

Synthesis and Application of Pyrrolidone-containing Shale Inhibitors

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Abstract. New generation polyamine inhibitors are amino-terminated polyethers with excellent inhibiting capabilities; they play a key role in borehole stabilization and reservoir protection. However, polyamine inhibitors are limited by their poor thermal stability, which can be attributed to the presence of ether bonds in their molecular structures. We propose a three-step synthesis approach for a novel pyrrolidone-containing polyamine inhibitor (DYNP) by introducing N-vinyl-2-pyrrolidone (NVP) on divinylloxyethane. This polyamine inhibitor exhibits an optimized molecular structure and has enhanced heat resistance. Characterizations by infrared (IR) spectroscopy and evaluation tests demonstrate several advantages of DYNP inhibitors, including excellent inhibiting capability (superior to similar materials such as polyamines), improved heat resistance (reasonable stability at temperatures up to 240°C), and good compatibility with both fresh water and salt water drilling fluids. These can be attributed to the presence of considerable amounts of amino groups in the repeating unit of DYNP molecules. The DYNP inhibitor was applied in over 20 boreholes in tight oil blocks in Daqing Oilfield to relieve hydration of formations with high shale contents. For instance, drilling in the 2033.5m horizontal section of Dragon 2 borehole was smooth, with a borehole diameter expansion ratio below 10%.

1. Introduction

Exposure to water during the drilling process leads to the hydration of shale formations, which have high levels of clay minerals. This results in an increase in both the clay particle interlayer distance and swelling pressure, which in turn lead to diameter reduction and sidewall exfoliation. To avoid this, additives such as inorganic salts, quaternary ammonium salt, and small cations are typically added into drilling fluids [1-7]. Nevertheless, conventional inhibitors do not satisfy the drilling requirements of deep mining and ultra-deep mining. In this article, we propose the design and synthesis of a novel pyrrolidone-containing polyamine inhibitor (DYNP) [8-12] that significantly improve inhibiting capability and heat resistance.



2. Structure of polyamine

Polyamines are aminated polyethers (either amino-terminated polyether or polyetheramine) with ether bonds ($\text{R}-\text{O}-\text{R}'$) in the backbone. In acidic environments, ether bonds are protonated and oxysalts are obtained. Eventually, ether bonds are broken. In strong basic environments, ether bonds are typically stable. However, the breaking of ether bonds (as shown in Fig. 1) is observed when the temperature exceeds 100°C . Therefore, the heat resistance of polyamine inhibitors is usually below 120°C [13].

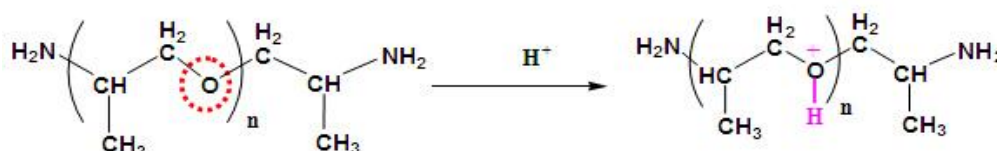


Fig 1. Breaking of ether bonds in polyamine.

3. Principles of molecular structure design and mechanism analysis

3.1 Principles of molecular structure design

In order to improve stability and thermal resistance, modifications are proposed to the molecular structure of an amine-terminated polyether. The proposed modifications are based on the following principles:

- High thermal resistance: $\text{R}-\text{O}-\text{R}'$ bonds in the backbone were replaced by CC bonds, and NVP groups were introduced.
- Strong inhibiting capability: the content of amine groups was further increased.
- Appropriate chain length: the chain length was optimized to increase the inhibiting capability while maintaining low toxicity. The molecular weight of inhibitor molecules was altered by adjusting the catalyst content and other reaction conditions.
- Good compatibility: no functional groups were involved that might readily react with drilling fluids [14-17].

3.2 Mechanism analysis

DYNP, a modified amine-terminated polyether, exhibits strong inhibiting capability for clay shale. First, the low molecular weight and appropriate chain length enabled the monolayer adsorption of these molecules and the formation of hydro-bonds between the inhibitors and the internal surface of clay crystalline lamellae, due to their ability to fit into the inter-lamella space in the clay. Second, hydrophobicity was increased by the adsorption of JY-2 molecules on the clay surface, thus preventing water adsorption and reducing hydration, dispersion and swelling of the clay. Third, the formation of H-bonds reinforced the adsorption of JY-2 molecules on the internal surface of the clay crystalline lamellae. The clay lamellae were held together by electrostatic attraction and the hydrogen bonding, and the water content in the inter-lamellae space was reduced. Water penetration and hydration of clay was thus mitigated. Finally, JY-2 exhibited improved inhibiting capability compared to other polyamine inhibitors due to its higher amine content [18].

4. Lab synthesis

4.1 Equipment and reagents

Equipment: stirrer, high-temperature/pressure autoclave.

Reagents: Divinyloxyethane, N-Vinylpyrrolidone, ethanediamine, H_2 , metallic catalyst and Raney nickel catalyst.

4.2 Procedure

Step I: Divinyloxyethane, NVP monomers and the initiator were placed in an autoclave and stirred in order to promote a reflux reaction. Polymer intermediate A was obtained, which contained carbonyl groups (Fig. 2).

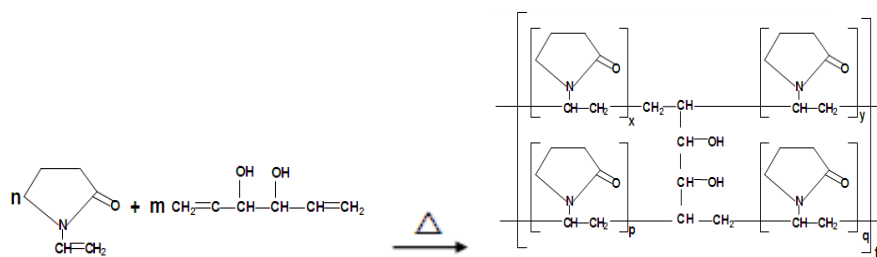


Fig 2. Schematic illustration of Step I.

Step II: Intermediate A and sodium borohydride (catalyst) were mixed in an autoclave to allow reduction of the carbonyl groups into hydroxyl groups via catalytic hydrogenation. Thus, intermediate B was obtained (Fig. 3).

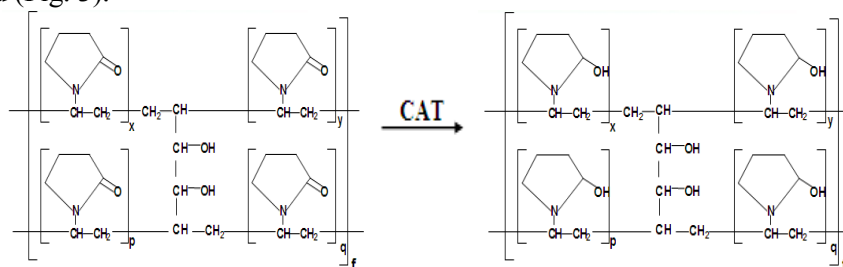


Fig 3. Schematic illustration of Step II.

Step III: Intermediate B and Raney nickel (catalyst) were mixed in an autoclave, followed by the addition of ethanediamine. The autoclave was protected by pure H₂ (2.6-3.2 MPa) and heated to 220-240 °C. The mixture was stirred for 4-5 h, cooled, and then filtered to obtain JY-2, an amine-based inhibitor containing several primary amine groups (Fig. 4).

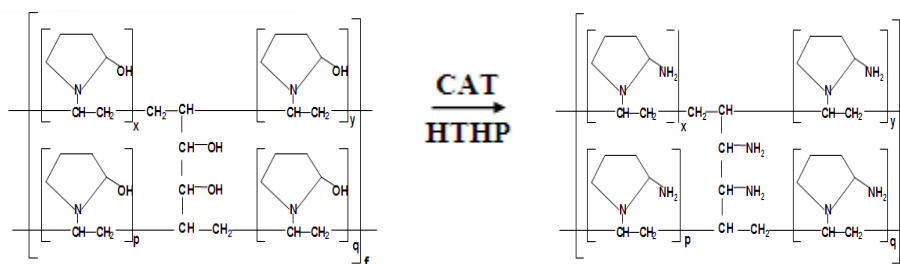


Fig 4. Schematic illustration of Step III.

5. Characterization

5.1 Characterization by FT-IR

The samples were characterized by FT-IR spectrometry (Nicolet-Nexus 670) using the KBr pellet method at a scanning range of 400-4000 cm⁻¹. As shown in Fig. 5, the peak at 3371.94 cm⁻¹ corresponds to the contraction vibration of non-associated N-H; the peak at 2989.56 cm⁻¹ corresponds to the stretching vibration of CH₂ groups; the band located at 600 cm⁻¹ - 750 cm⁻¹ corresponds to the out-of-plane rocking vibration of -NH₂ groups; the peak at 1270 cm⁻¹ corresponds to the stretching vibration of C-N groups; the peak at 1690 cm⁻¹ represents the strong absorption peak of -C-N- groups; and the peaks at 900 cm⁻¹, 1400 cm⁻¹ and 710 cm⁻¹ correspond to the bending vibration of methyl/methylene groups. Thus, the successful achievement of the designed molecular structure is confirmed by FT-IR spectral analysis, indicating the presence of target groups and the absence of fragile ether bonds.

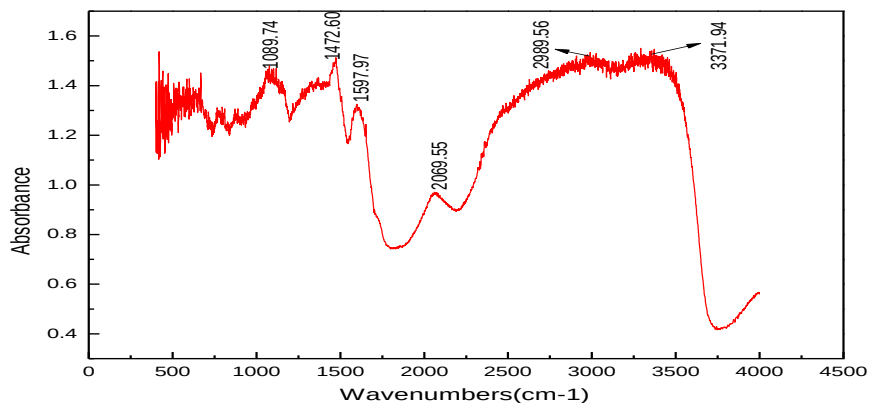


Fig 5. FT-IR spectra of synthesized samples.

5.2 Characterization by thermogravimetric analysis (TGA)

DYNP samples were characterized by TGA in order to investigate their thermal stability. Briefly, TGA of each sample was conducted in the temperature range of 30-600°C under argon, with an increasing temperature rate of 10 °C/min. As shown in Fig. 6, no significant degradation was observed at $T < 299.5$ °C, indicating that the functional groups were not deactivated by a temperature less than 300 °C. Hence, the DYNP samples are verified as thermally resistant.

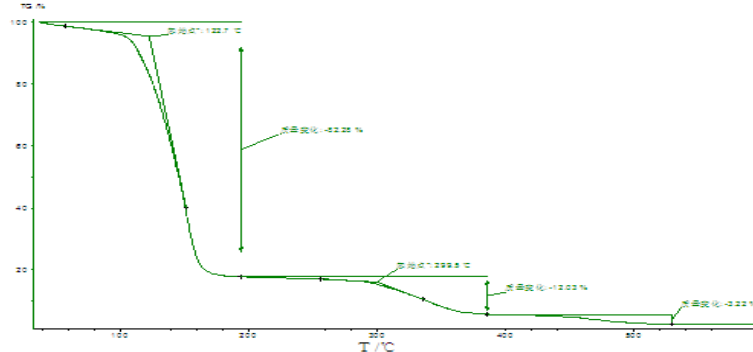


Fig 6. TGA curve of JY-2 samples.

6. Performance evaluation

The performances of samples from large-scale industrial fabrications were evaluated, as well as their compatibility with fresh water and saline water systems.

6.1 Inhibiting capability

The inhibiting capability of DYNP inhibitors was evaluated using microscopic analysis (X-ray Diffraction) and macroscopic analysis (via the linear expansion method and rolling recovery tests). The inhibiting capability of DYNP inhibitors was compared with that of polyols, KCl, and polyamino inhibitors.

6.1.1 Characterization by X-ray Diffraction

Inhibitors were added into bentonite suspensions containing 3% sodium, which were then stirred for 30 min and cured for 24 h. The wet precipitations were then characterized with X-ray diffraction in order to investigate the effects of the inhibitor mass concentration on the inter-layer space (d_{001}). As shown in Table 1, d_{001} decreased from 1.932 nm (sodium bentonite in water) to 1.418 nm at the JY-2 content of 0.5%. The variation in d_{001} was consistent with the diameter of JY-2 molecules (0.502 nm), and no further variations in d_{001} were observed as JY-2 continued to increase, indicating that the adsorption of JY-2 was preferred over that of water molecules. Indeed, JY-2 molecules adsorbed on the inner surfaces of lattices and water molecules were blocked due to the Standing Effect of JY-2

molecules. Additionally, a low content of JY-2 can deliver significant inhibition of clay hydration, and the inhibition effects of JY-2 on sodium bentonite were significantly better than those of PF-HCS and UHIB.

Table 1. Results of XRD characterization(nm).

	0	0.5%	1.0%	1.5%	2.0%
Polyols	1.932	1.807	1.783	1.782	1.781
KCl	1.932	1.812	1.796	1.802	1.801
Polyamine	1.932	1.431	1.434	1.432	1.434
DYNP	1.932	1.418	1.409	1.412	1.410

6.1.2 Linear expansion method

Fig. 7 shows the linear expansion curves of calcium clay mixed with different inhibitor solutions (1%, mass concentration) and pure water. As observed, the linear expansion corresponding to the DYNP inhibitor was significantly lower than that of other inhibitors, indicating effective reduction of the clay expansion by DYNP inhibitor.

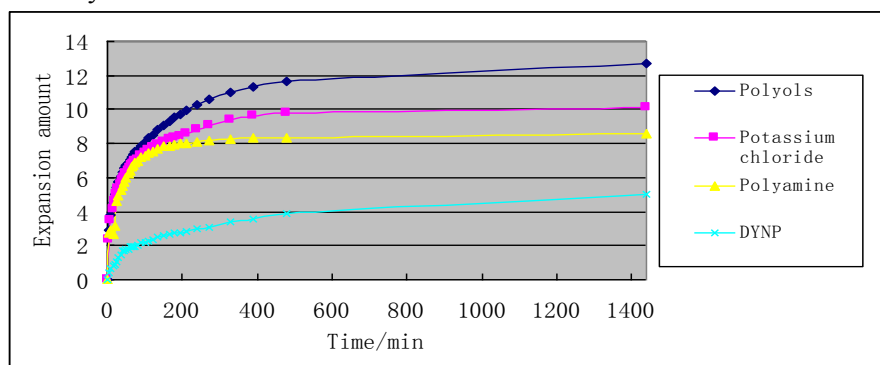


Fig 7. Linear expansion curves.

6.1.3 Rolling recovery test

Rolling recovery tests (repeated three times) were conducted on shale cuttings (6-10 mesh) from a specific horizon, using 1%(mass concentration) inhibitor solutions and pure water. As shown in Fig. 8, the primary, secondary, and tertiary recovery rates were 71.26%, 67.36%, and 56.82%, respectively, while the tertiary recovery rate of polyamines was 32.36%. This indicates that DYNP inhibitors have good heat resistance, resulting in strong adhesion on cuttings and effective long-term inhibition of shale hydration.

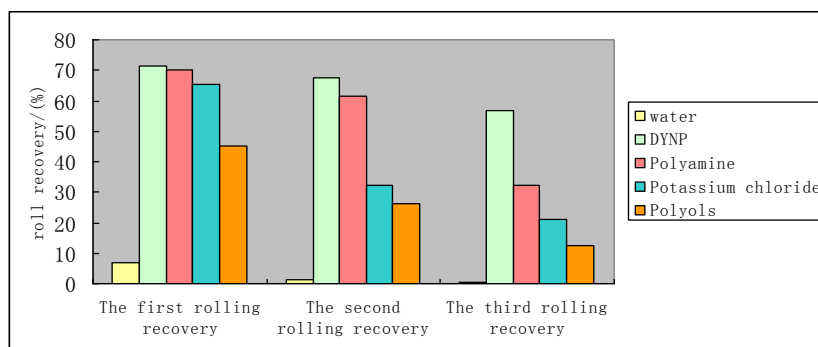


Fig 8. Rolling recovery ratios of different polyamine solutions.

In summary, the prepared DYNP inhibitor exhibits superior inhibiting capability towards shale hydration and excellent resistance of clay contamination.

6.2 Compatibility with drilling fluids

The compatibility of DYNP as an inhibitor with fresh water drilling fluid and KCl drilling fluid was evaluated and the results are summarized in Table 2. The presence of DYNP was observed to lead to significant improvements of the inhibiting capability of both drilling fluids with no effects on the rheology of drilling fluids. The optimized content of DYNP was demonstrated to be 1.5%. Therefore, it can be concluded that DYNP is compatible with both fresh water drilling fluid and KCl drilling fluid, and the recommended content is 1.5%.

Table 2. Compatibility of DYNP with fresh water drilling fluid and saltwater drilling fluid.

System	Conditions	AV/mPa·s	Φ6/Φ3	FL _{API} /mL	Recovery ratio (%)
Fresh water drilling fluid	Room temperature	21.5	6/3	3.2	53.6
	200°C×16h	22	5/4	3.1	
Fresh water drilling fluid +1.0%DYNP	Room temperature	21	6/5	2.9	87.2
	200°C×16h	21.5	6/4	3.0	
Fresh water drilling fluid +1.5%DYNP	Room temperature	22.5	7/5	2.8	96.3
	200°C×16h	22	6/5	2.7	
Fresh water drilling fluid +2.0%DYNP	Room temperature	21.5	6/4	2.7	97.2
	200°C×16h	20.5	6/5	2.8	
Saltwater drilling fluid	Room temperature	26.5	6/5	5.2	65.2
	200°C×16h	26	5/4	5.3	
Saltwater drilling fluid +1.0%DYNP	Room temperature	27	6/4	4.9	88.4
	200°C×16h	26.5	5/3	4.9	
Saltwater drilling fluid +1.5%DYNP	Room temperature	27	5/4	4.6	97.3
	200°C×16h	26	5/3	4.6	
Saltwater drilling fluid +2.0%DYNP	Room temperature	26.5	5/4	4.6	97.6
	200°C×16h	26.5	5/4	4.5	

6.3 Economic benefits

The market price of commercial polyamine is 30,000~50,000 RMB/t in domestic markets, while that in global markets exceeds 60,000 RMB/t. The market price of DYNP is 18,000 RMB/t, which is significantly lower than commercial polyamine.

7. Field application

The DYNP inhibitor was applied in over 20 boreholes in tight oil blocks in Daqing Oilfield. The tight oil blocks have mud stone and silty mudstone as their major components and are primarily distributed in Yaojiazuo and Quantouzu. The major clay minerals include illite (absolute content = 9.43~14.67, relative content = 79~91%) and aillite/smectite mixed layer (absolute content = 1.48~4.53, relative content = 6~26%). Sidewall exfoliation and collapse are commonly observed in the drilling process.

The Dragon 2 hole has a designed hole depth of 3500m and a horizon exceeding 1200 m. Drilling in this borehole is mainly in the shale formations mentioned above. Water-based drilling fluids with small cations as inhibitors were used. The pulp content was maintained at 2.0% and 50kg of inhibitor was added per day. Viscosity and shear stress of the drilling fluid increased drastically and pump suffocation were observed during drilling in the 2600m building up section of the shale formation. Repeated scrapings were observed in the 2973-3200m section, and drilling could only be executed with repeated down hole and drift redressing. In horizontal drilling, severe sidewall exfoliations were observed, resulting in scrapings (the length of largest falling block exceeded 4.7 cm). Drilling in this borehole was completed 400 m short of the designed depth.

The Dragon 2 borehole (7 km away from the Dragon 1 borehole) has a designed depth of 4045m and horizon length of 2033.5m. The drilling horizon of the Dragon 2 borehole is consistent with that of the Dragon 21 borehole. To avoid down hole collapse, 1.5%DYNP was used as an inhibitor and the amount of Al-based polymers added was increased to 5%. The DYNP inhibitor was used according to

standards (see Table 3) that were designed based on previous experiences to guarantee effective drilling. Once the drilling workface reached the building up section, designated procedures were strictly followed to ensure good inhibiting and sealing capability of the drilling fluids.

During drilling in the building up section and horizontal drilling (high shale contents), the viscosity and shear stress of the drilling fluid stayed constant and no rapid rise of adjacent boreholes was observed. Drilling of the 2033.5m horizon was achieved without severe diameter reduction, sidewall exfoliation, or scraping. The average diameter expansion rate is below 10%, demonstrating good inhibiting and sealing capability of the DYNP inhibitor, which satisfies the requirements of drilling in tight oil formations.

Table 3. Maintenance of drilling fluids used in Well Gu No.2.

Section	FV (s)	ρ (g/cm ³)	PV (mPa·s)	YP (Pa)	Dynami c plastic ratio	Gel (Pa)	Solid content t (%)	Sand content (%)	FL _{API} (mL)	Maintenance principles
Vertical section	45~ 55	1.20~ 1.35	12~ 22	4~ 10	0.25~ 0.55	1~2/ 6~10	8~ 13	< 1.0	2.0~ 2.5	Low viscosity, low density, rapid drilling Strong lubrication, strong inhibition,
Incline d section	50~ 65	1.35~ 1.40	20~ 30	10~ 18	0.4~ 0.7	2~5/ 10~1 5	10~ 20	0.5~ 1.5	2.0~ 2.5	strong encapsulation, appropriate shear, stabilized incline
Horizo ntal section	55~ 70	1.35~ 1.40	20~ 30	10~ 18	0.4~ 0.7	3~5/ 13~2 0	10~ 20	0.5~ 1.0	2.2~ 2.4	Improved sealing and well cleaning capacity, decreased friction and filtration loss

Table 4. Properties of drilling fluids used for field tests.

Depth /m	ρ /g/cm ³	FV /s	FL /mL	PV/mPa·s	YP /Pa	pH	Sand content/%	Contents of solid /%
1381	1.25	51	2.2	16	9	10	0.4	10
1809	1.31	53	2.8	21	10	9	0.4	15
2021	1.31	55	1.6	24	12	9	0.2	15
2604	1.35	67	1.4	28	17	8	0.2	14
2915	1.35	63	1.4	25	15	8	0.2	14
3334	1.4	69	2.2	23	23	8	0.2	15
3488	1.4	67	2	21	19.5	8	0.3	14

8. Conclusions

(1) Aiming at improving heat resistance of amino-terminated polyether inhibitors, a novel pyrrolidone-containing polyamine inhibitor (DYNP) was synthesized by introducing N-vinyl-2-pyrrolidone (NVP) on divinyl oxyethane. Characterizations by infrared (IR) spectroscopy and evaluation tests demonstrate several advantages of the DYNP inhibitor, including excellent inhibiting capability (superior to similar materials such as polyamines), improved heat resistance (reasonable stability at temperatures up to 240°C), and good compatibility with both fresh water and salt water drilling fluids.

(2) These advantages can be attributed to the presence of considerable amounts of amino groups in the repeating unit of DYNP molecules. Indoor tests revealed that the prepared DYNP inhibitors can effectively enhance the inhibiting capability of water-based drilling fluids and reduce hydration in

shale due to their excellent inhibiting capabilities and good compatibility with water-based drilling fluids. Field tests show that DYNP inhibitors can effectively relieve diameter reduction, sidewall exfoliation, and collapse of boreholes in water sensitive shale, and satisfy the requirements for drilling in horizontal boreholes in tight oil blocks.

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References

- [1] Arvind D P. Design and development of quaternary amine compounds: Shale inhibition with improved environmental profile[Z]. SPE 121737, 2009:1-9.
- [2] Leaper R, Hansen N, Otto M, et al. Meeting deepwater challenges with high performance water based mud[C]. Houston: AADE 2006 Fluids Conference Texas, 2006.
- [3] Arvind D P. Shale hydration inhibition agent and method of use:US, 7494958B2[P]. 2009—02—24.
- [4] Arvind D P. Shale hydration inhibition agent and method of use:US, 7572756 B2[P]. 2009—08—11.
- [5] Julio Montilva, et al. Improved Drilling Performance in Lake Maracaibo Using a Low—Salinity, High—Performance Water—Based Drilling Fluid[J]. SPE 110366, 2007.
- [6] PATEL A D, STAMATAKIS E, ERIC D. Shale hydration inhibition agent and method of use: US, 6609578[P]. 2003-08-26.
- [7] LARKIN J M, RENKEN T L. Process for the preparation of polyoxyalkylene polyamines:US,4766245[P].1988-08-23.
- [8] KLUGER E W, GOINEAU A M. Process for the reduction of dicyanoglycols:US,4313004[P].1982-01-26.
- [9] DYE W, DAUGEREAU K, HANSEN N, et al. New water-based mud balances high—performance drilling and environmental compliance[J]. SPE Drilling & Completion, 2006, 21(4): 255-267.
- [10] Qiu Z, Zhong H and Huang W. Properties and mechanism of a new polyamine shale inhibitor. Acta Petrolei Sinica, 2011, 32(4): 678-682.
- [11] Xiao W and Xiang X. Study and Application of a Water-Based Drilling Fluid System Containing Alcohol Ether. Chemical Engineering of Oil and Gas, 2000, 29(4): 198-199, 202.
- [12] Zhang K, He L, An S, et al.. An Introduction to the High Performance Water Base Muds Abroad. Drilling Fluid & Completion Fluid, 2007, 24(3): 68-73.
- [13] Wang J, Yan J, Ding T. Progresses in the Researches on High Performance Water Base Muds. Drilling Fluid & Completion Fluid, 2007, 24(1): 71-75.
- [14] Zhang Q, Chen F, Liu Y et al.. Development of High Performance Water Base Muds Abroad. Drilling Fluid & Completion Fluid, 2007, 24(3): 74-77.
- [15] Qu Y, Lai X, Yang Y et al.. Study Progresses in Water Base Drilling Fluid with Amine. Drilling Fluid & Completion Fluid, 2009, 26(3): 73-75.
- [16] Liu H, Liang C, Zhong D et al.. Application of High Performance Water Base Drilling Fluid in Well Hong69. Drilling Fluid & Completion Fluid, 2011, 28(2): 87-88.
- [17] Guo W, Peng B, Cao W et al.. Structure and Properties of Polyamine Shale Inhibitor for Drilling Fluid. Drilling Fluid & Completion Fluid, 2015 10(1): 26-29.
- [18] Ma P, Xiong K, Chen F et al.. Application of Polyglycol Amine Drilling Fluids in Well Ke 21-Ping 1. Drilling Fluid & Completion Fluid, 2012, 29(1): 85-88.