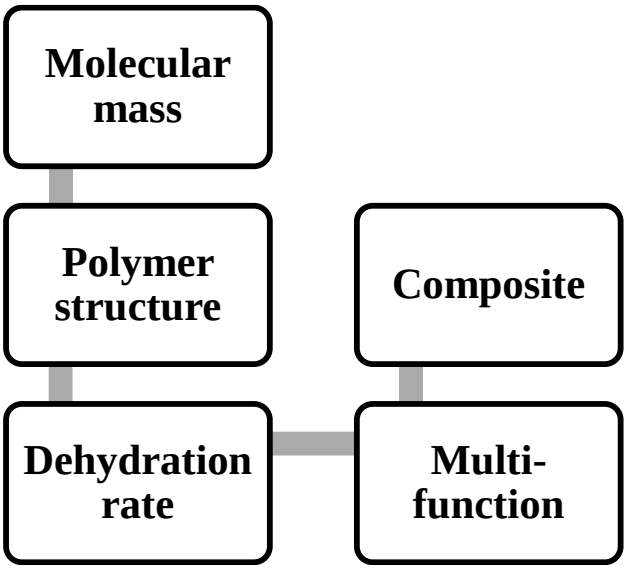

Figure 2. Key factors of improving emulsion breaker performance.

2. Types and structures of emulsion breakers for crude oil

2.1. Crude oil emulsion

Water cut crude oil will produce oil emulsion by mixing in the process of exploitation and transportation[2]. There are two immiscible phases, water phase and oil phase, in the crude oil emulsion, and there are surfactants. Based on the phase volume theory of crude oil emulsion, there are two types as shown in Table 2 below.

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Table 2. The types of crude oil emulsion.

Aspects	W/O type	O/W type
Volume of aqueous phase	＜26%	＞74%
Coalescence velocity	Oil drop ≫ water drop	Water drop ≫ oil drop
Emulsifier	Strong lipophilic	Strong hydrophilicity

2.1.1. Adverse effects of crude oil emulsion

First of all, the existence of crude oil emulsion will significantly increase the volume of liquid flow, which makes the design efficiency of crude oil extraction and transportation pipeline difficult to achieve. Secondly, because the presence of crude oil emulsion increases the viscosity, so the transportation power loss is significantly increased. In addition, the fuel consumption in the process of crude oil heating and the treatment of crude oil refining process are adversely affected by crude oil emulsion. Moreover, due to the existence of crude oil emulsion, the corrosion rate of crude oil production and transportation pipeline and processing equipment is accelerated, and it is easy to scale.

2.1.2. Dehydration of crude oil emulsion

The dehydration methods and Strategies of crude oil emulsion mainly include sedimentation separation, electric dehydration and wetting coalescence dehydration[3]. The sedimentation separation dehydration method mainly includes the centralized means as shown in Table 3 below. The electric dehydration method is mainly based on the characteristics of water as conductor and oil as insulator, so as to realize the deformation and coalescence of water in crude oil emulsion by adding electricity to form large water drops.

In addition, the principle of wetting coalescence dehydration is to make the water droplets in the emulsion contact with the strong hydrophilic substances, so that the water droplets can be adsorbed on the surface of the strong hydrophilic substances, so that the water will coalesce to form large water droplets and finally be settled and separated. The wet coalescence dehydration method is mainly suitable for the dehydration of W/O type crude oil emulsion.

Table 3. Precipitation separation dehydration of crude oil emulsion.

Measures	Detailed means	Functions
Increase the droplet size	Chemical emulsion breaker; High voltage electric field; Hydrophilic oil repellent solid materials	Decrease the stability of emulsion; W/O emulsion was treated; Make the water droplets coalesce.
Increase density difference	Blending with light oil Choose the right temperature Reduce the pressure	Reduce the density of crude oil; Increase the density difference; Make the bubbles expand.
Reducing crude oil viscosity	Mixed with low viscosity light oil; Heating.	Dilute crude oil; Reduce the viscosity of emulsion.

2.2. Types and structures of emulsion breakers for crude oil

Generally speaking, crude oil emulsion breakers need to have strong surface activity, good wettability,

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sufficient flocculation ability and excellent coalescence ability. In the molecular structure of crude oil emulsion breaker, the hydrophilic group and oleo Phil group of crude oil emulsion breaker need to keep balance, and the more hydrophilic groups, the better. The alkyl and hydrophilic groups on phenyl are in ortho or meta position.

2.2.1. Types of emulsion breakers for crude oil

Crude oil emulsion breakers can be divided into low molecular weight, high molecular weight emulsion breakers and ultra-high molecular weight emulsion breakers. In addition, it can be divided into diblock polymer and triblock polymer based on the different number of crude oil emulsion breakers[4]. Moreover, based on the solubility of crude oil emulsion breakers, water-soluble emulsion breakers and oil-soluble emulsion breakers can be divided into water-soluble emulsion breakers and oil-soluble emulsion breakers.

2.2.2. The W/O type crude emulsion emulsion breaker

The W/O type crude emulsion breaker is a block polyether with alcohol as the starting agent, so it is mostly suitable for paraffin base crude oil, but not for high viscosity crude oil of gelatin, asphaltene and high water cut crude oil. The crude oil emulsion breaker with polyethylenepolyamine as starting agent has many branched chains, high wettability and permeability, low dosage and good demulsification effect at low temperature. Its molecular expression is as shown in follows 3.

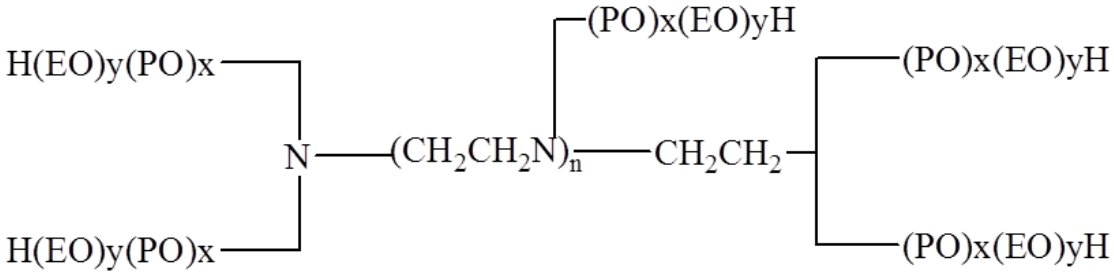

Figure 3. Molecular structure of polyethylenepolyamine as initiator.

The crude oil emulsion breaker with alkyl phenol formaldehyde resin as starting agent has a molecular structure similar to that of crude oil natural emulsifier, and has good permeation diffusion effect. Its molecular formula is shown in Figure 4 below.

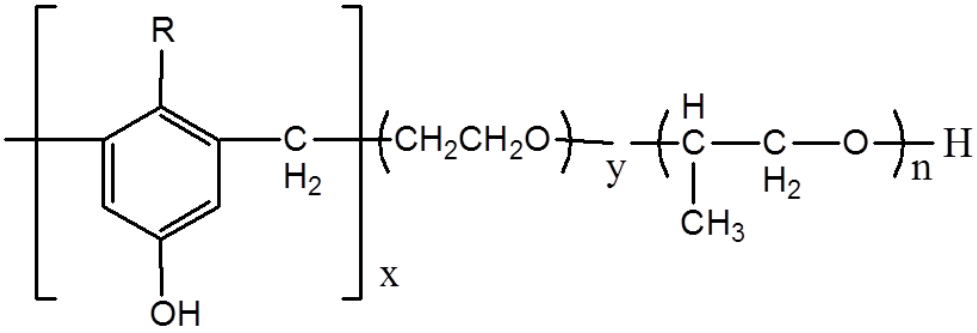

Figure 4. The molecular formula of alkyl phenolic resin as initiator.

The crude oil emulsion breaker with phenol amine aldehyde resin as the starting agent is the condensation product of alkyl phenol, ethylene amine compounds and formaldehyde, which is not sensitive to the type of crude oil emulsion[5].

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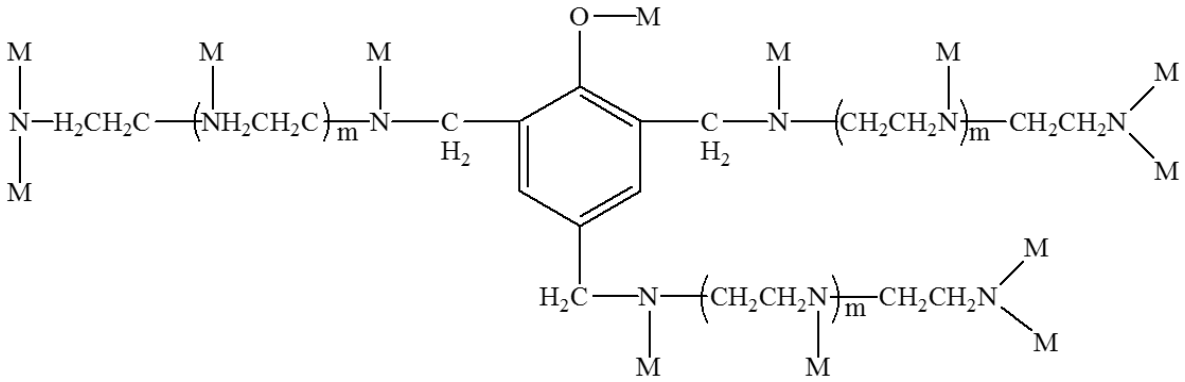

Figure 5. The molecular formula of phenolic amine aldehyde resin as initiator.

2.2.3. O/W emulsion breaker

The O/W type emulsion breaker has strong electropositive, flocculating ability and surface activity, thus forming an active material of the emulsion interfacial film, which is sufficient to neutralize the negative charge formed by the emulsifier, and could flocculate the emulsion particles and reduce the interfacial energy of the emulsion[6]. The O/W crude oil emulsion breakers of surfactants have various forms, such as quaternary ammonium salts, dithiocarbamates and polyamines.

2.3. Demulsification mechanism of crude oil emulsion breaker

The addition of crude oil emulsion breaker can make the emulsified water droplets close to each other and contact each other, so that the droplets coalesce and the emulsified water droplets are separated from the continuous phase. In the phase inversion mechanism, the emulsion breaker of crude oil is contacted with the oil water interfacial film to form an oil water interfacial film. The oil in water emulsion can become an oil in water emulsion. When it reaches a certain volume, it will settle out of the oil phase due to the difference of oil-water density. The demulsification mechanism of main crude oil emulsion breakers is shown in Table 4.

Table 4. The demulsification mechanism of crude oil emulsion breakers.

Mechanisms	Characteristics
Phase transfer reverse deformation	Form a new oil water interface mask; The water settles based on the density difference between oil and water
Flocculation - coalescence	Liquid bead flocculation, The number of emulsion beads decreased Oil water density difference, sedimentation separation.
Neutral mask charge	Neutralization of interfacial charge Adsorption bridging Flocculation and coalescence
Solubilisation	Solubilizing emulsifier molecules Demulsification of emulsified crude oil
Fold deformation	The inner part of the droplet is connected The droplets agglomerate and demulsify

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3. Development and application of emulsion breaker for crude oil

3.1. Development of emulsion breaker for crude oil

With the development of chemical industry and the continuous realization of new technology breakthroughs, the research of crude oil emulsion breakers has also made rapid progress, and a large number of new crude oil emulsion breakers have been improved and applied[7]. The representative achievements of these new emulsion breakers for crude oil include but are not limited to copolymers represented by methyl methacrylate, highly polar organic ammonia derivatives, cationic amide compounds and polymer emulsion breakers, three-component composite emulsion breakers and hydrophobically associating trimers. With the increasingly complex composition of crude oil emulsion, the function and composition of emulsion breaker also need to be improved. Therefore, the current research focus of crude oil emulsion breaker mainly focuses on several aspects as shown in Table 5 below.

Table 5. The research focus of crude oil emulsion breaker.

Focus	Characteristics	Functions
Molecular mass	Continuous improvement	Fast demulsification and low dosage
Demulsification effect	Mixed type emulsion breakers	Improving demulsification effect
Synthetic emulsion breaker	Branched chain emulsion breaker	Improved demulsification effect
Polymer emulsion breaker	Complexity and diversity	Multifunction
Ultra-high molecular weight	Synthesis in aromatic solvent	Synthesis in alkaline system
Cationic polyether type	Chlorinated polyether	Improved demulsification effect
Emulsion breaker for high pour point oil	Block polymer	Suitable for water cut and high pour point oil

At present, the development of domestic crude oil emulsion breakers is still at the level of block copolymers prepared by epoxide, only a slight expansion in the relative molecular weight, and no breakthrough change in the characteristics of polyether emulsion breakers has been achieved.

3.2. Restrictive factors of emulsion breaker research and development

With the continuous application of polymer flooding and ASP flooding technology in crude oil production technology, the water content of crude oil emulsion is continuously increased[8]. In order to reduce the adverse impact of crude oil emulsion on the production and transportation links and equipment, it is necessary to actively develop new crude oil emulsion breakers. However, the current research and development of crude oil emulsion breaker is affected by many factors, which are shown in the following figure 6.

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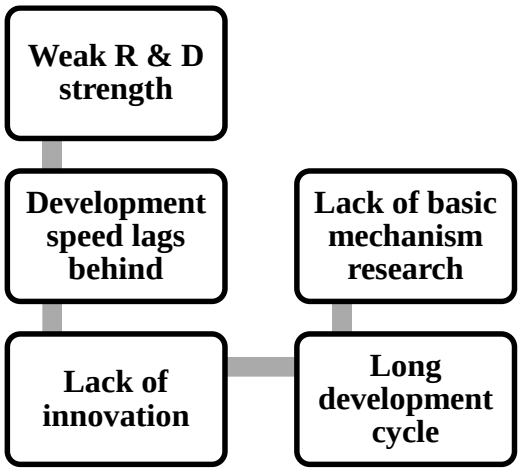

Figure 6. Restrictive factors of emulsion breaker research and development.

Among them, due to the difference of actual exploitation situation faced by each oilfield and the difference of crude oil refining units, the actual demand of crude oil emulsion breaker in each production and processing unit is also different[9]. In this case, the variety and variety of crude oil emulsion breakers make it difficult to concentrate the research and development, resulting in long development cycle, obvious lag effect and less application of new technology. Secondly, the innovative development and application of new high-efficiency emulsion breakers based on chemical structure breakthrough are still scarce, resulting in only slight modification of crude oil products. In addition, due to the lack of research on the demulsification mechanism of crude oil emulsion breaker, the key factors that affect the stability of oil water interfacial film are difficult to identify, and the stability of oil water interfacial film is difficult to control, leading to the difficulty in fundamentally realizing technological innovation of products.

In addition, in view of the outstanding phenomenon of demulsification and dehydration of crude oil produced liquid, it is required that the crude oil emulsion breaker has strong demulsification ability, good quality of wastewater after demulsification, and can better adapt to the processing and treatment of crude oil produced fluid containing polymer, alkali and surfactant. At present, the crude oil emulsion breaker still has a series of shortcomings, such as slow dehydration speed and high water content of dehydrated crude oil, which can only increase its dosage and bring a series of adverse consequences.

3.3. Application status of emulsion breaker for crude oil

At present, the exploitation and application of crude oil show several characteristics as shown in Figure 7 below, which makes the application of crude oil emulsion breaker have changed accordingly, which are specifically shown in the following aspects. On the other hand, most of the domestic oilfields are in the state of high water cut, high recovery and high oil recovery rate. Therefore, in order to improve the efficiency of crude oil extraction and ensure the stable increase of crude oil production, many oilfields apply emulsion breakers to solve the problem of oil-water treatment. However, with the continuous improvement of the difficulty of demulsification and dehydration of crude oil produced liquid, and the deepening of the emphasis on environmental ecology, the application of emulsion breakers is developing in the direction of high performance, high environmental protection and high efficiency.

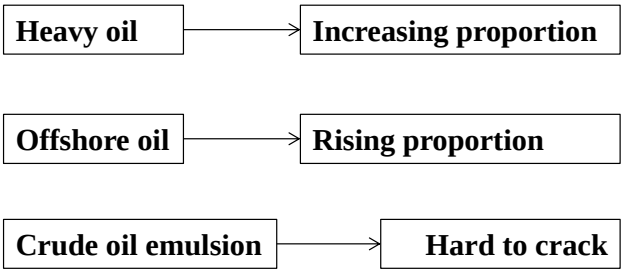

Figure 7. Two dimensional planar linear arrays.

At present, the application of crude oil emulsion breaker in crude oil emulsion still focuses on non-ionic polymers and the modification of crude oil products. The upgrading and improvement of emulsion breaker properties are mainly based on the technical route shown in Figure 8 below. The emulsion breakers have different synergistic effects,

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which make the emulsion breakers show better synergistic effect.

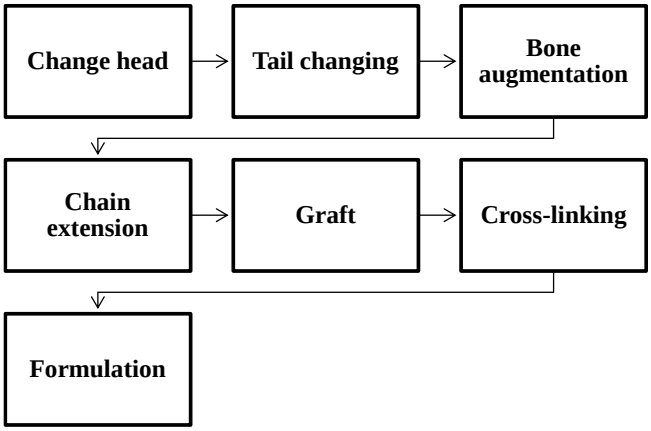

Figure 8. The upgrading and improvement technical route of emulsion breaker.

In addition, with the addition of additives, the emulsion breaker's effect can be retained and brought into play. At the same time, its performance and function are further broadened, such as viscosity reduction and wax prevention. In addition, a variety of initiators, molecular structures and corresponding block forms were synthesized to achieve hydrophilic, lipophilic and multi-directional properties. Moreover, the composite emulsion breaker has the characteristics of fast dispersion and dehydration of crude oil emulsion at the oil-water emulsion interface.

4. Adaptive harmonic current detection method on account of Neural Network

4.1. Evaluation of crude oil emulsion breaker

The evaluation indexes of crude oil emulsion breaker mainly include dehydration rate, dehydration rate, oil-water interface state, oil content of desalted water and optimal dosage of emulsion breaker. The evaluation index of crude oil emulsion breaker also includes the applicability of different crude oil, the effect of corrosion inhibition, scale inhibition, viscosity reduction and wax prevention, and the compatibility with other chemicals[10]. In addition, based on the performance test method standard of crude oil emulsion breaker, the demulsification effect of crude oil sample under the application of emulsion breaker was recorded and measured, and the oil content of oil and sewage was finally tested. Finally, the final evaluation of crude oil emulsion breaker effect is carried out by recording several indexes as shown in Figure 9 below.

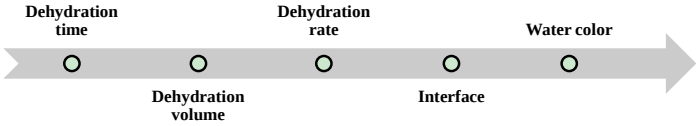

Figure 9. Evaluation indicators of crude oil emulsion breaker.

4.2. Development process of emulsion breaker for crude oil

The early crude oil emulsion breakers were mainly represented by caustic soda and petroleum sulfonate. These products had disadvantages such as large dosage, poor effect and easy to be affected by electrolyte. Subsequently, the crude oil emulsion breaker was modified and replaced by the oxidized propylene block copolymer and its modified products.

During this period, the crude oil emulsion breaker's acid, alkali, salt resistance and crude oil dehydration effect were significantly improved, and the amount of crude oil emulsion breaker was greatly reduced. With the application of emulsion breakers represented by amine polyoxyethylene compounds, the molecular weight of crude oil emulsion breakers is further improved, and the demulsification effect is also significantly enhanced, and the amount of emulsion breakers is also constantly reduced. The typical development history of crude oil emulsion breakers is shown in table 6 below.

Table 6. The typical development history of crude oil emulsion breakers.

Period	Dosage (mg / L)	Typical emulsion breakers	Characteristics

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1920s	1000	Sulfonated castor oil	Large dosage, poor effect,
1930s	1000	Sulfonated succinate	Susceptible to electrolytes
1940s	100-500	Fatty alcohol	The dosage is greatly reduced
1950s	100	Ethylene oxide	
1960s	20-45	Polyoxyethylene compounds	High molecular weight, good demulsification effect
20th-- Current	5-20	Alkyl polyoxyethylene ester	

4.3. Application and development direction of crude oil emulsion breaker

Because of the strong specificity of crude oil emulsion breaker, it is necessary to develop a special emulsion breaker for a specific oilfield, which will lead to poor universality of crude oil emulsion breaker and high cost. In order to solve this problem and phenomenon, the development and application of crude oil emulsion breaker with universal and multi applicability has become one of its important development trends. Based on the characteristics of crude oil emulsion breakers, such as interfacial activity, wetting and permeability, etc., the synergistic effect between crude oil emulsion breakers can be brought into play, and the demulsification performance has higher adaptability, so that the application cost can be significantly reduced, and the application efficiency can be continuously improved.

In addition, with the continuous growth of social demand for crude oil, the proportion of heavy oil extraction in the current crude oil exploitation activities is increasing. Based on this trend, the application and development of crude oil emulsion breakers in the future will inevitably develop in the direction suitable for heavy oil emulsion breakers. On the other hand, with the increasing proportion of offshore oil exploitation, more and more attention has been paid to the protection of marine ecology and environment. In order to reduce the impact of crude oil emulsion breaker on the ecological environment, the application and development prospects of biological demulsification technology in crude oil de oiling and demulsification engineering have been continuously strengthened and clarified. In general, the research and application of low temperature, environmental protection, compound emulsion breaker and ultra-high molecular weight emulsion breaker can further improve the demulsification efficiency, and have become an important development direction of crude oil emulsion breakers in the future.

5. Conclusion

In summary, with the continuous improvement of crude oil extraction and refining technology, the composition and properties of produced liquid are greatly different from those produced by traditional production methods, and the requirements for emulsion breaker performance are also constantly changing and improving. Therefore, the performance of crude oil emulsion breaker needs to be further optimized and improved. In the current situation of heavy crude oil and low-quality crude oil, the demand of crude oil processing and refining industry for crude oil emulsion breakers with good interfacial activity, strong flocculation rejection ability and good wetting permeability is also increasing.

In this paper, the types and structures of crude oil emulsion breakers, the demulsification mechanism of crude oil emulsion breakers and their harmfulness are analyzed. Secondly, through the analysis of the research and development and application status of crude oil emulsion breaker, the research and development progress of crude oil emulsion breaker, the restrictive factors of emulsion breaker research

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and development, and the application status of crude oil emulsion breaker are deeply studied. Finally, the development course, evaluation method and future development direction of crude oil emulsion breaker are analyzed by expounding the research and development direction of crude oil emulsion breaker.

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