Progress of Development and Application of Drag Reduction Agents for Slick-Water Fracturing

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Abstract. Fracturing technology is the key technology of shale oil and gas exploitation in the United States. The key of hydraulic fracturing lies in the formulation of fracturing fluid, which can improve the permeability of shale gas layer, reduce pumping resistance, optimize production conditions, reduce strata damage and other purposes. Slick-water is widely used in water-based fracturing for unconventional oil and gas exploitation, which can reduce the friction resistance. As the core of the slickwater fracturing fluid, the friction reducer determine the fluid’s performances. Combining with the related literature at home and abroad, this paper analyzes the mechanism of friction reducer, introduces the research and application progress of natural polysaccharide, surfactant and polyacrylamide. It is considered that both the instant powder polymer and W/W dispersion polymer have great application potential. The friction reducer with high-efficiency sand-carrying and salt resistance is the focus of future research.

Keywords. Unconventional reservoirs, slickwater, anti-blocking agents, polymers, resistance reduction rates.

1. Introduction
With the development of conventional energy extraction and fracturing technology, the target of oil and gas exploration at home and abroad has been shifted from conventional to unconventional. Unconventional reservoir materiality is poor, porosity is small, penetration rate is low, no natural production capacity, oil and gas resources include oil sands, heavy oil, shale oil, dense sandstone gas, coal seam gas, shale gas, etc., rich in world content, need to carry out reservoir transformation in order to obtain industrial output. Slippery water fracturing is one of the most effective ways to realize its economic exploitation. Slippery water is a common water-based fracturing fluid, in clear water to add anti-blocking agents, filter-reducing agents, support agents, surfactants, fungicides, clay stabilizers, etc. formed, 96%-99% by water composition, also known as water fracturing liquid or water fracturing solution. Belongs to the non-Newtonian fluid, shows the sticky elasticity, the resistance effect is significant, can use large displacement, large-scale, high pump pressure operation mode to communicate the natural cracks of the formation to achieve reservoir transformation, with easy return can be reused, not easy to form filter cake, small damage to the formation and so on. As one of the most important additives, anti-resisting agent has become a hot research topic of fracturing liquid in modern times [1-2].

Based on the relevant literature at home and abroad, this paper summarizes the development course, classification, resistance reduction mechanism and research and development application, and looks forward to the development direction.
2. The Development Course of the Anti-Blocking Agent

In 1948, Toms [3] observed a decrease in chlorobenzene flow resistance with a small amount of polymethyl acrylates (PMMA), and the polymer's resistance reduction, also known as the Toms effect, was first observed. Savins in 1963 [4] defined the resistance reduction agent as a small amount added to the fluid to increase transport capacity, energy consumption reduced substances, referred to as DRA, the resistance reduction effect is generally characterized by the resistance reduction rate. Adding one millionth of a millionth of a long-chain flexible resistance reduction agent to the liquid can reduce turbulence friction loss by up to 80%, because the realization of resistance reduction can bring great economic benefits, resistance reduction agent has become a common concern, widely used in oil and gas, biomedicine, fire protection, sewage treatment, regional heating and other fields [5].

Fracturing fluid with reducing inhibitors first appeared in the late 1950s and early 1960s [6], and has since been mainly used in cross-linking gel systems for reservoir modification. With the transition from conventional to unconventional oil and gas exploration, anti-fracturing fluid has received renewed attention and has shown great superiority in the fracturing operations of shale gas layers. In 1997, Mitchell first adopted a water-skiing fracturing system to carry out a large-scale volume modification of the Barnett shale, the success of which provided an effective means of unconventional oil and gas exploration [4]. Large-scale applications began in the field in 1998 and accounted for 30 per cent of total fracturing fluid use in the United States in 2004. It has been rolled out worldwide [7-9].

3. Reduce the Resistance Classification

The advantages and disadvantages of anti-blocking agent determine the performance of fracturing fluid, which is the core factor restricting reservoir mining [10-12]. After the success of the application of water-skiing fracturing fluid, there has been an increase in research reports on anti-blocking agents at home and abroad. At present, the most used water-based anti-blocking agent is formulated for water-based water-based anti-obstruction agent, according to molecular structure and source, can be divided into the following types.

3.1. Polyacrylamide (PAM)

Polyacrylamide is a synthetic polymer and is most widely used in oil and gas fields. There are sol-like, solid powder-like and emulsion-like forms. The production cost of sol-like anti-resistance agent is low, but the resistance reduction rate is slow, and it is less used in fracturing fluid. Powdered polyacrylamide is easy to store and transport, the synthesis process is mature, the degradation rate is high, but the dissolution rate is slow, in the water first dissolved and then dissolved, the dissolution will not be sufficient fisheye caused reservoir damage, site construction can be overcome by means of instruments and equipment to overcome its dissolution problem. The United States developed a hybrid equipment power consumption is low, all aspects of better performance, the technical level in a leading position. China's current use of the most car-mounted hybrid car CSGT-240, the use of jet mixer for water powder mixing, the maximum dispensing capacity of 10m³/min, the general use of two vehicles at the same time dispensing to meet the construction needs. The powder-like anti-resistor CFZ-1, produced by Yanfei, et al., can be completely dissolved within 5min and has a certain viscosity to meet the requirements of continuous mixing on-site. The combination of instant powder-type anti-resistors and continuous mixing devices can greatly reduce costs and operational complexity. Emulsion-like polymers are micron-grade and can generally dissolve quickly in water within 3 min, including the following two types [13-15].

3.1.1. W/O Inverted Polymer Damper. Through inverting emulsion polymerization, the monomer water solution is added to the oil phase step by drop, emulsified and dispersed in the oil with the aid of oil-coated water emulsifier, the polymerization caused by the addition of the trigger agent, conforming to the free radical reaction mechanism, chain triggering, chain growth and chain termination of the three element reactions, and finally the water-soluble polymer particles are evenly dispersed in the oil phase emulsion. The distribution state of the oil and water was shown in figure 1. W/O-type inverting
polymer relative to the molecular mass is large, solid content is about 25%-40%, the inner phase is water-soluble polymer, the outer phase is petroleum alkanes, dilution, the polymer in water can be quickly hydrated release. With good solubility and thickening ability, the synthetic path is easy to operate, the raw material source is wide, the field application is the most. Inverted emulsion polymerization when the amount of surfactant is large, polymers need to be phased before they can be dispersed in water to play a role, and the emulsion contains a large number of oil phases, will bring about environmental pollution problems, for which W/W dispersion polymer anti-blocking agent is proposed.

![Figure 1. The distribution state of the oil and water.](image)

3.1.2. W/W Dispersion Polymer Anti-Resistor. Through the water dispersion polymerization method, a high concentration of electrolyte solution is added to the water solution containing monomer as a phase separator, isolation and electrostatic action with the polymer chain, the polymer formed after adding the promoter can be dissolved directly in water by dispersion mechanism, forming a uniform and stable W/W solution. The particle size is usually 10μm. The synthesis process is simple, the dissolving rate is fast, the safety is high, and the environmental impact is small. W/W-type anti-resistant than W/O type, does not contain organic solvents and surfactants, dissolves quickly, low cost, small environmental pollution. But most of them are still in the research and testing stage, and they are not being put into use on a large scale. The field application effect should be further studied so that it can replace the traditional W/O-type anti-resisting agent [16-17].

Changing the composition of polymer monomers can give the anti-resistance agent better performance. Monomers containing sulfonate roots, which can form strong hydrogen bonds with water and have greater stability, include vinyl acrylates, acrylic sulfonate, 2-acrylamide-2 methyl sulfonate (AMPS), etc., with AMPS being the most widely used. Ring monomers can increase the rigidity of polymers, including chitosan, vinyl glycoside, acrylamide, etc., can increase thermal stability. Adding a small amount (molar fraction <2%) hydrophobic group to the molecular main chain, usually 12-18 alkys, can obtain hydrophobic polyacrylamide (HAPAM), which can be physically cross-linked to form a reversible spatial mesh structure, which in turn can increase the ability to resist shearing. When the concentration is lower than CAC (critical polymerization concentration), the polymer chain mainly takes place in-molecule action, the higher the content of hydrophobic monomer, the more curly the polymer, is not conducive to reducing resistance. When CAC is reached, intermolecular bonding occurs, DR increases, and when CAC is exceeded, viscosity decreases and DR decreases slightly.

3.2. Natural Polymers
Natural polymer inhibitors are biodegradable, the most representative of the natural macromolecules xenon gum (XG) and polysaccharide gum (GG), the price of the two are equivalent, the gum depends on imports, and xylitol can be produced for their own use.

Xyrogen is an efficient thickener that quickly dissolves in water to form a stable rigid rod-like double helix structure. Small influence by acid alkaline, with false plasticity, and compared with polymers with molecular weight, the ability to resist shear is stronger, but the resistance performance
is generally, low temperature is difficult to break the glue, high temperature is easily oxidation degradation and loss of effect. The high salt resistance makes it show great application potential in the field of fracturing fluid formulation. Minghua, Lu Congjun, etc. [18] in 2016 using mineralization of 28074mg/L of sea water formulation quality score of 0.4% modified xylogen fracturing liquid, with low resistance, good stability, sand carrying capacity, safety and environmental protection, can meet the compact reservoir fracturing needs at 60 to 130 degrees C, and simple formulation, low cost, with broad application.

Linear gel and its derivatives in high concentration as a thickener to increase adhesion, low concentration can be used as a resistance reduction agent, in polyacrylamide-type anti-blocking agent before the epidemic, widely used in the formulation of fracturing fluid, low cost, is the earliest use of water-skiing anti-blocking agent. Usually when the mass concentration is 10mg/L, the effect of reducing resistance begins to appear, the mass concentration increases, the resistance reduction rate increases, at 300 mg/L is 30%, the resistance reduction rate is low, a small amount of crosslinking agent is added, can simultaneously improve the resistance reduction and sand carrying capacity of the acolyte [19-24]. However, when the glue is returned, the residue content is high, the damage to the reservoir is large, and it is easily decomposed by microorganisms, and the storage time is limited. Some researchers combine flexible polymers with gel to improve performance, R. Deshmukh [25] grafted 7 kinds of polyacrylamide onto the gum, found that the shear resistance and resistance of the gum have been improved, the longer the polymer chain, the better the performance, all grafted gum in ten days did not appear microbial degradation phenomenon.

3.3. Surfactant
According to the charged properties of hydrophilic groups, surfactant-type anti-resisting agents can be divided into four types, respectively, cation, anion, non-ion and gender ion surfactant as the main agent.

Among them, the anti-ion surfactant is poor anti-salt, will react with calcium and magnesium ions in the water to produce precipitation, non-ion surfactants have turbidity point, poor temperature resistance, high price of both sexes surfactants, and the preparation process is cumbersome. The application potential of cation surfactant in the reduction of resistance has been widely studied, even at low concentrations, can occur a stable resistance reduction effect. Among them, seasonal ammonium salt has better anti-temperature anti-shearing properties and is currently the most commonly used surfactant type anti-resisting agent. Xing L and others [26] prepared a solid cation surfactant CFZ-1, the mass score of 0.15%-0.2%, can reduce the resistance 68%-72%. Eight wells have been successfully applied in ultra-low seepage dense reservoirs, and Tammano S [27] have a 70% resistance reduction rate when the mass score is 0.6%, which is synthesized by the main agent of 1dane dimethyl oxide. When the amount of surfactant added is greater than the critical beam concentration, different forms of glue bundle can be formed to make the solution sticky elasticity and drop resistance, if the shear rate is too large, the beam structure is destroyed, the reduction resistance rate is reduced. The high dose of surfactant required to achieve resistance reduction, viscosity can only reach 10%-40% of the same polymer concentration, limiting the transport of proppants, coupled with the higher price of surfactants, resulting in increased fracturing costs, rarely used as a water-skiing anti-blocking agent. Added to fracturing fluid is mainly used to change rock wetting and reduce surface tension, promote liquid re-discharge and thus reduce strata damage.

4. The Mechanism of Action of the Anti-Blocking Agent
Slippery water fracturing uses high displacement, large amount of liquid operation. In some oil fields, the injection rate reaches 25 to 30 m³/min, the water injection of a single well is 2x 105 m³, turbulence is formed in the tube, a large number of vortex is produced, and the polymer solution with the addition of a resistance reduction agent can play an effective role. The following image shows the curve of
frictional resistance of polymer solutions (non-Newtonian fluids) and Newtonian fluids that produce a drop-resistance effect with Reynolds.

In the small Reynolds number, the shear rate is low, the viscous fluid is layered motion, at this time the anti-resistor molecules are disorderly, with the increase of Reynolds, the polymer solution curve deviates from the Newtonian fluid curve, began to occur drop resistance, the fluid interface within the unit length of the pipeline in the turbulence state is distorted and deformed, the curly anti-blocking molecule fully dispersed, the long chain is naturally stretched along the direction of flow, and is linearly arranged, the curve continues to deviate until the drop resistance effect reaches its maximum value, when the Reynolds number is too large, the polymer molecular structure is degraded by a larger shear, the two curves are close to each other until coincident, the drop rate gradually reduced to zero. Therefore, the drop effect exists only in turbulent areas within the limited Renault numerical range [28].

The earliest theory of drop resistance is the pseudo-plastic hypothesis put forward by TOMS, which holds that the viscosity of the fluid decreases with the increase of the shear rate, so the resistance decreases with the flow of the fluid. An in-depth study of non-Newtonian fluids found that polymethylene acrylic, which also has a damping effect, was a typical shear-thickened liquid, a theory overturned.

Since then, a large number of scholars have carried out in-depth study of the mechanism of descent, the complexity of near-wall turbulent flow mechanics and polymer dynamics, so that there is no definite model to explain. There are two more accepted mechanisms.

4.1. Turbulence Inhibits Drop Resistance
The polymer stretches in the near-wall flow area, and the stress generated by the stretch is opposite to the vortex force, resulting in vortex suppression. Zhang [29] used three-dimensional direct numerical simulation to find that the positive and negative torque of the polymer can inhibit the frequency and intensity of the vortex burst, reduce the vortex regeneration, thereby reducing turbulence pulsation, so that the flow in the quasi-stratospheric flow state. Using numerical simulation, Toonder [30] used particle image velocity measurement technology to study the flow velocity and turbulence distribution of liquid after adding the anti-blocking polymer, and found that radial turbulence intensity decreased and axial turbulence intensity increased. Polymer molecules mainly act on the area near the pipe wall, also known as buffer zones, resisting some radial forces of fluid microns and converting them into axial forces that flow in a smooth direction, reducing the exhaustive consumption and reducing the coefficient of friction of the flow by changing the turbulence structure and flow rate distribution.

4.2. Sticky Elastic Resistance Reduction
All polymers with a resistance reduction effect have a sticky elasticity at higher concentrations. Maxwell's equation shows that the vortex of the fluid is obviously inhibited with the increase of adhesive elasticity. Sticky elasticity gives it the ability to store energy, absorbs kinetic energy near the wall and converts it into its own elastic energy, giving the fluid a certain buffering effect, when the polymer molecule relaxes long enough, the energy is released into the buffer layer to weaken the near-wall turbulence. The anti-resisting agent can also form an elastic bottom layer in the pipe, with the increase of concentration, the bottom layer thickens, creating isolation between the pipe wall and the liquid, reducing the pipe wall resistance, thus achieving the drop effect. Some researchers have found that at low flow rate, the resistance reduction performance is mainly affected by viscosity, while at high flow rate, it is mainly controlled by elasticity. Liu [31] used a transmission electron microscope to observe the micro-resistance mechanism of the anti-blocking agent, indicating that the dispersed particles and continuous mesh-like structure of the anti-blocking agent have a good resistance reduction effect at low and high flow rates, respectively, as shown in figure 2.
Figure 2. (a) Pure liquids; (b) Liquids with anti-blocking agents added.

The mechanism of drop resistance is not completely clear at present, but it is certainly related to the tensile properties of polymer flexible long chain molecules.

5. Summary and Outlook
Reducing mor resistance has always been the most important goal in the process of oil and gas extraction, based on the above-mentioned research on water-skiing fracturing anti-blocking agent, anti-blocking agent can be extended through the molecular chain to achieve resistance reduction. Natural polymer de-inhibitors come from a wide range of sources and are biodegradable, but have limited resistance reduction capacity. The amount of surfactant is large and the cost is high. Polyacrylamide is the most widely used, there are different kinds, the effect of resistance reduction is obvious, can meet the requirements of different site construction. Both at home and abroad have produced related products, on-site applications have achieved certain results. A wide range of foreign products, BJ Service produced the most widely used anti-blocking agents, limited domestic product categories, most of which are in the laboratory research stage, can reach 70% resistance reduction rate of products less.

Although the water-skiing fracturing liquid can achieve a large reduction resistance, but the sand carrying capacity is weak, not suitable for long-term effective exploitation of oil and gas. It is necessary to increase the adhesive elasticity to increase the production capacity under the condition of meeting the drop resistance, to use slippery water for volume modification, to improve the refive rate of fracturing fluid, to reduce the damage of the reservoir water lock, and to increase recycling. In view of environmental protection problems and water pressure, it is necessary to develop an economic and environmentally friendly anti-resisting agent with excellent de-resistance performance at high mineralization, low damage to the formation and high efficiency with sand. Dispersed polymerized W/W anti-resistant does not contain surfactants and oil phases, dissolves fast and low cost, and has broad application prospects.

China should learn from foreign experience, when formulating fracking fluid, for reservoir characteristics, water characteristics, fracturing equipment and other chemical additives and other comprehensive considerations, the combination of resistance reduction and production capacity, the introduction of different properties of the monomer polymer inhibitor molecular structure design and improvement, or add other material interaction, the optimal site construction design, so as to achieve the lowest cost of maximum recovery results.

Acknowledgments
The project is supported by National Science and Technology major projects (2017ZX05023003).

References
[1] Wang L, Wang D and Shen Y 2016 Study on properties of hydrophobic associating polymer as drag reduction agent for fracturing fluid Journal of Polymer Research 23(11) 235.
[2] Abubakar A, Al-Wahaibi T and Al-Wahaibi Y 2014 Roles of drag reducing polymers in single- and multi-phase flows Chemical Engineering Research & Design 92(11) 2153-2181.
[3] Toms B A 1948 Some observations on the flow of linear polymer solutions through straight tubes at large Reynolds numbers First International Congress on Rheology.
[4] Deshmukh S R and Singh R P 1987 Drag reduction effectiveness, shear stability and biodegradation resistance of guargum based graft copolymers Journal of Applied Polymer Science 33(6) 1963-1975.
[5] Palisch T T, Vincent M C and Handren P J 2021 Slickwater fracturing: food for thought SPE Production & Operations 25(3) 327-344.
[6] Nechaev A I, Gorbunova M N, Lebedeva I I, et al. 2017 Synthesis by radical polymerization and structure of drag reducing terpolymers based on acrylamide, acrylonitrile, and 2-acrylamido-2-methylpropanesulfonic acid Russian Journal of Applied Chemistry 90(9) 1524-1531.
[7] Zhao B Y and Mao J 2019 Review of friction reducers used in slickwater fracturing fluids for shale gas reservoirs Journal of Natural Gas Science and Engineering 62 302-313.
[8] Asdin M A, Suali E, Jusnukin T, et al. 2019 Review on the applications and developments of drag reducing polymer in turbulent pipe flow Chinese Journal of Chemical Engineering 27(8)
[9] Michael S, Kyle F and Steve T 2016 Dry polyacrylamide friction reducer: not just for slick water SPE Hydraulic Fracturing Technology Conference (Texas: SPE).
[10] Hong C H, Zhang K and Choi H J 2010 Mechanical degradation of polysaccharide guar gum under turbulent flow Journal of Industrial and Engineering Chemistry 16(2) 178-180.
[11] Deshmukh S R and Singh R P 1987 Drag reduction effectiveness, shear stability and biodegradation resistance of guargum-based graft copolymers Applied Polymer 33 1963-1975.
[12] Liang X, Yang K and Xu H 2019 Preparation and properties of amphoteric polyacrylamide/modified montmorillonite nanocomposites and its drag reduction performance Colloids and Surfaces A: Physicochemical and Engineering Aspects 574 94-104.
[13] Feng C, Yasuo K and Bo Y 2008 Experimental study of drag-reduction mechanism for a dilute surfactant solution flow International Journal of Heat and Mass Transfer 51(3) 835-843.
[14] Broniarz L, Rozanski S and Rozanska Z 2007 Drag reduction effect in pipe systems and liquid falling film flow Reviews in Chemical Engineering 23(3-4) 149-245.
[15] Ronald R, Harsha S and Friction L 2013 Reducers as water management aids in hydraulic fracturing SPE Production and Operations Symposium Oklahoma City, Oklahoma, USA, SPE.
[16] Robert G and Eric F 2018 Geochemical formulary and analysis of hydraulic fracturing water quality to determine the optimal fracturing fluid design SPE/AAPG Eastern Regional Meeting Pittsburgh, Pennsylvania, USA, SPE.
[17] Shen L, Leonid V and David H 2018 Can friction reducers transport sand during fracturing treatment SPE/AAPG/SEG Unconventional Resources Technology Conference Houston, Texas, USA, URTEC.
[18] Leonid V, Andrey B and Shen L 2018 Far-field diversion system designed for slickwater fracturing SPE Liquids-Rich Basins Conference - North America Midland, Texas, USA, SPE.
[19] Arjun S, Martin J and Imad Z 2014 Successful slickwater fracturing in ultrahigh TDS water by novel environmentally preferred friction reducer International Petroleum Technology Conference Kuala Lumpur, Malaysia, IPTC.
[20] Alexandra M, Nikolay S and Ahmed F 2019 Completing ultra extended-reach wells: overcoming the torque and drag constraints of brine Abu Dhabi International Petroleum Exhibition & Conference Abu Dhabi, UAE, SPE.
[21] Mehdi H and Clark P E 2017 Drag reduction behavior of hydrolyzed polyacrylamide/xanthan gum mixed polymer solutions Petroleum Science 14(02) 412-423.
[22] Mortazavi S M M 2016 Correlation of polymerization conditions with drag reduction efficiency of poly(1-hexene) in oil pipelines Iranian Polymer Journal 25(8) 731-737.
[23] Den Toonder J M J, Hulsen M A, Kuiken G D C, et al. 1997 Drag reduction by polymer additives in a turbulent pipe flow: numerical and laboratory experiments Journal of Fluid Mechanics 337 193-231.

[24] Lawrence C, Edomwonyi O and Panagiota A 2019 Separated oil-water flows with drag reducing polymers Experimental Thermal and Fluid Science 102 467-478.

[25] Deshmukh S R and Singh R P 1987 Drag reduction effectiveness, shear stability and biodegradation resistance of guar gum - based graft copolymers Journal of Applied Polymer Science 33(6) 1963-1975.

[26] Xing L, Ke Y C, Hu X, et al. 2019 Preparation and properties of amphoteric polyacrylamide/modified montmorillonite nanocomposites and its drag reduction performance Colloids and Surfaces A: Physicochemical and Engineering Aspects 574 94-104.

[27] Tamano S, Kitao T and Morinishi Y 2014 Turbulent drag reduction of boundary layer flow with non-ionic surfactant injection Journal of Fluid Mechanics 749 367-403.

[28] Nesyn G, Yu M and Suleimanova V 2012 Polymer drag-reducing agents for transportation of hydrocarbon liquids: Mechanism of action, estimation of efficiency, and features of production Polymer Science 54(1) 61-67.

[29] Zhang L J, Huang X D, Fan X M, et al. 2019 Rapid fingerprinting technology of heavy oil spill by mid-infrared spectroscopy Environmental Technology 42(2) 270-278.

[30] Toonder J D, Hulsen M A, Kuiken G, et al. 1997 Drag reduction by polymer additives in a turbulent pipe flow: numerical and laboratory experiments Journal of Fluid Mechanics 337 193-231.

[31] Liu Z Y, Zhou F J and Qu H Y, et al. 2017 Impact of the microstructure of polymer drag reducer on slick-water fracturing Geofluids 2017 9080325.