



US00RE33856E

United States Patent [19]
Giddings et al.

[11] E **Patent Number: Re. 33,856**
[45] **Reissued Date of Patent: Mar. 24, 1992**

[54] **TERPOLYMER COMPOSITIONS FOR AQUEOUS DRILLING FLUIDS**

4,650,593 3/1987 Slingerland 252/8.51
4,676,317 6/1987 Fry et al. 523/130 X

[75] **Inventors: David M. Giddings, Sugar Land; Charles D. Williamson, Houston, both of Tex.**

FOREIGN PATENT DOCUMENTS

72445 2/1983 European Pat. Off. .

[73] **Assignee: Nalco Chemical Company, Naperville, Ill.**

OTHER PUBLICATIONS

Amer. Petroleum Institute, publication RP 13 (B), 6th Ed., Apr. 1976, pp. 1-33, "Standard Procedure for Testing Drilling Fluids".

[21] **Appl. No.: 144,260**

[22] **Filed: Jan. 15, 1988**

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Related U.S. Patent Documents

Reissue of:

[64] **Patent No.: 4,678,591**
Issued: Jul. 7, 1987
Appl. No.: 848,527
Filed: Apr. 7, 1986

[57] **ABSTRACT**

A method of improving high temperature fluid loss and rheology stabilization of high calcium brine clay-containing oil well drilling fluids which comprises adding thereto a stabilizing amount of a water-soluble terpolymer composition comprising:

[51] **Int. Cl.⁵ C09K 7/02**
[52] **U.S. Cl. 507/106; 507/107; 507/108; 507/120; 507/121**
[58] **Field of Search 252/8.51, 8.511, 8.514; 524/705, 735**

Ingredients	% by weight
NaAMPS	72-3.8
N,N-dimethylacrylamide	13.5-0.7
Acrylonitrile	9.5-0.5

[56] **References Cited**

U.S. PATENT DOCUMENTS

2,650,197 8/1953 Rahn 252/8.511
2,718,497 9/1955 Oldham et al. 252/8.51
2,935,504 5/1960 King et al. 252/8.511
3,266,887 8/1966 Kramer et al. .
3,639,263 2/1972 Troscinski et al. .
3,700,728 10/1972 Moschopedis et al. 252/8.51 X
3,985,659 10/1976 Felicetta et al. 252/8.511
4,374,738 2/1983 Kelly 252/8.511
4,502,964 3/1985 Giddings et al. .
4,547,299 10/1985 Lucas 252/8.51

said composition containing lignin, modified lignin, brown coal or modified brown coal in an amount ranging between 5-95% with the lignin, modified lignin, brown cell or modified brown coal having been present during the polymerization of the water-soluble polymer.

2 Claims, No Drawings

TERPOLYMER COMPOSITIONS FOR AQUEOUS DRILLING FLUIDS

Matter enclosed in heavy brackets [] appears in the original patent but forms no part of this reissue specification; matter printed in italics indicates the additions made by reissue.

INTRODUCTION

A serious problem is encountered when clay-based oil well drilling fluids are subjected to conditions of high temperature and high pressure in conjunction with utilization of high calcium-containing brines which are used to prepare these drilling fluids. When these conditions exist, conventional drilling fluid polymeric additives such as acrylamide polymers, when used as stabilizers for these fluids, tend to be rendered ineffective.

In U.S. Pat. No. 4,502,964, there is shown an improved high temperature fluid loss additive and rheology stabilizer for high temperature oil well drilling fluids which comprises a water-soluble terpolymer having the following compositions:

Ingredients	Mole %	
	Preferred	General
2-acrylamido-2-methylpropane-sulfonic acid, sodium salt (AMPS ¹)	53.5	51-59
N,N-dimethylacrylamide	16.6	6-28
acrylonitrile	29.8	20-35

¹AMPS, a registered trademark of Lubrizol, Inc., 2-acrylamido-2-methylpropane sulfonic acid, Na salt.

These polymers are further described in this patent as having a molecular weight below one million. They preferably have a molecular weight range within the range of 10,000-500,000. The other properties of these polymers and their efficacy as high temperature fluid loss additives are further described in this patent. The disclosure of U.S. Pat. No. 4,502,964 is incorporated into this disclosure by reference and forms a part hereof.

Resinex, a sulfonated lignite complexed with a sulfonated phenolic resin, is a commercially available high temperature, high pressure fluid loss additive for drilling muds. It is effective in controlling filtration properties in both fresh and sea water muds with high concentrations of soluble calcium.

If it were possible to provide high temperature fluid loss additives having superior activity to the activity of either the polymers described U.S. Pat. No. 4,502,964 or the Resinex additive, an advance in the art would be afforded.

THE INVENTION

In accordance with the invention, there is provided a method for improving high temperature fluid loss and rheology stabilization of high calcium brine clay-containing oil well drilling fluids which comprises adding thereto a stabilizing amount of a water-soluble terpolymer composition comprising: polymer prepared by polymerizing the following monomer ingredients:

Ingredients	% by weight
NaAMPS	72-3.8
N,N-dimethylacrylamide	13.5-0.7

-continued

Ingredients	% by weight
Acrylonitrile	9.5-0.5

said composition containing lignin, modified lignin, brown coal or modified brown coal in an amount ranging between 5-95% with the lignin, modified lignin, brown coal or modified brown coal having been present during the polymerization of the water-soluble polymer.

THE LIGNIN, MODIFIED LIGNIN, BROWN COAL OR MODIFIED BROWN COAL

A variety of material falling within this generic description may be used in the practice of the invention. One of the most common materials is lignite which is a brown coal in which the original structure of the wood is still recognizable. It is commonly known that lignite may be reacted with sulfuric acid or SO₃ to produce a sulfonated lignite. A related product that may also be substituted is lignin which is a byproduct formed in the processing of wood for the manufacture of paper.

It can be modified to provide a lignosulfonate or a cyano derivative as described in U.S. Pat. No. 3,639,263.

Another related product is leonardite which is a naturally oxidized product with higher oxygen and moisture content than lignite.

Another brown coal-type material is humic acid which is a completed polycyclic polycarboxylic acid which can be converted into its salt form e.g. alkali metal, ammonia or amine, or it can be sulfonated. Such products as well as other derivatives of humic acid are described in U.S. Pat. No. 3,266,887. The disclosure of which is incorporated herein by reference.

The polymer portion of the composition used to practice the invention is prepared in accordance with the teachings of U.S. Pat. No. 4,502,964. The reaction temperature and times may be varied with the reaction time being temperature dependent, e.g. the higher the temperature the shorter the reaction time. Generally, temperatures within the range of about 35°-80° C. may be employed. Although, the temperature and reaction times vary, they are further governed by the amount of catalyst as well as the ratio of the reactants. Often, routine experimentation must be used to optimize the process.

As indicated, the compositions are prepared by conducting the polymerization in the presence of the lignin, modified lignin, brown coal or modified brown coal.

The amount of brown coal combined with the polymer as indicated ranges between 5-95%, preferably 20-50% and most preferably 20-35% by weight.

One of the surprising facts of the invention is that the entire broad range of lignin, modified lignin, brown coal or modified brown coal used shows excellent results are achieved in providing fluid loss control.

The composition of this invention provides good results at dosages ranging between 0.5-10 lbs. per barrel. A preferred dosage range is between 1-5 lbs. per barrel. The dosages are varied depending upon the conditions and type of formation being treated.

Method for Preparing the Compositions of the Invention Composition I		
Component	Weight Percent	
(1) Deionized Water	55.77	
(2) Causticized Lignite	9.53	
(3) 50% Na AMPS Solution	28.87	
(4) Dimethylacrylamide	2.71	
(5) Acrylonitrile	1.90	
(6) EDTA	.10	
(7) Sodium Bisulfite	.56	
(8) Ammonium Persulfate	.56	
	100.00	

Charge (1) and (2) to reactor with stirring, heat to 60° C. and continue stirring at 60° C. for 30 minutes. Charge (3)-(6). Close in reactor, pull vacuum, break with nitrogen, repeat. Charge catalyst pair (7) and (8), portion-wise (approximately 0.14 weight percent) at one hour intervals. A small exotherm (10°-15° C.) may occur and the solution should gain viscosity. It appears that a Brookfield viscosity greater than 200 centipoise is necessary for peak product performance. Continue adding catalyst doses until residual monomer levels are at acceptable levels (less than 1% for AMPS and dimethylacrylamide, and less than 25 ppm for acrylonitrile). Typical residuals for open pot laboratory reactions are as follows:

Monomer	Residual
ACN	1.7 ug/g
AMPS	.07%
diMeAcAM	<.05%

Using this general preparative method, the following compositions in Table I were prepared:

TABLE I

Composition No.	Product Compositions Weight Percents			Lignite
	NaAMPS	N,N-dimethylacrylamide	Acrylonitrile	
1	50.5	9.5	6.7	33.3
2	60.7	11.4	7.9	20
3	72.0	13.5	9.5	5
4	3.8	0.7	0.5	95
5	54.3	12.4	—	33.3
6	47.2	18.4	1.1	33.3
7	48.6	14.7	3.4	33.3
8	51.6	6.7	8.4	33.3
9	56.9	2.1	7.7	33.3
10	59.3	—	7.4	33.3
11	66.7	—	—	33.3

The following variations contain the same base polymer with different lignin/lignite variations:

NaAMPS (50.5%), N,N-dimethylacrylamide (9.5%), acrylonitrile (6.5%), lignin/lignite variation (33.3%).

Composition No.	Lignin/Lignite Variation
12	Ca lignosulfonate
13	Na lignosulfonate
14	Lignin
15	Sulfomethylated lignite
16	Sulfonated lignite

FLUID TEST PROCEDURES

The variations were tested in a high temperature, high pressure fluid loss additive test which is described

in detail in the American Petroleum Institute publication RP13(B). Improved fluid loss control was observed for the variations tested. The results in both unaged muds and muds aged overnight at 350° F. are shown in Table II. The base mud used for testing consisted of:

280 g	water
15 g	bentonite
40 g	kaolinite
4 g	chrome lignosulfonate
294 g	barite
10.6 g.	sea salt

Using the above test procedures, the compositions of Table I were evaluated with the results being shown in Table II.

TABLE II

Composition No.	Concentration (lbs/bbl)	HTHP Fluid Loss (ml)	
		Unaged	Aged 350° F.
Blank	—	dry @ 27 min	dry @ 28 min
1	2	80	70
2	2	64	62
3	2	76	66
4	2	142	134
5	2	90	70
6	2	78	60
7	2	74	62
8	2	96	66
9	2	98	94
10	2	112	94
11	2	84	70
12	2	dry @ 29 min 30 sec	82
13	2	134	102
14	2	dry @ 27 min	96
15	2	dry @ 29 min 30 sec	124
16	2	124	96

The products of the invention, either in solution or in dry form, provide effective and improved performance as fluid loss additive in oil field drilling fluids. These products show especially improved performance at elevated temperatures. These additives may be used in a wide range of drilling fluid types including the following:

- (1) fresh water muds
- (2) fresh water muds contaminated with calcium or other multivalent ion
- (3) sea water muds
- (4) gypsum muds
- (5) lime muds

Having thus described our invention it is claimed as follows:

1. A method of improving high temperature fluid loss and rheology stabilization of high calcium brine clay-containing aqueous oil well drilling fluids which comprises adding thereto a stabilizing amount of a water-soluble terpolymer composition comprising: a polymer prepared by polymerizing the following monomer ingredients:

Ingredients	% by Weight
[NaAMPS] 2-acrylamido-2-methylpropane sulfonic acid, sodium salt	72-3.8
N,N-dimethylacrylamide	13.5-0.7
Acrylonitrile	9.5-0.5

said composition containing lignin, modified lignin, brown coal or modified brown coal in an amount rang-

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ing between 5-95% with the *lignin, modified lignin,*
brown coal or modified brown coal having been present
during the polymerization of the water-soluble poly-
mer, where the lignin, modified lignin, brown coal or
modified brown coal is from the group consisting of
lignites, sulphonated lignites, lignins, leonardites, ligno-

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sulfonates, alkali metal humic acid salts, humic acids,
and sulphonated humic acids.

【2. The method of claim 1 where the lignin, modified
lignin, brown coal or modified brown coal is present in
an amount ranging between 5-95% by weight.】

3. The method of claim 1 where the lignin, modified
lignin, brown coal or modified brown coal is present in
an amount ranging between 20-35% by weight.

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UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : RE. 33,856
DATED : March 24, 1992
INVENTOR(S) : Giddings, et al

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

In the ABSTRACT, the third line from the end, after
brown and before or, change "cell" to --coal--.

Signed and Sealed this
Twenty-second Day of June, 1993

Attest:



MICHAEL K. KIRK

Attesting Officer

Acting Commissioner of Patents and Trademarks