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Advanced developments in environmentally friendly lubricants for water-based drilling fluid: a review

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The problem of high friction and high torque is one of the most troublesome problems for engineers in extended reach wells and long horizontal wells. Generally, the friction coefficient of oil-based drilling fluid is around 0.08, while the friction coefficient of water-based drilling fluid exceeds 0.2, which is much higher than that of oil-based drilling fluid. With the increasingly stringent environmental regulations, water-based drilling fluids have gradually become a better choice than oil-based drilling fluids. Therefore, lubricants become a key treatment agent for reducing the friction coefficient of water-based drilling fluids. Although there have been many related studies, there is a lack of comprehensive reviews on environmentally friendly water-based drilling fluid lubricants. In general, water-based drilling fluid lubricants can be mainly divided into solid lubricants, ester-based lubricants, alcohol-based lubricants, and nano-based lubricants. Vegetable oil ester-based lubricants, biodiesel lubricants, and dispersible nano-lubricants are all promising environmentally friendly water-based drilling fluid lubricants. Understanding the lubrication mechanism of different types of lubricants and clarifying the evaluation methods of lubricants is an important prerequisite for the next development in high-performance water-based drilling fluid lubricants. Therefore, the purpose of this paper is to give a comprehensive overview of water-based drilling fluid lubricants in recent years, in order to fully understand the development and lubrication mechanism of water-based drilling fluid lubricants, and provide new ideas for subsequent research on water-based drilling fluid lubricants.

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1. Introduction

With the continuous increase in global energy demand, the exploration and development of oil and gas resources have gradually developed into deeper and more complex formations, and the demand for extended-reach wells, high angle deviated long horizontal wells, and multi-branch wells is increasing.¹ Different from vertical wells, these types of well have serious problems of high torque and high friction, which can easily cause problems such as increased rotary resistance of the drilling tool, difficulty in tripping, and even differential pressure sticking (Fig. 1). In addition, the friction caused by the metal-to-metal surface contact between the drill string and the casing can cause casing wear and reduce casing service life.²⁻⁵ Therefore, it is very important to handle the contradiction between drilling safety and downhole friction. As the circulating fluid

between the downhole drilling tool and the borehole wall, drilling fluid plays an important role in reducing friction.⁶⁻⁹ The drilling fluid forms a filter cake on the surface of the well wall so that the contact between the drill pipe and the well wall becomes the contact between the drill pipe and the filter cake. By improving the lubricity of the filter cake, the frictional resistance to the drill pipe can be reduced. In the downhole, drilling fluid reduces friction by reducing the contact area between the drill bit, drilling tool, and drilling cuttings.

The friction coefficient of diesel is much smaller than that of water. Generally, the friction coefficient of diesel-based oil-

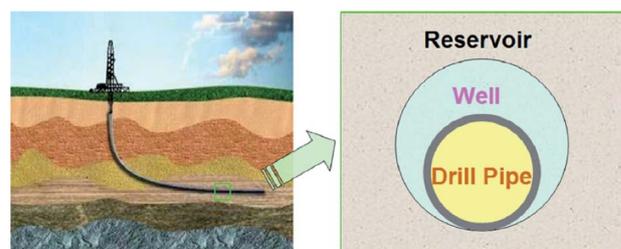


Fig. 1 Schematic diagram of horizontal well drill pipe state (copyright@2021 Liu et al.).¹⁰

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based drilling fluids (OBDF) is lower than 0.1, and the friction coefficient of water-based drilling fluids (WBDF) is higher than 0.2. However, the biggest problem with OBDF is that it is not friendly to the environment.^{3,11,12} The new generation of biomass synthetic-based drilling fluids (SBDF) has significantly improved the problem of environmental pollution of OBDF. However, insufficient temperature resistance and high cost are its main disadvantages.^{13–15} Compared with OBDF and SBDF, WBDF has greater advantages in environmental protection and cost, but its lubricity is difficult to meet the needs of horizontal wells.¹⁶ Therefore, it is necessary to add lubricant to WBDF to effectively improve its lubricating performance. A good drilling fluid lubricant offers several valuable friction-reducing physicochemical properties, including high lubricity, low corrosion, low pour point, low flammability, low foaming, no fluorescence, high solubility, high heat and oxidation stability, and no toxic and biodegradable.¹⁷

Traditional drilling fluid lubricants usually include inert solid particles, oil, graphite, and so on. Inert solid particles are similar to rolling bearings in drilling fluids.¹⁸ Incompressible spherical particles are embedded in the filter cake, which converts the simple sliding friction between the drilling tool and the filter cake into rolling sliding friction, reducing the friction contact area.¹⁹ However, most of the inert solid particles cannot be degraded after entering the pores of the reservoir and easily cause damage to the reservoir. In addition, it is easy to be removed by solid control equipment and high recovery cost is also an important problem faced by inert solid lubricants. Liquid lubricants minimize the frictional contact area by forming a lubricating film between the drilling tool and the surface of the well wall.^{20,21} Crude oil and diesel were used as the most direct lubricants in the past. However, Ahmet's research showed that whether used alone or with lubricants, diesel and heavy oil will have a negative impact on the lubrication performance of drilling fluids.²² In addition, the difficulty and cost of disposal of waste drilling fluid after oil mixing are greatly increased, which is also likely to cause adverse effects on the environment. As the environmental protection requirements become more stringent, oil mixing measures have been gradually banned. Non-environmentally friendly lubricants will directly lead to the non-environmental protection of WBDF, which directly affects the surrounding ecological environment, and also poses a threat to the health of construction workers.²³ In the past few years, various alternatives to crude oil and diesel oil have been reported to improve the lubricity of WBDF, such as animal and vegetable oil esters, nanomaterials, graphene, and polyols, *etc.* Although a large number of lubricants have been studied in various industries, the lubricants used in WBDF are only a minority. The reason is that the lubricants used in WBDF not only need to have high-efficiency lubrication performance but also meet the conditions of the use of drilling fluids. Compatibility with other components of drilling fluid, temperature and salt resistance in the formation, biodegradability, *etc.* are all important considerations for researchers to develop WBDF lubricants.

The purpose of this paper was to review and summarize the research status of environmentally friendly lubricants for water-

based drilling fluids in recent years. Through the classification of lubricants, the advantages and disadvantages of various lubricants were clarified, the current research difficulties were pointed out and future research directions were also proposed. The paper is structured as follows. After the introduction, the characterization techniques of water-based drilling fluid lubricants are summarized, and then the environmentally friendly WBDF lubricants are classified and discussed, including solid lubricants, and ester-based lubricants, alcohol-based lubricants, and nano-lubricants. Finally, the challenges and prospects of environmentally friendly WBDF lubricants are proposed.

2. The need for environmentally friendly lubricants

The need to protect the ecological environment has gradually become one of the most important issues to be considered in the drilling process. As shown in Table 1, there are many deficiencies in the traditional ways to improve the lubricity of water-based drilling fluids. Oil mixing is banned because it is not environmentally friendly. As the using conditions become more severe, lubricants are also required to be used under more complex formation conditions. Extreme pressure elements such as sulfur and phosphorus can improve the wear resistance of lubricant molecules. Zinc dialkyl dithiophosphate (ZDDP) is a typical lubricating additive that enhances the extreme pressure and anti-wear properties of lubricants. The downhole temperature and pressure can provide the necessary conditions for the decomposition of ZDDP, thereby forming a polyphosphate film on the surface of the drilling tool.²⁴ However, the decomposition of ZDDP will also generate toxic compounds containing S/P, which will pollute groundwater and soil also have corrosive effects on drilling tools.²⁵ The application of nanoparticles in drilling fluids is becoming more and more important due to their adjustable chemical and physical properties.⁹ Nanomaterials are also a potential lubricant. The size, morphology, and surface functionalization of nanoparticles have a key impact on their performance. At the same time, synthesis conditions, processing, and chemical composition will also determine the toxicity of nanoparticles.^{26,27} Nanomaterials can easily penetrate deep into the formation through drilling fluid, and the penetration of toxic nanomaterials into the formation water will cause damage to the ecological environment.

Therefore, it is necessary to strictly control the impact of drilling fluid treatment agents on the ecological environment. Toxicity and biodegradability have become important considerations for the development of drilling fluid lubricants. On the other hand, the film-forming properties of the friction surface play an important role in determining the lubricating effect of the lubricant, which is closely related to the chemical composition and structure of the lubricant molecule. The new generation of excellent WBDF lubricants should include the following characteristics: high lubricating film strength, high solubility, strong oxidation stability and thermal stability, low corrosion,



Table 1 Summary of traditional drilling fluid lubricants

Traditional lubricants	Shortcomings
Inert solid particles Crude oil, diesel	Not degradable and prone to damage to the formations Deterioration of performance of water-based drilling fluid, environmental pollution, and high disposal cost of drilling fluid after mixing with the oil
Zinc dialkyl dithiophosphate (ZDDP)	The decomposition of ZDDP produces toxic compounds containing S/P, causing environmental pollution
Mineral oil-based lubricant	Aromatics contain fluorescence, which affects logging work

low flammability, and low foaming rate, non-fluorescence, non-toxic and biodegradable, and compatibility with drilling fluid components.¹⁷ A lot of research has been devoted to replacing the hazardous lubricants currently used with environmentally friendly drilling fluid lubricants.

3. Techniques for characterizing the lubricants of WBDF

The lubricating performance of drilling fluid usually includes two aspects: the lubricating performance of the drilling fluid itself and the lubricating performance of the filter cake. Therefore, the indicators for evaluating the lubrication performance of drilling fluids mainly include the friction coefficient of the drilling fluid itself and the friction coefficient of the filter cake (also known as the adhesion coefficient of the filter cake). This section describes the various characterization techniques used to evaluate WBDF lubricants.

3.1 Friction coefficient (COF) of drilling fluid

An extreme pressure (EP) lubrication instrument is usually used to measure the friction coefficient of the drilling fluid. The equipment simulates the rotation speed of the drill pipe and the pressure of the drill pipe on the well wall. A standard lubrication coefficient test system includes a friction block and a uniformly rotating annular rotator. The ring-block friction system is immersed in the container containing the drilling fluid to be tested to simulate metal-metal type friction, and the torque N when the friction block is pressed on the rotating ring is measured.^{6,28} Calculate the friction coefficient (f) of the drilling fluid by formula (1), and calculate the friction coefficient reduction rate (Δf) by formula (2):²⁹

$$f = 0.01 \times N_1 \times \frac{34}{N_2} \quad (1)$$

$$\Delta f = (f_0 - f_1) / f_0 \quad (2)$$

where N_1 and N_2 are the torque readings of the drilling fluid and distilled water respectively; f_0 and f_1 are the friction coefficients of the drilling fluid before and after the lubricant is added. Ordinary WBDF requires f to be less than 0.2, but for shale horizontal wells, f needs to be less than 0.1. The decrease of the friction coefficient indicates that in the presence of drilling fluid, the wear between the solid particles in the drilling fluid

and the drilling tool is reduced, which not only helps to reduce the torque of the drill string but also prolongs the life of the drilling tool.

The traditional EP lubrication instrument can only test the friction coefficient of the drilling fluid under normal temperature and pressure. However, the rotation speed of the drill pipe and high-temperature conditions will also affect the performance of the lubricant. To overcome the shortcomings of traditional EP lubrication instruments, various friction and wear-testers can be used to evaluate the friction and wear performance of lubricants at a certain temperature, pressure, and speed.³⁰

3.2 Adhesion coefficient of filter cake

The surface of the filter cake formed by the drilling fluid on the borehole wall has a certain viscosity, which causes the drilling tool to receive frictional resistance when relative movement occurs on the surface of the filter cake. This frictional resistance is called the adhesion coefficient of the filter cake. That is, the adhesion coefficient is used to characterize the lubricating performance of the filter cake. Too large of adhesion coefficient is easy to cause the drilling stick and drilling tool to wear. In this experiment, first, measure the fluid loss of the drilling fluid to form a filter cake, the pressure difference is 3.5 MPa, and the fluid loss time is 30 min. Then the adhesion plate and the filter cake are compacted, and the maximum torque value M that makes the slip between the adhesion plate and filter cake is measured. The adhesion coefficient (K_f) of the filter cake is calculated by the formula (3), and the adhesion coefficient reduction rate (ΔK_f) is calculated by the formula (4):^{29,31}

$$K_f = 0.845 \times M \times 10^{-2} \quad (3)$$

$$\Delta K_f = (K_f - K_{f1}) / K_f \times 100\% \quad (4)$$

where K_f and K_{f1} are the adhesion coefficients of the drilling fluid before and after adding the lubricant.

Generally, the lubrication coefficient of the drilling fluid refers to the friction coefficient of the drilling fluid, which represents the friction between the drilling tools or drilling tools and the solid phase in the drilling fluid in the presence of the drilling fluid. The adhesion coefficient of drilling fluid refers to the friction between the filter cake formed on the surface of the well wall and the drilling tools. The decrease of the filter cake lubrication coefficient indicates that the



adhesion coefficient between the drill tool and the filter cake is reduced, that is, the resistance of the filter cake to the rotation of the drill string is reduced. The adhesion of the drill string and the filter cake will not only increase the drilling friction but also easily cause downhole accidents such as sticking. However, most of the current lubricant studies take the friction coefficient of the drilling fluid as the main evaluation criterion, and the adhesion coefficient of the filter cake is not considered enough, which also causes difficulties in the practical application of the lubricant. For lubricants, according to corporate standards, when the lubricant can reduce the friction coefficient or adhesion coefficient by more than 50%, it is effective.^{29,31}

3.3 Fluid loss test

Filtration property is one of the key performances of the drilling fluid system, which is reflected by the size of the fluid loss and the quality of the filter cake. Among them, the quality of the filter cake is directly related to the lubrication performance of the entire drilling system. The thick filter cake will narrow the annulus gap and cause contact between the drill pipe and filter cake. When the drill pipe is embedded in the filter cake, sticking will occur. A thin filter cake helps reduce friction in the drilling system. Therefore, if the addition of lubricant can further reduce the thickness of the filter cake, it can also be considered that the lubricant improves the lubricity of the drilling fluid. Of course, for the filtration volume, a good lubricant should not cause an increase in the filtration volume, which means the deterioration of the performance of the drilling fluid.

3.4 Wetting test

A huge load or pressure may squeeze the lubricant out of the contact surface in a complex drilling environment. Therefore, lubricant is required to wet the friction surface (drill tool steel). The contact angle is used to reflect the wettability of the lubricant on the steel surface. A small contact angle means that the lubricant has a strong tendency to adhere to the steel surface, which is conducive to the formation of a lubricating film.³

3.5 Scanning electron microscope and energy spectrum analysis

The scanning electron microscope (SEM) is an important instrument for analyzing worn surfaces which can see the degree of wear on the friction surface.^{32,33} The formation of a lubricating film on the worn surface can be analyzed by the change of the element content of the worn surface.³⁴ Lubricants that can reduce the width or depth of wear scars on the friction surface are considered good.

3.6 Rheology test

The compatibility of the lubricant with other additives in the drilling fluid is the key prerequisite for its use. A good lubricant should not deteriorate the rheological properties of the drilling fluid.

4. Classification of environmentally friendly water-based drilling fluid lubricants

Traditional drilling fluid lubricants can be divided into two categories: solid lubricants and liquid lubricants. With the strengthening of environmental protection policies, the development of lubricants tends to use more environmentally friendly materials. The lubricating properties of some new types of nanomaterials, such as nanoparticles, nanofluids, nanographene, *etc.*, are gradually being known and partly applied to drilling fluids. Therefore, the nano lubricants are divided into one category. As shown in Fig. 2, lubricants are mainly divided into three categories: traditional solid lubricants, liquid lubricants, and new nano-lubricants, which will be discussed in detail in the following chapters.

4.1 Solid lubricant

Aiming at the problems of traditional inert solid lubricants which are difficult to degrade and easy to be removed by solid control equipment, some new solid lubricants have been developed. They are no longer simple inert solid particles, usually in powder form, which are convenient for transportation but can be evenly dispersed in drilling fluid and adsorb on the contact surface.

The production process of sodium bisulfite will produce chemical residues with a complex chemical composition, including inorganic residues and organic residues. Experiments showed that organic residues containing thiodiglycol, 2,2'-dithiodiethanol and 1,4-thioxane have good lubricity and are suitable for use as lubricating additives. The inorganic residues need to be removed because they are easy to contaminate the formation. Zhang *et al.* heated the recovered chemical residues at 100 °C to obtain organic residues and prepared solid lubricant (slube) together with graphite, regenerated asphalt, and surfactants. The soft layered and porous structure of graphite (flake graphite and expanded graphite) and the fibrous structure of recycled asphalt are beneficial to improving the lubricity of the slube and the compatibility of the slube in the drilling fluid. On the other hand, both temperature and salt (NaCl and CaCl₂) have an adverse effect on the lubrication performance of the slube.²⁹

The wax emulsion with low-fluorescence, non-toxic, and non-corrosive can form a uniformly distributed film on the drilling tools and well wall, so it shows good lubricity in the drilling fluid. However, the wax emulsion has poor storage stability, is easy to solidify in winter, and has many defects in terms of filterability and cost, which is not conducive to popularization and application. Zhou *et al.* fully reacted the oil-in-water nano-wax emulsion with a special water-soluble polymer material (polyphenylene sulfide) in a kneader by semi-dry technology to obtain the self-dispersed nano-emulsified wax solid lubricant Ewax. 1 wt% Ewax can reduce the adhesion coefficient (K_f) of the freshwater bentonite base slurry by 73.5% and the extreme pressure friction coefficient (f) by 77.6%. The



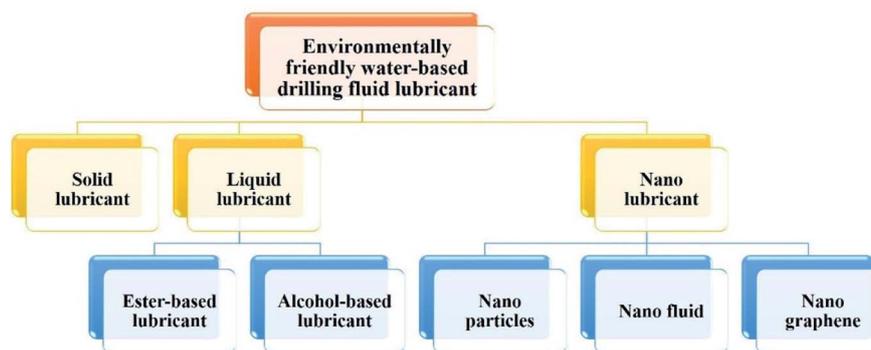


Fig. 2 Types of environmentally friendly water-based drilling fluid lubricant.

coverage of Ewax on the surface of the special polymer is the reason for the excellent lubricity, which makes the surface of the polymer smoother. More particular, Ewax is superior to other similar liquid wax emulsions in terms of fluid loss control, heat resistance, and salt resistance, and is environmentally friendly. It also solves the problems of liquid wax emulsions freezing in winter and poor storage stability.³¹

Starch is a common drilling fluid additive because it is cheap, environmentally friendly, and non-toxic. Its various modified products can be used as key treatment agents such as rheological and fluid loss additives in drilling fluids. Sifferman *et al.* prepared a dry powdered starch lubricant composition by mixing starch and various olefin lubricants by jet cooking. This production process enables the interaction between starch and the lubricant droplets to produce an aqueous starch dispersion of suspended lubricant droplets with a diameter of 1–10 microns. After drying and grinding, the non-oily powder containing 28% lubricant is obtained. The preparation process without an emulsifier avoids environmental problems and eliminates the problem of foaming. The lubricity test showed that the starch lubricant composition not only reduces the friction coefficient of the drilling fluid to a level similar to that of the ODBF, but also gives the drilling fluid good fluid loss performance.³⁵ The powdered lubricant product is convenient to transport and reduces the cost.

Mario *et al.* designed a new type of solid lubricant based on the principle of tribology and tested the new type of solid lubricant with a friction meter to produce a continuous Stribeck curve, to evaluate the performance of the lubricant in the whole lubrication state. The new solid lubricant reduces the contact area of the friction surface by rolling and provides a chemical bonding film on the contact surface to reduce the shear stress between the surfaces. In this study, a tribometer was used to test the dynamic and static friction coefficients for the first time, providing a more comprehensive characterization for the performance evaluation of drilling fluid lubricants.³⁶

The compatibility of lubricant and drilling fluid is one of the prerequisites for its application. The effects of the above solid lubricants on the rheological properties of water-based drilling fluids such as apparent viscosity (AV), plastic viscosity (PV), yield point (YP), gel strength (Gel), *etc.* are shown in Table 2.

Traditional solid lubricants generally do not affect the rheological properties of drilling fluids because they do not react with the components of the drilling fluid. However, the surface modification of the solid lubricant enables it to interact with other components of the drilling fluid. Therefore, it is very important to investigate its influence on the rheological properties of the drilling fluid. As shown in Table 1, the starch lubricant has a great influence on PV, YP, and Gel of drilling fluid, so other treatment agents need to be added to control the rheology of drilling fluid during its use.

The current research focuses on new solid lubricants and is mainly focused on the modification of the original solid lubricants and the innovation of the production process. By reducing the particle size of solid lubricants, the risk of being removed by solids control equipment can be reduced.

4.2 Liquid lubricants

Typical liquid lubricants mainly refer to lubricants stored in liquid form, which can interact with other additives of drilling fluid to affect the performance of the drilling fluid. Therefore, the evaluation index of liquid lubricant is not only its lubricating ability but also its compatibility with other components of drilling fluid, oxidation stability, high-temperature, and high-pressure stability, salt resistance, and so on. The newly developed liquid lubricants can be mainly divided into ester-based lubricants and alcohol-based lubricants. Next, we will introduce their research progress in detail.

4.2.1 Ester-based lubricants. Lubricants based on mineral oil or vegetable oil are the most traditional and common drilling fluid lubricants. Mineral oil is a mixture of liquid hydrocarbons refined from petroleum. Due to the presence of many aromatic hydrocarbons in mineral oil, lubricants prepared with mineral oil as base oil usually have high fluorescence. More importantly, mineral oil is difficult to biodegrade and is likely to cause serious pollution to the environment. Therefore, researchers turned their attention to vegetable oils with low toxicity, good biodegradability, good resource reproducibility, and low fluorescence intensity.³⁷ Organic oil esters derived from vegetable oils have the lowest volatile vapor content and do not contain aromatic substances, sulfur, or paraffin, which can prevent any long-term impact on the health of workers and the



Table 2 Summary of the effect of solid lubricants on the rheology of drilling fluids

Lubricant	Rheological properties/compatibility
Slube ²⁹	The increase of slube concentration has no obvious effect on PV and YP of drilling fluid
Ewax ³¹	The addition of Ewax has little effect on the AV, PV, and gel of the drilling fluid, but can slightly increase the YP of the system
Starch ³⁵	Starch lubricant would cause a significant increase in PV, YP, and gel values of drilling fluid
Novel solid lubricant ³⁶	Not mentioned

surrounding environment during use. Therefore, vegetable oil can provide a sustainable source of environmentally friendly additives for the oil and gas industry to achieve safe and environmentally friendly drilling operations.²³ Vegetable oils that can be used as the base oil of environmentally friendly lubricants mainly include castor oil, olive oil, rapeseed oil, soybean oil, palm oil, and linseed oil. There are a lot of unsaturated fatty acids in vegetable oil, and the hydroxyl bond makes it attractive to the metal surface, which is conducive to the formation of a high-strength lubricating film on the friction surface.^{38,39} Mahto compared the lubricating effects of linseed oil and commercial motor oils in bentonite drilling fluids. The results showed that linseed oil performed a better lubricating effect than non-vegetable oil-based lubricants. More importantly, linseed oil can maintain the rheology of the drilling fluid and control fluid loss.⁴⁰

However, unmodified vegetable oils usually have the following problems: (1) vegetable oil has poor thermal stability and is easy to saponify in an alkaline environment, generating bubbles and causing changes in drilling fluid performance; (2) lubricants after saponification consume quickly and are not durable, causing cost increase; (3) the poor oxidation stability of vegetable oil makes it easy to deteriorate, resulting in reduced or even loss of lubricating performance.^{41,42} Therefore, vegetable oils are generally modified for use. The main components of vegetable oils are esters produced by straight-chain higher fatty acids and glycerin. Liquid lubricants prepared from modified vegetable oils and synthetic esters can be called ester-based lubricants.

Sinopec Petroleum Engineering Research Institute used plant esters and elemental sulfur grafting to prepare hydroxy fatty acid ester SMJH-1. The friction coefficient reduction rate of the base slurry containing 1.0% SMJH-1 before and after aging reached 91.4% and 90.7%, respectively. Sulfur-containing vegetable esters form a lubricating film on the metal surface through the C=S bond, thereby reducing the friction coefficient. On the other hand, high temperature promotes the formation of C=S bonds on the clay surface and strengthens the clay-metal contact. During the sliding process, the clay particles fill into the uneven surface of the sliding surface, reducing the average roughness of the sliding surface, further reducing the friction coefficient.¹

Waste vegetable oil is available in large quantities and has a sustainable source of supply. Using waste vegetable oil to prepare lubricants can not only reduce costs but also help solve

the problem of waste vegetable oil disposal in the food and catering industry.²³ The optimized waste vegetable oil MVO-3 has good low-temperature fluidity, high flash point, low aromatic content, and self-lubrication. The modified expandable graphite GIC has a composite layered structure with a strong adsorption capacity. In the presence of emulsifiers and dispersants, the composite lubricant SDL-1 was prepared with the mass ratio of MVO-3 to GIC of 38–40. After emulsification, MVO-3 composed of macromolecular esters can be adsorbed on the solid surface to form an oil film to improve the lubricity of the solid surface. On the other hand, the modified GIC particles were compressed between the wellbore and the drill pipe so that the friction between the drill pipe and the wellbore changed from dry friction to sliding friction, thereby reducing friction and torque. In addition, the graphite flake particles would expand and deform at high temperatures, further reducing the contact probability between the drill pipe and the wellbore. SDL-1 has remarkable lubrication and anti-wear properties. Only 0.5% of SDL-1 can reduce the friction coefficient by more than 80%, and the temperature resistance exceeds 180 °C.³⁰ Amanullah and Arfaj prepared a green water-based drilling fluid lubricant ARC Eco-Lube with waste vegetable oil. The waste vegetable oil is esterified by methanol, and then separated, washed, and heated to obtain pure vegetable esters, which reduces the viscosity of the waste vegetable oil and improves its lubricating potential. 3% ARC Eco-Lube can significantly reduce the friction coefficient of drilling fluid. In addition, the excellent thermal stability of ARC Eco-Lube ensures its safety during transportation and operation.⁴³ To enhance the thermal oxidation stability of vegetable oils, acidic ion exchange resins were used as heterogeneous catalysts to perform *in situ* epoxidation of methyl esters prepared from waste vegetable oils to synthesize WCOME bio-lubricant base oils. The modified epoxy has significantly improved viscosity and thermal oxidation stability.⁴² Ma *et al.* prepared a non-toxic and biodegradable environmentally friendly lubricant F-1 by modifying the by-product of bio-oil phyto-acidified oil (AO). The reduction rate of extreme pressure lubrication coefficient of F-1 in fresh water and 4% NaCl brine drilling fluid can reach 86.84% and 85.76%, respectively. After aging at 150 °C, F-1 can obtain a higher reduction rate of extreme pressure lubrication coefficient than before aging. The vulcanization and esterification process of vegetable acidified oil not only improves the temperature resistance of the lubricant but also helps to reduce the foaming rate.⁴⁴



Castor oil contains up to 95% ricinoleic acid, which has better low-temperature viscosity and high-temperature lubricity than most other vegetable oils. However, common esters and natural vegetable oil lubricants are generally incompatible with completion fluids (saltwater). Therefore, Arvind *et al.* developed a new castor oil-based phospholipid lubricant. The lubricant has a fatty alkyl chain as a lipophilic tail and a phosphoric acid part as a hydrophilic head. Experiments showed that 0.5 vol% of the phospholipid lubricant can effectively reduce the friction coefficient of a variety of brines. The HLB value of the lubricant can be customized by changing the type and number of fatty alkyl chains in the phospholipid so that the application of the lubricant in different brines can be adjusted.⁶ Livescu *et al.* modified castor oil by sulfonation and the obtained sulfonated castor oil can not only improve fluid lubricity but also has excellent temperature resistance. Besides, sulfonated castor oil has high stability and can maintain lubricity for a long time.⁴⁵

Zhang *et al.* prepared a special intermediate product SPP-REO with good lubricity, heat resistance, and salt resistance by three-step chemical modification (vulcanization, pentaerythritol esterification, and phosphate esterification). The summer special lubricant BLC-1 and winter special lubricant BLC-2 were prepared by mixing SPP-REO as base oil with modifier and defoamer and other auxiliary materials. The lubricant is especially suitable for brine-based drilling fluid with advantages in protecting reservoirs and stabilizing the wellbore.⁴⁶

Elements, phosphorus (P), nitrogen (N), sulfur (S), and boron (B) are usually used as extreme pressure and anti-wear elements to be introduced into the lubricant molecule to improve the extreme pressure and anti-wear properties of the lubricant. Sulfurized fatty acids with S element can improve the extreme pressure and antiwear properties of rapeseed oil. The element S present in organic molecules is less toxic and is not easily converted into sulfur oxides, reducing the possibility of environmental pollution. The active S in the sulfurized fatty acid generates active sulfur-free radicals in the process of friction, which promotes the formation of the protective layer on the surface of the drill steel. Under low load, ordinary fatty acids with strong polarity can easily form an adsorption film on the friction surface, reducing the friction coefficient. However, under extreme pressure conditions, the protective film formed by adsorption gradually fails. At this time, the chemical reaction film formed on the friction surface by active sulfur radicals can continue to play a lubricating effect. Studies have shown that all fatty acids with an alkyl chain length greater than 10 can improve anti-friction performance under extreme pressure by introducing S element.⁴⁷

Another non-fluorescent cationic extreme pressure lubricant JDLUB-1 is composed of synthetic base oil, oil-soluble spherical nano-silica, and sulfur phosphomolybdenum additives. During the lubrication process, the positively charged lubricant droplets can be adsorbed on the surface of the N80 steel casing sample to form an adsorption film composed of oil-soluble nano-silica and sulfur-phosphorus-molybdenum compounds, which has a low melting point and low shear strength. It can

effectively reduce the friction coefficient between the drilling tool and the wellbore during the friction process.⁴⁸

Biodiesel is green energy that has received increasing attention. It is defined as monoalkyl esters of animal and vegetable oils or fats and can be regarded as a substitute for petroleum diesel.⁴⁹ There are no aromatics in biodiesel, non-toxic and non-fluorescent, with excellent biodegradability and good environmental performance.¹⁷ The contact angle of biodiesel on G105 steel is small and the surface interfacial tension is low, which means that it has a strong tendency to adsorb on steel and is easy to disperse in water. Gerhard and Kevin found that biodiesel (fatty compounds) has better lubricity than petroleum diesel (hydrocarbons) because fatty compounds give oxygen atoms polarity. In biodiesel, oxygen can enhance lubricity better than nitrogen and sulfur. Among them, the type of oxygen-containing groups has a great influence on the lubricity of biodiesel. The study concluded that the order of oxygen-containing groups to enhance lubricity is as follows: COOH > CHO > OH > COOCH₃ > C=O > C-O-C.⁵⁰

It is worth noting that although biodiesel can effectively reduce the friction coefficient of drilling fluids, due to the high kinematic viscosity, biodiesel has a huge impact on the rheological parameters of drilling fluids. Biodiesel also foams severely after aging, which is not conducive to the control of drilling fluid performance. Therefore, biodiesel also needs to be modified or used in combination with other additives. The biodiesel-based lubricant BL is obtained by modifying biodiesel with sulfur-containing substances and polyhydroxy polymers. BL can be adsorbed on the surface of steel and barite, reducing the friction between the barite and the surface of the drilling tool. High temperature can further improve the lubricity of freshwater fluids because BL reacts with the steel surface at high temperatures, which enhances the strength of the lubricating film. Combination with other lubricant additives (ZDDP, hydroxyl, and carboxyl modified graphite MG) can improve the effectiveness of BL. The lubrication mechanism can be attributed to the synergy between BL and other materials. For example, when used in combination with ZDDP, both the combinations of BL/ZDDP = 9 : 1 and 8 : 2 exhibited improvements in lubricity compared to pure BL. BL can be adsorbed on the solid protective film formed by the reaction of ZDDP with the steel surface, thereby reacting with sulfur and phosphorus compounds to form a composite film, which further increased the strength of the film and enhanced lubricity. The combination of solid lubricants and liquid lubricants allows the two different mechanisms of action to be coordinated and complement each other. When the weight ratio of BL/MG was 6 : 4, both in freshwater and seawater drilling fluids showed higher lubricity than pure BL or MG. The solid lubricant MG sheet can be adsorbed on the recesses on the steel surface to reduce the surface roughness of the steel. In this case, combined with the film-forming action of the liquid lubricant BL, the lubricity of the steel surface can be further improved.³

Although lubricants based on vegetable oils already have low fluorescence intensity, they are still looking for ways to eliminate fluorescence. The main sources of fluorescence are the double bonds, conjugated double bonds, benzene, and fused



ring structures with Π electrons in the molecular structure. Among them, benzene and fused ring structures have strong fluorescence characteristics. The mechanism of eliminating fluorescence is to reduce the number of double bonds and Π bonds in the molecular structure of vegetable oils. Nitric acid has strong oxidizing properties, which can destroy the Π bond structure and reduce the fluorescence intensity. Zhou *et al.* used liquid nitric acid and solid nitric acid as fluorescence eliminators to modify lubricants prepared with animal and vegetable oils as base oils and developed a low-fluorescence drilling fluid lubricant E167. After adding concentrated nitric acid, the fluorescence intensity of the lubricant is significantly reduced. At the same time, E167 also has high-temperature resistance and low foaming properties. It can still exhibit good lubricity after aging at 180 °C.⁴¹ Lachter's group proposes that a mixture of xanthan gum (XC) and monoglycerides can enhance lubrication in water-based drilling fluids. They propose that monoglycerides can form complexes with polysaccharides, which help to disperse less water-soluble surfactants in aqueous media, thereby exhibiting synergistic lubricating effects.²⁸ Alkylglycerol ethers exhibit the molecular structure of amphiphilic compounds with polar groups similar to esters. Therefore, this group again investigated nonionic surfactants alkyl glycerol ethers with different alkyl chain lengths as lubricants for water-based drilling fluids. Alkyl glycerol ethers exhibit higher friction reducing ability with increasing alkyl chain length. However, they must form complexes with xanthan gum, which facilitates ether dispersion and adsorption to metal surfaces in the aqueous phase and forms a lubricating film. Alkyl glycerol ethers with larger alkyl chain lengths are less soluble in water and therefore interact more strongly with xanthan gum, promoting interfacial activity, and resulting in better lubricating effects.⁵¹

The effects of the above ester-based lubricants on the rheological properties of water-based drilling fluids are shown in Table 3. As shown in Table 3, most ester-based lubricants are compatible with other drilling fluid treatment agents, that is, they will not cause significant changes in the rheological properties of the drilling fluid. However, there are also some studies without rheological evaluation, which would affect the applicability evaluation of the developed lubricant.

The vegetable oil molecule contains unsaturated bonds and a variety of functional groups, so it is easy to obtain enhanced lubricating ability through structural modification, such as high-temperature resistance and strong anti-wear ability. The introduction of S, N, P, B, and other elements can improve the binding capacity of the base oil and metal or clay, thereby improving the extreme pressure lubrication performance of the lubricant. However, current research focuses on improving the lubricating performance of ester-based lubricants under complex conditions, but less attention has been paid to its compatibility in drilling fluids. The synergistic effect of lubricant molecules and other drilling fluid treatment agents needs to be further researched.

4.2.2 Alcohol-based lubricants. The cloud point effect of polyols is very effective in inhibiting the hydration and dispersion of shale, and it is a common drilling fluid additive. Some studies have shown that it also has a certain lubricity. Alessandro *et al.* used a complex polyol fluid derived from the reaction of methyl glucoside and polyglycerol in oil wells in the Gulf of Mexico, which can not only improve the stability of the well wall, but also effectively improve the lubricity of WBDF and SBDF.⁵² The study by Mueller *et al.* showed that fatty alcohols composed of linear or branched monoalcohols with at least 12 carbon atoms can significantly improve the lubricity of over-alkaline water-based silicate drilling fluids. Carboxylic acid

Table 3 Summary of the effect of ester-based lubricants on the rheology of drilling fluids

Lubricant	Rheological properties/compatibility
SMJH-1 (ref. 1)	Not mentioned
SDL-1 (ref. 30)	SDL-1 had no significant effect on the rheology of freshwater and saltwater drilling fluids
ARC Eco-Lube ⁴³	Not mentioned
WCOME bio-lubricant ⁴²	Not mentioned
F-1 (ref. 44)	F-1 did not affect the AV and PV of water-based drilling fluids
Castor oil-based phospholipid lubricant ⁶	Castor oil-based phospholipid lubricant will cause a significant increase in PV, YP, and gel before and after the aging of drilling fluid, especially YP, which can improve the rock-carrying ability of the drilling fluid
BLC-1/BLC-2 (ref. 46)	Neither BLC-1 nor BLC-2 affected the rheological properties of the drilling fluid
JDLUB-1 (ref. 48)	JDLUB-1 is compatible with common drilling fluid additives within 130 °C, and would not cause the deterioration of drilling fluid rheological properties
Biodiesel-based lubricant BL ³	Whether it is freshwater drilling fluid or seawater drilling fluid, the AV change caused by BL is less than 5 mPa s, that is, the rheological effect of BL on drilling fluid is negligible
E167 (ref. 41)	E167 only caused a slight increase in AV and YP in freshwater or saltwater drilling fluids
Alkyl glycerol ethers ⁵¹	Not mentioned



esters can interact with fatty alcohols to further improve their lubricating properties. The significant advantage of fatty alcohol is that it can inhibit foaming and weaken the impact on other properties of drilling fluid.⁵³

Polyethylene glycol is also an environmentally friendly, non-toxic, and excellent inhibitor. A recent study explored its potential as a WBDF lubricant. Studies have shown that only 0.1 wt% polyethylene glycol can reduce the friction coefficient of the filter cake by 44.5%. The hydrophobic paraffin in the polyethylene glycol molecule is adsorbed on the surface of the bentonite to form a hydrophobic film and play a lubricating effect; secondly, as shown in Fig. 3, the adsorption of polyethylene glycol inhibits the hydration and dispersion of bentonite, and increases the particle size of bentonite. The increase of particle size will lead to the reduction of specific surface area and friction resistance, thereby enhancing the lubrication performance. Polyethylene glycol has good compatibility with commonly used drilling fluid additives (sodium carboxymethyl cellulose, methyl methacrylate, *etc.*) and does not foam. However, insufficient temperature resistance is a problem that polyethylene glycol needs to solve.¹⁰

Qin *et al.* analyzed the improvement effects of polyaspartic acid (PA) and polyethylene glycol (PEG) on the lubricity and rheological properties of water-based drilling fluids. The mixture of 5% PEG with a molecular weight of 6000 and 10% PA can reduce the friction coefficient of the water-based drilling fluid to 0.094, and at the same time, the adhesion coefficient of the filter cake can also be reduced to the minimum, so as to achieve the lubricating performance close to that of the oil-based drilling fluid. PA is hydrolyzed to form polar groups to chelate and adsorb on the metal surface and form a lubricating film, while the hydroxyl group at the end of the PEG molecule can further connect with the ether bond on PA to form a hydrogen bond, thereby forming a second layer of lubricating film. The synergistic effect of the two lubricating films minimizes the friction of the contact surface and improves the anti-wear performance of the drilling fluid. According to the SEM image of the filter cake, it can be seen that the solid particles in the filter cake without lubricant are dispersed in irregular prisms, while the solid particles in the filter cake with lubricant are tightly packed, and in a regular spherical shape (Fig. 3b), thus forming a “ball bearing effect” on the surface of the mud

cake, effectively reducing the frictional resistance between the drilling tool and the mud cake.⁵⁴

The effects of the above lubricants on the rheological properties of water-based drilling fluids are shown in Table 4. The use of polyalcohols alone generally does not cause a large change in the rheological properties of the drilling fluid, but its use in combination with other lubricants may cause changes in the rheological properties. Therefore, further research is needed on the synergistic effect of alcohol-based lubricants and other lubricants.

Hydroxyl groups are beneficial to bond with metal surfaces and improving lubricity. Polyols can inhibit the hydration of bentonite and can play a lubricating effect to a certain extent, but its lubricating effect under more complicated conditions has not been studied in depth.

4.3 Nano-lubricants

Nanotechnology has developed rapidly in the past ten years and has been widely used in all walks of life. The small size of nanomaterials gives it unique advantages in plugging micropores in the formation. The use of nanomaterials as drilling fluid additives to improve the stability of the wellbore has been widely successful.^{55,56} In addition to the advantages in size, nanomaterials also have a high specific surface area, which facilitates the interaction between nanomaterials and frictional contact points.⁵⁷ Recent studies have shown that under uniaxial tests, the friction coefficient of nano-solids is smaller than that of pure oil, and the ultimate pressure of nano-lubricants is twice that of pure oil.^{58–60} According to the difference in nanomaterials, nano lubricants can be divided into three types: nanoparticles, nanofluids, and nanographene.

4.3.1 Nanoparticles. Silica (SiO₂) nanoparticles are one of the most common drilling fluid nano additives. Taraghikhah *et al.* tested the effect of different concentrations of SiO₂ nanoparticles on the lubrication properties of WBDF. The results showed that only 1 wt% of SiO₂ nanoparticles can achieve lubrication enhancement.⁶¹ However, Petar *et al.* obtained the opposite conclusion. They proposed that regardless of the type and concentration of nanoparticles,^{26,62} the use of SiO₂ nanoparticles alone cannot improve the lubricity of WBDF without any lubricant. In drilling fluids containing lubricants, both SiO₂ and titanium dioxide (TiO₂) nanoparticles can reduce

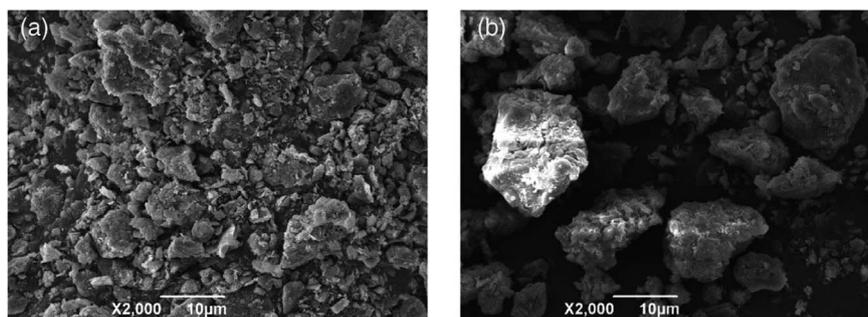


Fig. 3 SEM images of bentonite (a) before and (b) after treatment with polyethylene glycol solution (copyright@2021 Liu *et al.*).¹⁰

Table 4 Summary of the effect of alcohol-based lubricants on the rheology of drilling fluids

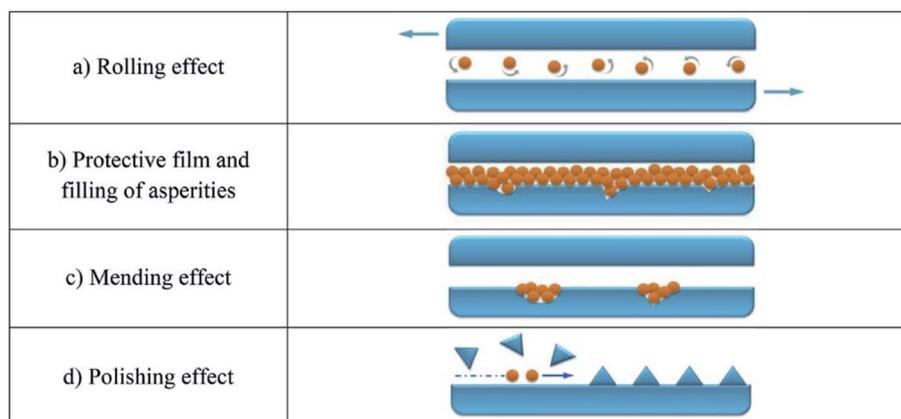
Lubricant	Rheological properties/compatibility
Complex polyol fluid ⁵²	It has been used in oil wells in the Gulf of Mexico, and the complex polyol fluid produced by the reaction of methyl glucoside and polyglycerol can improve the stability of the wellbore
Fatty alcohol ⁵³	Fatty alcohols can inhibit foam generation and reduce the impact on other properties of drilling fluids
Polyethylene glycol (PEG) ¹⁰	PEG lubricant has no obvious effect on AV, PV, and YP of drilling fluid, and has been successfully applied in Sulige gas field
Polyaspartic acid (PA) and polyethylene glycol (PEG) ⁵⁴	The use of PA and PEG alone has little effect on the rheological properties of water-based drilling fluids. However, the combined use of PA and PEG has a synergistic effect on the rheology of the drilling fluid. In the presence of 10% PA, the addition of PEG increases the viscosity of drilling fluid but has little effect on PV and YP. The gel of the drilling fluid will increase with the increase of the PEG concentration, that is, the suspending ability of the drilling fluid will increase

the lubrication coefficient of the drilling fluid.⁶³ The reason why the two works reached opposite conclusions can be attributed to the different lubricity evaluation methods used by the two. Taraghikhah *et al.* tested the lubrication coefficient of the filter cake, while Petar *et al.* used an EP lubrication instrument to test the friction coefficient of the drilling fluid itself. So, using SiO₂ nanoparticles alone can improve the lubricity of the filter cake but cannot improve the lubricity coefficient of the drilling fluid itself. Dhiman *et al.* put forward a different point of view. They believe that the mechanism of nano-particles affecting the lubricity of drilling fluids is not the rolling bearing effect or the adsorption film-forming effect, but the effect of the nanoparticles on the association state of the clay platelets. If the nanoparticles can enhance the dispersion of the clay platelets, the lubricity of the drilling fluid can be improved. Conversely, if the nanoparticles cause the flocculation of the clay platelets, it will reduce the lubricity of the drilling fluid.⁶⁴

Metal borate is an important tribological additive. Borate nanoparticles have excellent wear resistance, anti-friction ability, and oxidation resistance. The study by Saffari *et al.* showed that adding borate nanoparticles to the drilling fluid increased its extreme pressure property by more than five times

compared to the reference samples. As shown in Fig. 4, the spherical structure of nano-borates, such as magnesium, zinc, aluminum, and titanium borate, can change the wear properties of the friction surface from simple sliding friction to mixed rolling-sliding friction. The excellent wear resistance of nano borate enables it to stably form a strong protective friction film on the friction surface under extremely high salty high pressure and temperature. The nanomaterial deposited on the concave part of the friction surface can compensate for the worn surface and reduce the surface roughness. Finally, the nanoparticles can also separate the sliding material to prevent direct contact between the contact surfaces. Among the different nano-borates, the biodegradable nano-borate showed the most excellent performance in preparing high-quality friction films and reducing the friction coefficient.⁵⁷

Organic borate esters are excellent ester-based lubricants with good wear resistance, but their application is limited due to their easy hydrolysis property. Hydrolysis can lead to the formation of abrasive boric acid, which is not conducive to lubrication. Shutesh *et al.* reacted nanoparticles with boron and suspended them in an ester-based organic carrier to prepare a boron-based nanomaterial enhanced additive PQCB. PQCB

Fig. 4 Possible mechanisms of lubrication using nano-additives (copyright©2018 Saffari *et al.*).⁵⁷

can improve the lubricity of drilling fluid in challenging formations with temperatures up to 200 °C. 5% PQCB can reduce the torque of the 10 lb gal⁻¹ drilling fluid system by 80% and that of the 13.5 lb gal⁻¹ drilling fluid system by 52%. In addition to improving lubricity, PQCB can also enhance the rheology of drilling fluids and eliminate the problem of foaming. For the lubrication mechanism, PQCB mainly reduces friction by forming a highly wear-resistant friction film on the drilling tool.⁶⁵

Polystyrene/organic montmorillonite nanocomposites (PS/OMMT) were prepared by *in situ* emulsion polymerization of styrene. PS/OMMT mixed with silicone oil can provide nanocomposite lubricant with temperature resistance up to 200 °C for drilling fluids. PS/OMMT nanocomposite particles can be used as micro bearings to transform sliding friction into rolling friction. As the friction temperature increases, the nanoparticles can be slightly melted, forming a layer of nano-film with certain toughness and strength on the metal surface. It is worth mentioning that the nanocomposite particles can also reduce the foaming of drilling fluid.⁶⁶

Molybdenum disulfide (MoS₂) nanoparticles are a typical two-dimensional layered material with the typical lubricating ability and are widely used as lubricating additives.⁶⁷ However, the dispersibility of solid MoS₂ in the oil phase is poor and cannot fully exert its effective lubricating ability. Lu *et al.* proposed to couple organic chains (1-dodecanethiol, DDT) with MoS₂ nanosheets to improve the lubrication properties of MoS₂ in liquid lubricants. The organic acid ammonium in JS-LUB can be effectively adsorbed on the friction surface to form a stable oil film. The layered structure of MoS₂ nanosheets plays an important role in improving lubricity. Compared with commercial lubricants, JS-LUB does not foam and also does not affect the rheology of the drilling fluid, it can reduce the filtration loss and effectively increase the ROP.⁶⁸

The effects of nanoparticles on the rheological properties of drilling fluids are shown in Table 5. Nano-SiO₂/TiO₂ is already a commonly used additive for drilling fluids, and its influence on the rheological properties of drilling fluids is mainly controlled by its concentration. Other composite nanoparticles also generally do not degrade the rheological properties of drilling fluids.

Nanoparticles have more unique properties than traditional solid lubricants due to their small particle size and large specific surface area. Direct use of nanoparticles has a poor lubricating effect due to their low dispersibility. Surface modification can enhance the dispersion of nanoparticles and their adsorption on the friction surface. Among them, borate or borate ester nanomaterials have the highest lubricating potential due to their excellent lubricating effect and unique environmental advantages.

4.3.2 Nanofluids. The emulsion is also a lubricant for reducing friction.⁶⁹ Yang *et al.* developed a nano-level emulsion lubricant for Daqing Oilfield. The oriented adsorption of nano-emulsified lubricant on the well wall is shown in Fig. 5. Nano-emulsion particles can not only be adhered to the surface of the well wall or drilling tool and form a dense lubricating film but also can be adsorbed on the clay particles to improve the structure of the clay, thus reducing the friction caused by interlayer sliding of drilling fluid.⁷⁰ In addition, the nano-emulsion can change the particle network structure in the drilling fluid by adhering to the surface of the solid particles, thereby improving the rheological properties of the drilling fluid, increasing the YP value of the drilling fluid, and thus enhancing the rock-carrying ability of the drilling fluid.

4.3.3 Nano graphene. Graphene is the thinnest two-dimensional material in the world, with high hardness and high specific surface area. Its special physical and mechanical properties make it an additive in a high-performance solid lubricant or liquid lubricant. First, the interlayer shear force of graphene is very small, and its extreme mechanical strength can inhibit the wear of the friction surface. Secondly, graphene can isolate liquids and gases (such as water or oxygen), thus slowing down the oxidation and corrosion of the friction surface.^{71,72} However, the original graphene is hydrophobic and cannot be directly used as an additive for WBDF lubricants. The tribological properties of graphene change with its surface chemistry. Therefore, it is necessary to modify the surface of graphene to improve its hydrophilicity and adjust its lubricating properties.

Liang *et al.* improved the dispersion stability of graphene in water by the nonionic surfactant Tritonx-100.⁷³ As shown in Fig. 5a, in the presence of hydrophilic surfactants, the graphene in contact with the sliding surface is embedded in the wear

Table 5 Summary of the effect of nanoparticles on the rheology of drilling fluids

Lubricant	Rheological properties/compatibility
Nano-SiO ₂ /TiO ₂ (ref. 61–64)	The influence of nano-SiO ₂ /TiO ₂ on the rheological properties of drilling fluid depends largely on its concentration and temperature
Metal borate ⁵⁷ PQCB ⁶⁵	Not mentioned Higher PV, YP, and gel can be obtained after adding PQCB to the drilling fluid. The addition of PQCB to the weighted drilling fluid helps to increase the low shear rate viscosity and enhance the rock-carrying ability of the drilling fluid
Polystyrene/organic montmorillonite nanocomposites (PS/OMMT) ⁶⁶ JS-LUB ⁶⁸	PS/OMMT can keep the rheological properties of drilling fluid stable in the temperature range of 200 °C JS-LUB had no obvious effect on the density and rheological properties of the drilling fluid



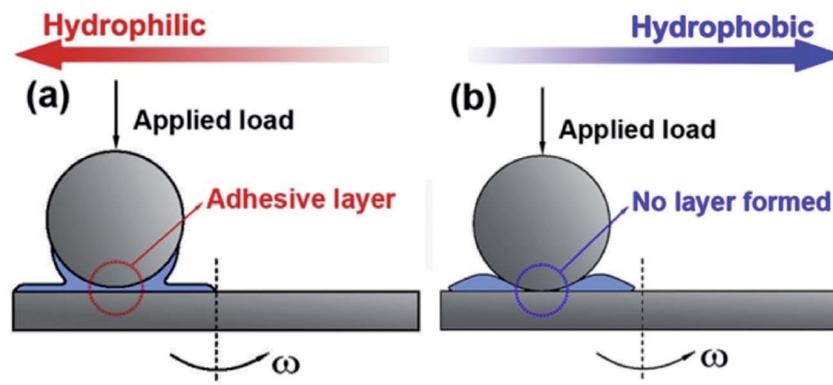


Fig. 5 (a) Lubrication mechanism of graphene in hydrophilic and (b) hydrophobic cases (copyright©2016 Liang *et al.*).⁷³

trace to form a protective film on the worn surface. In contrast, graphene films cannot be formed in the hydrophobic case (Fig. 5b).

Taha and Lee have developed a nanographene product, which is a mixture of proprietary surfactants and nanographene. Compared with typical ester-based lubricants, the nano-graphene can reduce the torque of conventional salt polymer drilling fluids by 70–80%, while the ester-based lubricant can only achieve 30–40% torque reduction in the same case. Nanographene is biodegradable, and it remains stable at temperatures up to 300 °C, it can also be used in medium-salinity drilling fluids with chloride content up to about 140 000 mg L⁻¹.⁷⁴ Perumalsamy *et al.* compared the effects of ester-based lubricant (PC60) and nanographene on the rheology and lubricity of water-based drilling fluids. Compared with PC60, the stability of nanographene after aging is reduced, increasing the coefficient of friction. Therefore, the lubricity of graphene after aging needs to be further enhanced. However, ester-based lubricant (PC60) has a greater tendency to foam than nanographene in water-based drilling fluids, which is not conducive to the stability of drilling fluid rheology.⁷⁵ Tian *et al.* improved the high-temperature stability of graphene using sodium dodecylbenzene sulfonate (SDBS) modification so that it still maintains high lubricity at a high temperature of 240 °C. SDBS not only improves the hydrophilicity of graphene but also has certain anti-wear properties. The sulfonate group of SDBS-modified graphene promotes the deposition of graphene and bentonite, forming a deposition film composed of graphene, Al₂O₃, SiO₂, Fe₂O₃, and FeSO₄, thereby improving the tribological properties of the drilling fluid.⁷⁶

Liu *et al.* also investigated the improvement of the lubrication properties of drilling fluids by graphene and graphene oxide. The uniform and stable dispersion of graphene or graphene oxide are obtained by using a dispersant and an ultrasonic dispersion method. The results showed that graphene oxide with better dispersibility can significantly improve the lubricity of drilling fluids than graphene. Only 0.075 wt% of graphene oxide can reduce the lubrication coefficient by 12.6% and the wear area by 21.7%. However, the content of graphene oxide should not be too much. When the amount of graphene oxide added exceeds 0.1%, its lubricity decreases due to the

decrease in dispersibility. When the amount of graphene oxide added exceeds 0.2%, too much graphite oxide will be deposited on the friction surface which will increase the surface roughness, which has a negative impact on the expected friction reduction.⁷² Our group also studied the lubricating properties of graphene oxide (GO) and the deep eutectic solvent (Gly-DES) composed of choline chloride and glycerol in drilling fluids. Our experimental results showed that the combination of only 0.1% GO and 2% Gly-DES can reduce the adhesion coefficient by more than 50%, increase the GO content to 0.25%, and the friction coefficient can also be reduced by more than 50%. The micro-morphological observation of the metal friction surface showed that GO mainly affected the width of the wear scar while Gly-DES affected the depth of the wear scar more. Therefore, the synergistic effect of the two can greatly reduce the volume of wear scars, that is, reduce friction. In addition, GO and Gly-DES do not increase the filtration volume of drilling fluids, whether used alone or in combination.⁷⁷

Wang *et al.* used the cationic surfactant CTAC to modify the surface of natural flake graphite to improve the dispersibility of graphite in water-based drilling fluids. The authors evaluated the lubricating properties of modified graphite by the viscosity coefficient (VC). The results show that the modified graphite exhibits the best lubricating effect when the addition amount is 0.05%. In addition, the modified graphite had no obvious effect on the rheological parameters of the drilling fluid.⁷⁸

Table 6 showed the effects of the investigated nanographene lubricants on the rheological properties of drilling fluids. The results showed that graphene, graphene oxide, and modified graphene all have no obvious effect on the rheological properties of drilling fluid. Nano graphene has obvious effects in reducing drill string torque and corrosion, and its dispersion in drilling fluid is the current research focus. However, the high cost of graphene has largely limited its development and application.

5. Lubrication mechanism

Overview of the research on a large number of lubricants, the lubrication mechanism can be summarized as shown in Table 7.



Table 6 Summary of the effect of nanographene on the rheology of drilling fluids

Lubricant	Rheological properties/compatibility
Graphene ^{75,79}	Graphene enhanced lubricant has little effect on the rheological parameters of drilling fluid
Sulfonated modified graphene ⁷⁶	Not mentioned
Graphene oxide (GO) ^{72,77}	GO has no obvious effect on the rheological properties of drilling fluid
CTAC modified graphene ⁷⁸	CTAC modified graphene has no obvious effect on the rheological properties of drilling fluids

However, the current research on the lubrication mechanism is not deep enough, and the discussion on the film formation mechanism is still lacking.

6. Challenges and future prospects

The friction between the drilling tool and the wellbore trajectory is the main cause of torque and friction, that is, the friction between the drilling tools and the friction between the drilling tools and the filter cake on the well wall. Improving the lubricity of the surface of the drilling tool and filter cake on the borehole wall is the main way for drilling fluid lubricant to reduce torque and friction. Due to strict environmental regulations, WBDF is considered an alternative to OBDF and SBDF. Because of the low lubricity problem of WBDF, the development of eco-friendly high-performance water-based lubricants is essential to reduce the friction of WBDF. Natural animal and vegetable oils, ester-modified products, and nanomaterials have become more environmentally friendly alternatives to traditional hydrocarbons. They can significantly reduce friction in the WBDF environment. Among them, vegetable oil-based lubricants and biodiesel are considered promising WBDF lubricants, which provide the possibility for the green and sustainable development of the oil and gas drilling industry. Nanomaterials that solved the dispersion problem are also a reliable choice for WBDF lubricants.

A good water-based drilling fluid lubricant should have the following characteristics: firstly, it can effectively reduce the friction coefficient or filter cake lubrication coefficient of the drilling fluid. In addition, it should also have the characteristics of no fluorescence, non-toxic, biodegradable, no pollution to the environment, and no impact on the basic performance of drilling fluid. Few water-based drilling fluid lubricants fully satisfy the above characteristics, and there are still many difficulties and challenges in the research of lubricants.

- There are still huge challenges in simplifying the preparation process of solid lubricants.
- The structural modification of oil ester molecules such as vulcanization modification, sulfonation modification, and introduction of cyclic rigid structure is an effective method to improve the temperature resistance of lubricant molecules. Considering environmental factors, the introduction of a rigid ring structure or more environmentally friendly temperature-resistant elements (such as B) into the lubricant molecule is the future development direction, rather than the introduction of S/P and other elements that are likely to cause environmental problems.
- The complete elimination of fluorescence is one of the biggest challenges of water-based drilling fluid lubricants. From the perspective of molecular design, it is the most effective means to eliminate the main sources of fluorescence, that is,

Table 7 Summary of lubrication mechanism

Lubrication mechanism	Representative lubricant	Characteristics
Rolling of particles	Nano-borates, ⁵⁷ nano SiO ₂ , ⁶³ PS/OMMT ⁶⁶	Spherical particles convert the sliding friction between the friction surfaces into rolling friction, thereby reducing the friction coefficient. In addition, the particles are deposited in the recesses of the friction surface, which can reduce the surface roughness
Adsorption of friction surfaces	Modified vegetable ester, ^{1,30,48} biodiesel, ³ polyethylene glycol ¹⁰	Lubricants are physically adsorbed to the friction surface through hydrogen bonds, electrostatic interactions, intermolecular forces, <i>etc.</i> , or chemically adsorbed to the friction surface through metal bonds such as C=S bonds. The presence of the adsorption film reduces the mutual contact of the friction surfaces to reduce the coefficient of friction
Sliding of the layered structure	Flake graphite, ²⁹ graphene, ⁷² MoS ₂ (ref. 68)	The lubricant molecules with a layered structure are deposited on the friction surface, so that the direct contact between the friction surfaces is converted into the relative slippage of the lubricant molecular layer, thereby reducing the friction coefficient



double bonds, conjugated double bonds, and condensed ring structures with Π electrons in the molecular structure.

- As for biodiesel-based lubricants, their serious impact on drilling fluid performance is an important factor restricting their application and development. The impact and regulation of biodiesel-based lubricants on drilling fluid performance need to be the focus of future research.

- Nano lubricants have greater advantages in terms of temperature resistance and compatibility with drilling fluids, but the biggest challenge it faces is to solve the problem of dispersion in water. Surface modification is an effective solution.

- Temperature and pressure usually affect the lubricating effect of lubricants. For example, under high temperature or extreme pressure conditions, the physical adsorption film of the lubricant is gradually broken, resulting in deterioration of lubricity. At this time, only the lubricant that forms a chemically bonded film can still exert its lubricating ability under extreme conditions. In addition, lubricants are also affected by other complex conditions during use, such as high-salt and high-calcium environments. However, in the current research, there are few analyses of the influence of complex formation conditions and other additives of drilling fluid on lubricant lubrication performance, which also largely limits the application of these research results on the site.

- The performance evaluation methods of lubricants are also one of the difficulties that limit the research and application of lubricants. The current evaluation of the drilling fluid lubrication performance is mainly measured by friction coefficient, which is too simplistic. Many new tools based on tribological principles have been used in the design of lubricants in other industries, such as tribometers, Stribeck curves, high-frequency reciprocating drills, *etc.*, which can more comprehensively characterize the performance of lubricants under different conditions. During the drilling process, the rotation of the drill string, the temperature and pressure of the formation, and the viscosity, density, and salinity of the drilling fluid will all affect the performance of the lubricant. Excellent water-based lubricants are not necessarily suitable for WBDF, because WBDF has complex additive components. Only considering the friction properties of the lubricant in water is not enough, it is also necessary to consider its compatibility with other components in the drilling fluid. On the other hand, the current tools for evaluating the lubricity of drilling fluids are too simple, and more tools used to simulate the actual state of the formation and drilling tools should be applied to the evaluation of the lubrication properties of drilling fluids. The exploration of the lubrication mechanism is an important means to improve the effect of lubricants.

- Finally, the cost of environmentally friendly lubricants is the last hurdle that restricts its large-scale application. Vegetable oils are widely available and inexpensive. If the modification procedure can be further simplified, ester lubricants obtained by modification of vegetable oils are still one of the most economical lubricants at present. Alcohol-based lubricants are also one of the cost-acceptable lubricants, but because their lubricating effects under complex conditions have not

been thoroughly studied, the application range of alcohol-based lubricants is still not wide enough. Nanoparticles such as SiO_2 and TiO_2 have already been commercially produced and widely used in drilling fluids. However, the modification work to improve the lubricity and stability of nanoparticles is bound to further increase their cost of use, which depends on the modification scheme of nanoparticles. Finally, although nano-graphene, one of the recent research hotspots, has an excellent lubricating effect, its preparation cost is much higher than other lubricants, so its large-scale application cannot be realized. The issue of cost is a key factor in whether lubricants can move toward production, and only a few studies have examined the cost of the developed lubricants, which should receive more attention in future studies.

7. Conclusions

Due to the strict environmental regulations, the oil and gas drilling industry is developing in the direction of safety and environmental protection. This paper mainly discusses the research progress of environmentally friendly WBDF lubricants. The preparation, performance, and lubrication mechanism of solid lubricants, ester-based lubricants, alcohol-based lubricants, and nano-lubricants are discussed in detail. Several techniques to characterize the lubrication properties of drilling fluids are also summarized.

- Solid lubricants have unique advantages in transportation and storage. The new solid lubricant is no longer a simple inert solid but is mainly transported and stored in solid form, dispersed in the drilling fluid, and improved lubricity through adsorption and film formation.

- Modified vegetable oil esters have high stability and reduce the friction coefficient by forming a lubricating film on the metal surface or filter cake. Ordinary physical adsorption membranes are easily destroyed under high temperature or extreme pressure conditions. Under heavy load conditions, it is necessary to form a chemical adsorption film to maintain lubricity.

- The excellent adsorption of biodiesel on the surface of steel and the good dispersibility in water make it a potential WBDF lubricant. The type of oxygen-containing groups has an important effect on enhancing the lubricity of biodiesel. The high viscosity and foaming properties of biodiesel require special attention, as they may cause the deterioration of drilling fluid performance.

- To avoid the above shortcomings, the structural modification of vegetable oil and biodiesel molecules is an effective way to improve its ability to maintain lubrication under complex conditions. However, it should be noted that the compounds converted from elements such as S/P are toxic. Therefore, more environmentally friendly, temperature-resistant, and wear-resistant elements should be selected, or introduce other rigid groups.

- Compared with ester-based lubricants, polyols or fatty alcohol-based lubricants have a significant advantage in that they can inhibit foaming and have less impact on other



properties of drilling fluids. However, they have the limitation that they are not suitable for high-temperature environments.

- Nanomaterials have significantly higher-pressure resistance than oil. Nanoparticles can be inserted between friction materials to separate frictional contact surfaces and convert sliding friction into rolling-sliding friction. Besides, the deposition of nanomaterials on the depressions of the friction surface can also reduce the surface roughness of the friction surface.

- Graphene and molybdenum disulfide nanomaterials, as layered materials, are easy to deposit on the friction surface to form a lubricating film, which is an excellent lubricating material. The problem with both is poor dispersion. The surface-modified graphene and molybdenum disulfide nanomaterials have the potential to develop into highly efficient WBDF lubricants.

- The current research still lacks a more comprehensive and more suitable application conditions evaluation method for lubrication performance. It is recommended to consider lubrication performance analysis tools in other industries. No matter what kind of lubricant, it must be selected based on the actual application state of the drilling fluid. The complex WBDF composition and drilling conditions need to be considered more comprehensively and systematically in the development and selection of lubricants.

Conflicts of interest

There are no conflicts to declare.

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