# THERMAL-RESISTANT CHEMICALS FOR DRILLING FLUIDS

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## *ABSTRACT*

The most complete qualitative and quantitative information on the new developments in the field of drilling chemistry - thermal-resistant chemicals for drilling fluids based on humic acid of brown coal is presented in this paper. The structure, properties of humic acids of brown coal and ways of its modification are described. New thermal-resistant import-substituting polymer-lignite chemicals for drilling fluids are presented and the possibility of using the complexing ability of humic acids of brown coal to obtain thermal-resistant polymer-lignite chemicals was investigated. The properties and possibilities of new chemicals are described; the results of their laboratory tests and testing are given.

**Keywords:** drilling fluids (DF), thermal-resistant chemicals, humic acid (HA) of brown coal, high-thermal-resistant fluid-loss reducer.

## *INTRODUCTION*

Increased requirements for environmental safety of materials used in drilling, more correspond to chemical agents based on natural substances - vegetable oils, animal fats, brewing waste, coal industry [1-3].

The list of products includes - demulsifiers, corrosion inhibitors, scaling inhibitors and solvents, inhibitors and solvents of asphalt resin paraffin deposits (ARPD), bactericides, depressant additives. These chemicals are represented by a wide range of different classes of chemical compounds - metal salts, mainly alkaline, fatty acid esters, chlorinated, sulfonated and condensed fatty acids, polymer compositions.

Along with sintering and preparation of plant growth stimulants from coal waste one of the ways to solve emerging environmental problems in the development of brown coal deposits is processing them into modern thermal-resistant polymer-lignite chemicals, which will make it possible to transfer waste into the category of commercial products. Brown coals are not usually sufficiently unified; they are prone to strong grinding during mining and storage and to rapid oxidation up to spontaneous combustion. This leads to the fact that a significant part of the coal mined (sometimes up to 30-40%) is substandard in size, does not find a sale and goes into the category of waste, increasing the load on the environment and reducing the profitability of deposit operations. It should also be noted that the upper, oxidized part of brown coal is often transferred to the waste category because of its low calorific value.

Coal-alkaline reagent (CAR) is the most accessible and effective reagent of general improving effect for drilling fluids when drilling oil and other wells for various purposes. It should be noted that despite on the huge reserves of brown coal with various properties, there

is no production of coal-alkaline reagents in Kazakhstan. Therefore, the basic needs in it are satisfied by exporting from Ukraine, the Russian Federation and far-abroad countries.

## *MATERIALS AND METHODS*

In experimental laboratories of the enterprises LLC "NGO "Khimburneft", (Krasnodar) and LLC "Russkaya Gornopromyshlennaya Kompaniya" (Moscow) modern thermal-resistant polymer-lignite chemicals of the brands LIG-FIL, LIG-VIS and LIG-STAB were developed, which are nanomodified polymer-lignite compounds based on humic acids (HA) of brown coal.

Structure condensed systems, including alicyclic and aromatic rings with bearing side chains, functional groups both in the core and in the side chains are a basis of the HA [4-6]. $^{1}H$ and $^{13}C$, humic, fulvic acids, humins, brown coal bitumoids have been studied using methods of quantitative NMR spectroscopy. Humic fractions of brown coal contain aromatic and aliphatic structures, with alkyl-aromatic structures forming the basis of skeletal fragments and resistant to further decomposition. Among the variety of offered formulas of HA macromolecules, the structure of HA molecule construction from a condensed nucleus and loose periphery is the most reliable. [7-10] A structural formula of the brown coal HA macromolecule containing a nucleus from condensed aromatic rings of humic acids is fragmentary shown in Fig.1.

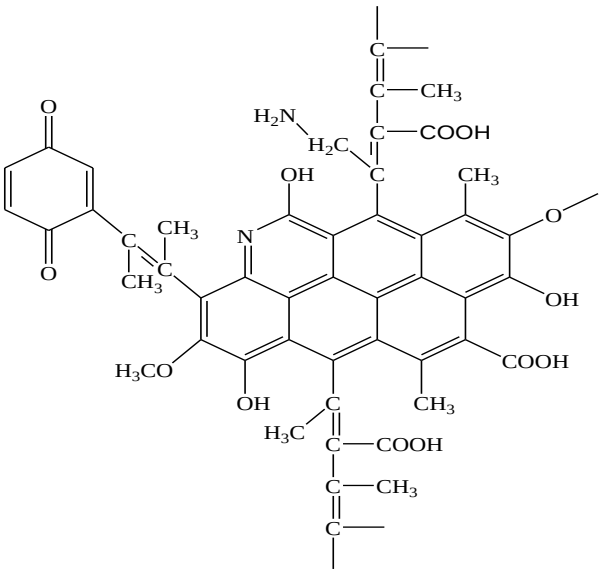



Fig. 1.Fragment of the molecule of brown coal HA

## *RESULTS AND DISCUSSION*

In content of carbon (C), hydrogen (H), oxygen (O) and nitrogen (N), the elemental composition of brown coal HA is specific and differs from other natural raw materials (see Table 1). Depending on the nature of humate-containing raw materials and the stage of metamorphism the atomic ratios of H/C, O/C, and C/N in the HA macromolecules are, respectively, within 0.6-1.2; 0.3-0.6 and 14-60. In this connection, the concept of a structural cell of HA with a minimum molecular mass (MM) of 1500 a.m.u. is introduced at two to four nitrogen atoms. The presence of positively charged nitrogen atoms in the polyanionic

structure of the macromolecule determines the ampholytic nature of the HA polyanion in a water solution.

Table 1– Characteristics of HA from humate-containing raw materials

| Source of HA | Atomic ratios | | | Content, mEq/100 g. | | |
|---|---|---|---|---|---|---|
| | H/C | O/C | C/N | COOH + phenolic-OH | COOH | CO-quinoline |
| Brown forest soil | 1.02 | 0.36 | 19.46 | 620 | 260 | 106 |
| Peat | 1.09 | 0.36 | 21.43 | 570 | 230 | 126 |
| Brown coal | 0.80 | 0.33 | 51.83 | 715 | 276 | 205 |
| Oxidized Coal | 0.62 | 0.33 | 57.92 | 730 | 348 | 337 |

Ampholytic nature of HA is a favorable factor of intermolecular interaction with polyelectrolytes of polyanionic and ampholytic character (carboxymethyl cellulose, polyanionic cellulose, polyacrylamide, hydrolyzed polyacrylonitrile). The presence of positively charged centers on the surface of HA macromolecules facilitates the associative coupling of these macromolecules in the "grapes cluster" when concentrating water solutions, provides a plasticizing effect of humates in relation to polyacrylates and a fluxing action on drilling and grouting mortars [6,7].

Abroad various methods of HA modification have been developed and are being applied in industry to improve the thermo-salt resistance, the inhibitory ability of humic reagents in water-based DF and in oil-based solutions. Potassium modifications of HA have found an application in DF systems of inhibitory action. For example, the company "M.I. Drilling Fluids" (USA) developed a system of DF "K-Mage-Sistem", which included:

- potassium-humate K-160, which increases the content of potassium ions in the DF up to 2000 mg/l.
- potassium-lignite XP-20 chrome-containing, used for high-temperature control of rheological properties and fluid loss of DF with a temperature of 260°C and above;
- sulphomethylated humate, condensed with phenol-formaldehyde resin of Resinex brand for DF fluid loss control in bore-hole bottom conditions, thermal-resistant up to 200°C.

The combination of these humic reagents with polyanionic cellulose (PAC) or acrylic copolymers as stabilizers and major fluid loss reducers makes it possible to use "K-Mag-System" systems to drill small diameter holes through highly colloidal clay rocks.

Potassium humates K-17, XP-20, XP-20 CF and Resinex are a part of another system of DF – "Duratherm" of high density and with a low content of active (colloidal) fraction of the solid phase. Being a water alternative to oil-based solutions, this system satisfies the conditions of deep well drilling, complicated by high temperatures with subsequent opening of productive formation by high-density DF in a case of abnormally high reservoir pressure. The advantage of systems like "Duratherm" over others (including oil-based solutions) lies in high temperature stability at low values of plastic and effective viscosity at the bore bit outlet, followed by a fast restoration of the initial viscosity, ensuring a good cutting-carrying capacity of drill cuttings. The high thermal stability of the polymer system containing humates is maintained due to the antioxidant capacity of phenolic hydroxyls and nitrogen-containing groups of HA, which reduce by 30-50% the irreversible mechanic destruction of acrylic polymers and cellulose-based reagents.

LLC "Russkaya Gornopromyshlennaya Kompaniya" and LLC "NGO "Khimburneft" jointly developed and produced a series of thermal-resistant import-substituting polymer-

lignite chemicals for treating drilling fluids at the construction of wells in the oil and gas industry:

1. "LIG – FIL" - high-thermal-resistant fluid loss reducer and a stabilizer of rheological properties of the drilling fluid *(Foreign analogues: "SHALE-CHEK", "POLYRX" M- IDrillingFluids, USA; DEERES-2000, Borregaard, Norway; "Polydrill®", BASF, Germany).*

2. "LIG-VIS"a viscosity reducer (diluent - a low thixotropic viscosity regulator) of drilling fluids (*Foreign analogues:"SPERSERNE – SF" M- I DrillingFluids, USA; "BORRE-THINCFL", Borregaard, Norway).*

3. "LIG – STAB" – a polymer inhibitor of shale, clays and unstable clay deposits and mudstones *(Foreign analogues: "KLAYSTAB", "CLAYTROL", "SULFATROL", drilling fluid system"NEWDRILL" (USA); Alcomer® ,BASF, Germany)*[8-9].

Polymer-lignite chemical reagent "LIG-FIL" as a thermal-resistant fluid loss reducer is manufactured according to Technical Conditions (TU) 2458-001-33686171-2015 with indicators given in Table 2.

Table 2 – Quality indicators of chemical reagent "LIG-FIL"

| Title of quality indicator | Regulatory requirements |
|---|---|
| 1. Appearance | Powder of brown color |
| 2. Moisture content,%, no more than | 10.0 |
| 3. pH indicator of 1% water solution | 9-10 |
| 4. Static filtration indicator at 0.7 MPa of 8% clay suspension containing 1.0% of a chemical reagent, $cm^3$, no more than | 8.0 |
| 5. Static filtration indicator at 0.7 MPa of 8% clay suspension containing 1.0% of a chemical reagent, after thermostating in an autoclave at 180°C for 2 hours, $cm^3$, no more than | 14.0 |

In the laboratory of LLC "Kortex Services" a study was made An investigation of the influence of polymer-lignite reagent "LIG-FIL" concentration change from 0.5 to 3% on technological parameters of fresh polymer-clay drilling fluid based on polyacrylamides (base solution) with a density of 1.12 $g/cm^3$. It has been established that the optimum concentration of polymer-lignite material "LIG-FIL" in fresh polymer-clay drilling fluid corresponds to 1.5 mass %. After heating for 8 hours at 85°C, the drilling fluid keeps its original properties (Table 3).

Table 3 – Dependence of drilling fluid properties on "LIG-FIL" reagent concentration

| Drilling fluid composition | Density, g/cm$^3$ | pH | $F_{30}/F_{HTHP}$ cm$^3$ | Relative viscosity on Marsh, second | Angle $\theta_{600/300}$ grade | Plastic viscosity PV, cP | Dynamic stress yield point YP, fnt/100ft$^2$ | Static shift stress Gels $10^{1s}/10^{10min}$, fnt/100ft$^2$ |
|---|---|---|---|---|---|---|---|---|
| 1. Influence of concentration of polymer-lignite material "LIG-FIL" on filtration and structural-rheological characteristics | | | | | | | | |
| Shelf liquid | 1.10 | 8.57 | 7.2 | 78.0 | 45/31 | 14 | 15.7 | 5.2/7.6 |
| 0.5% "LIG-FIL" | 1.11 | 8.76 | 6.4 | 81 | 55/36 | 19 | 16.9 | 5.0/5.8 |
| 1.0 % "LIG-FIL" | 1.12 | 8.3 | 5.5 | 84 | 58/39 | 19 | 19.4 | 4.8/6.3 |
| 1.5% "LIG-FIL" | 1.12 | 8.82 | 4.5 | 87 | 74/48 | 26 | 22.7 | 4.9/5.18 |
| 2.0% "LIG-FIL" | 1.12 | 8.92 | 4.5 | 90 | 83/51 | 32 | 19.6 | 4.8/6.1 |
| 3.0% "LIG-FIL" | 1.12 | 8.62 | 4.7 | 96 | 104/66 | 38 | 26.8 | 4.8/6.3 |
| 2. Influence of temperature on filtration and structural-rheological characteristics | | | | | | | | |
| Shelf liquid | 1.10 | 8.34 | 7.8 | 84 | 48/31 | 17 | 14.9 | 6.3/8.0 |
| 1.5% "LIG-FIL" | 1.12 | 8.78 | 4.8/15 | 92 | 81/55 | 26 | 29 | 5.0/6.3 |
| 1.5 % "LIG-FIL" (after warming up at 85°C. 8h) | 1.12 | 8.64 | 4.6/14 | 86 | 77/51 | 26 | 27 | 4.5/5.5 |

The polymer-lignite chemical reagent "LIG-VIS" as a thermal-resistant viscosity reducer is manufactured according to Technical Condition (TU) 2458-002-33686171-2015 with indicators given in Table 4.

Table 4 - quality indicators of the chemical "LIG-VIS"

| Title of quality indicator | Regulatory requirements |
|---|---|
| 1. Appearance | Powder of brown color |
| 2. Moisture content.%. no more than | 35.0 |
| 3. pH indicator of 1% water solution | 8-9 |
| 4. Decreasing the static shift stress after 10 minutes of rest (SSS10) of 10%clay suspension containing 1.0% of the chemical, %, no less than | 80.0 |

Table 4 continuation

| | |
|---|---|
| 5. Reduction of the dynamic shift stress of 10% clay suspension containing 1.0% of the chemical, %. no less than | 60.0 |
| 6. Solubility in water, mass %. no less than | 80 |

The polymer-lignite chemical reagent "LIG-VIS" - viscosity reducer of drilling fluids is a complex chemical agent based on water-soluble salt-resistant oligomer of acrylic series, potassium humate and organosilicon modifying additives. The polymer-lignite chemical reagent "LIG-VIS" effectively regulates the structural-and-mechanical properties of fresh and mineral drilling fluids, has a thinning effect and stabilizes filtration properties of the drilling fluid at increased temperatures (Table 5).

Table 5 – Structural-and-mechanical properties of drilling fluids with a chemical reagent "LIG-VIS"

| Indicators | Notation, measurement units | Initial clay solution containing 10% OCMA (OSMO-ISO-9002, API) | Initial clay solution +1% "LIG-VIS" |
|---|---|---|---|
| Solution temperature | $^0C$ | +23.0 | +23.0 |
| The density at BBD-1 (± 0.01 g/cm$^3$) | ρ, *g/cm$^3$* | 1.08 | 1.08 |
| Relative viscosity on BB-1(± 0.5 sec) | $RV^{700/500}$, *sec* | 94 | 68 |
| Fluid loss for 30 minutes at 0.7 MPa on API | $F_{30}$, *cm$^3$* | 13.2 | 7.5 |
| Static shift stress at 3 rpm after 10 sec / 10 min at rest (Gels) FANN | $SSS_{10s/10m}$, *dPa* | 124/143 | 7/12 |
| Plastic (structural) viscosity (PV) FANN | $\eta_{pl}$, *MPa·s(sP)* | 11 | 8 |
| Dynamic stress shift point YP (YP) FANN | $\tau_o$, *dPa* | 95 | 19 |
| Thickness of mud filter cake | $C_{mud}$, mm | 1.0 | 1.0 |
| pH indicator | pH | 8.36 | 8.96 |
| Concentration of solid phase, retort model 87101 FANN on API | c, vol. % | 10.0 | 10.0 |
| Lubricant content | Vol. % | 0.0 | 0.0 |
| Concentration of colloidal particles | c, vol. % | 2.6 | 2.55 |

Table 5 continuation

| | | | |
|---|---|---|---|
| Absorption capacity according to the method MBT (content of colloidal) OFI model 168-00 | Cc, $kg/m^3$ | 37.05 | 32.1 |
| Nonlinearity indicator | n | 0.76 | 0.73 |
| Coefficient of consistency | K, $Pa \cdot c^n$ | 0.67 | 0.80 |
| Specific electrical resistance | R, *Ohm m* | 0.93 | 0.62 |
| Moisturizing ability indicator | $P_o$, cm/*h* | 2.84 | 2.89 |
| Coefficient of drilling fluid friction according to API on EP/LubricityTester , 16.95 nm | $Co_{fr}$ | 0.22 | 0.22 |
| Coefficient of mud filter cake friction on FPC4E (15 min) | $Co_{fr}$ | 0.53 | 0.47 |
| Filtration of HPHT on API at 165 $^oC$, 3.0 MPa | $F_{HPHT}$,$cm^3$ | 14.0 | 12.6 |

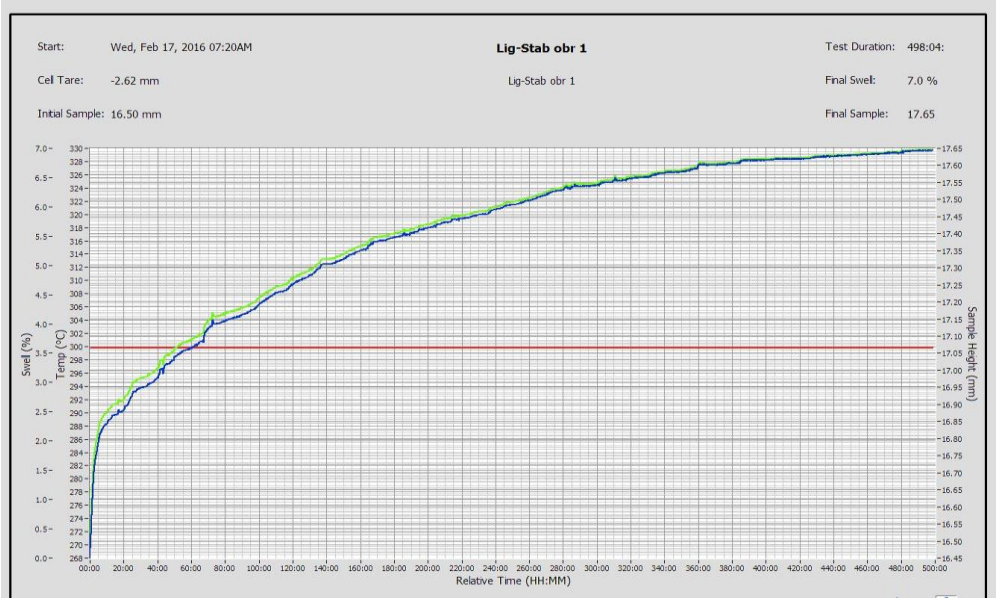
Laboratory tests of real loaded polymer clay drilling mud (2.10g/cm$^3$) of the well No. 25 Sernovodskaya PC "Rosneft" established that processing with a thermal-resistant polymer-lignite chemical reagent thinner "LIG-VIS" in an amount of up to 3 mass % provided a decrease in structural-rheological indicators: SSS 10sec/10min to values (Gels) 54/108 lb/100ft$^2$ and improvement of the fluid filtration properties - the filtration indicator to 1.0 cm$^3$ (0.7 MPa).

Polymer-lignite chemical reagent "LIG-STAB" - inhibitor of unstable clay minerals according to TC (TU) 2458-003-33686171-2015 has the following quality indicators (see table 6):

Table 6 - Quality indicators of the chemical "LIG-STAB"

| Title of quality indicator | Regulatory requirements |
|---|---|
| 1. Appearance | Powder of brown color |
| 2. Moisture content, %, no more than | 30.0 |
| 3. Indicator of inhibitory effect of 3% water solution of chemical agent ($P_o$), no more than, cm/h | 2.80 |
| 4. pH indicator of 1% water solution | 7.0 -9.5 |
| 5. Solubility in water, mass %, no less than | 70 |

Fig. 1 shows the results of testing the polymer-lignite chemical "LIG-STAB" in potassium chloride biopolymer drilling fluid as an inhibitor of unstable Kynov deposits of argilliferous and argillaceous minerals performed on the tester of longitudinal swelling OFITE "SWELLMETER" in the accredited laboratory of drilling fluids of LLC "NGO "BentoTechnologii" (Almetyevsk, Tatarstan).




| | |
|---|---|
| Swell | |
| Distance | |
| Temperature | |

Fig. 1. Swelling curve of Kynov argilliferous deposits in biopolymer potassium chloride biopolymer drilling fluid containing the inhibitor of shale "LIG-STAB"

All brands of the modern series of thermal-resistant polymer-lignite chemicals "LIG-FIL", "LIG-VIS" and "LIG-STAB" have a full set of documents (technical conditions, certificates of conformity, safety data sheets); they belong to Grade 4 of GOST 12.1.007-7 "Low-risk substances" and are recommended for commercial use when drilling exploratory and operational oil and gas wells in various mining and geological conditions of Russia and abroad.

## *CONCLUSION*

1. The performed investigations have shown that the developed thermal-resistant import-substituting polymer-lignite chemical reagents for the treatment of drilling fluids exceed the foreign analogues by a number of parameters.

2. It has been established by experiments that the ampholytic nature of HA is a favorable factor of intermolecular interaction with polyanionic and ampholyte polyelectrolytes (carboxymethyl cellulose, polyanionic cellulose, polyacrylamide, hydrolyzed polyacrylonitrile). The presence of positively charged centers on the surface of the HA macromolecules promotes to the associative coupling of these macromolecules in the "grapes

cluster" when concentrating water solutions, provides a plasticizing effect of the humates in relation to polyacrylates and a fluxing action on drilling and grouting mortars.

3. The possibility of obtaining high-quality chemical reagents of brands: "LIG-FIL", "LIG-VIS" and "LIG-STAB" for oil production, having qualitative indicators, profitable price policy and environmental safety was established.

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