Title: SHALE INHIBITORS FOR THE PETROLEUM INDUSTRY

Abstract: The present invention relates to shale hydration inhibitors for the petroleum industry consisting of the addition product of 80 to 99.5 parts by weight (pbw) of carboxymethyl cellulose with 0.5 to 20 pbw of an organic amine, to the method for their preparation and to the use thereof.
DESCRIPTION

SHALE INHIBITORS FOR THE PETROLEUM INDUSTRY

TECHNICAL FIELD

[0001] The present invention relates to shale hydration inhibitors for the petroleum industry, to the method for their preparation and to the use thereof.

BACKGROUND ART

[0002] Shale hydration inhibitors are compounds which are effective for the inhibition of swelling of clays (also called shales) which comes into contact with the fluids used in the drilling and construction of oil and gas wells for the petroleum industry.

[0003] Drilling systems involve the use of two main kinds of mud: water based mud (WBM) and oil based mud (OBM).

[0004] Drilling muds (or drilling fluids) are very complex system; they involve the use of different chemicals such as emulsifiers, wetting agents, brines, oils, rheological modifiers, fluid loss control additives and weighting agents.

[0005] The mud performs a number of functions, such as removing drill cuttings, lubricating the bit, coating the wellbore surface to avoid flow of fluids in and out of the wellbore, helping to support the weight of the drill pipe and casing.

[0006] In today’s operations, drilling fluids are pumped under great pressure through a long pipe, reach the very bottom of the drill hole through the center of the drilling bit, then they are returned to the surface through the small annulus between the outside of the pipe itself and the borehole wall or casing.

[0007] When the formation yields solids that are shale minerals which swell this can potentially compromise drilling time and increase costs.

[0008] Shales are typically composed of sheets which can have exposed surface hydroxyls.

[0009] Multivalent atoms may create a negative potential at the shale surface and in this case, a cation can be adsorbed onto the surface. These cations may be exchangeable.

[0010] Substitutions within the shale structure and the presence of exchangeable cations affect the tendency of the shale to swell in water. For example
surface hydration gives swelling with water molecules adsorbed on shale surfaces. All types of shales can swell in this manner.

[0011] Another type of swelling is called osmotic swelling, when interlayer ion concentration leaches water between the shale unit layers, swelling the shale. Only some shales can undergo osmotic swelling.

[0012] All types of shale swelling can cause a series of problems. This increases drag between the drill string and the sides of the borehole and can cause loss of fluid circulation and sticking of the drill string and bit.

[0013] This is why development of effective shale swelling inhibitors is important to the oil and gas exploration industry.

[0014] Many shale inhibitors are known, having different mechanisms of action; they include inorganic salts such as potassium chloride, aliphatic amines and ammonium salts, such as those described in US 6,247,543 (M-I LLC, US), US 5,197,544, (Halliburton Co., US) and US 4,842,073 (Halliburton Services, US) and natural polymer derivatives, such as those described in EP 1,038,937 (Metsa Specialty Chemicals Oy, Finland).

[0015] Ammonium quaternary salts and linear aliphatic amines are shale inhibitors of considerable commercial relevance, due to their effectiveness at dosage of 1-4 wt%, but unfortunately their smell is unpleasant, for at least some of them the biodegradability is low and the toxicity to animals and human of concern. It would therefore be highly desirable to have a shale inhibitor for water based drilling fluids, which minimises the dangers of environmental pollution and toxicity, its effectiveness being equal or even better than those of the known inhibitors.

DISCLOSURE OF INVENTION

[0016] It has now surprisingly been found that certain adducts of carboxymethylcellulose with organic amines are excellent shale hydration inhibitors for the petroleum industry.

[0017] It is therefore a fundamental object of the present invention a solid shale hydration inhibitor in the form of powder consisting of the addition product of 80 to 99.5 parts by weight (pbw) of carboxymethyl cellulose having DS from 0.8 to 1.3 with 0.5 to 20 pbw of an organic amine selected from: diamines with a saturated C2-C8 alkyl chain, such as 1,6-hexamethylenediamine, 1,2-ethylenediamine, 1,3-propylenediamine,
1,4-butanediamine, 1,5-pentanediame, 1,2-diaminocyclohexane; 2-(dimethylamino) ethanol; diethylene triamine; triethylene tetramine; polyalkoxy diamine represented by the general formula

\[ \text{NH}_2-\text{R}-[\text{OR'}]_x-\text{OR}-\text{NH}_2 \]  

in which \( x \) has a value from about 1 to about 20 and \( R \) and \( R' \) are alkylene groups having 1 to 6 carbon atoms.

[0018] Preferably the organic amine is a polyalkoxy diamine represented by the general formula

\[ \text{NH}_2-\text{R}-[\text{OR'}]_x-\text{OR}-\text{NH}_2 \]  

in which \( x \) is from 2 to 3, and \( R \) and \( R' \) are \( \text{CH}_2\text{CH(CH}_3) \).

[0019] Unexpectedly, the results obtained in the shale inhibiting tests revealed that the above described adducts of carboxymethyl cellulose with organic amines are much more effective than carboxymethyl cellulose and organic amine contained in the fluid in the same amounts but added as single compounds.

[0020] Furthermore, the specific weight ratio between carboxymethyl cellulose and organic amine in the adduct of the invention allows to minimise the amount of amine to be used in order to reach excellent inhibition levels. Adducts of carboxymethyl cellulose and organic amine obtained with higher or lower amounts of amine results in inferior inhibiting performance.

[0021] It is also observed that the viscosity of an aqueous solution containing the adduct of the invention is lower than the viscosity of the solution containing carboxymethyl cellulose and organic amine in the same amounts but added as single compounds.

[0022] The observed phenomena suggests that a weak unexpected linkage between carboxymethyl cellulose and organic amine is present in the adduct of the invention.

[0023] According to a particularly preferred embodiment of the invention the solid shale hydration inhibitor in the form of powder consists of the addition product of 92 to 99 pbw of carboxymethyl cellulose having Brookfield viscosity at 20 °C, 2 % by weight (wt%), and 60 rpm comprised between 10 and 200 mPa*s with 1 to 8 pbw of the organic amine.

[0024] It is another object of the present invention the method for the preparation of the above described solid shale inhibitor in the form of powder by
mixing to homogeneity 80 to 99.5 pbw, preferably 92 to 99 pbw, of carboxymethyl cellulose in the form of powder having DS from 0.8 to 1.3 with 0.5 to 20 pbw, preferably from 1 to 8 pbw, of an organic amine selected from: diamines with a saturated C₂-C₈ alkyl chain, such as 1,6-hexamethylenediamine, 1,2-ethylenediamine, 1,3-propylenediamine, 1,4-butandiamine, 1,5-pentanediame; 1,2-diaminocyclohexane; 2-(dimethylamino) ethanol; diethylene triamine; triethylene tetramine; polyalkoxy diamine represented by the general formula \( \text{NH}_2 - R - (\text{OR'})_x \text{OR} - \text{NH}_2 \) (I)

in which \( x \) has a value from about 1 to about 20, preferably from 2 to 3 and \( R \) and \( R' \) are alkylene groups having 1 to 6 carbon atoms, preferably \( \text{CH}_2 \text{CH} \( \text{CH}_3 \) \).

[0025] The carboxymethyl cellulose useful for the realisation of the present invention is commercially available technical or purified carboxymethyl cellulose.

[0026] Advantageously, the carboxymethyl cellulose is a technical grade PAC (polyanionic cellulose) having a percentage of active substance of 65-75 wt%, a content of water of about 2-10 wt%, the remaining part being mainly glycolate, acetate and inorganic salts deriving from the its preparation.

[0027] PACs, or polyanionic cellulos, are carboxymethyl cellulos well known in the field of oil drilling and considered to be premium products because typically have a high degree of carboxymethyl substitution and a special anionic distribution.

[0028] PACs are field tested and especially developed to improve the effectiveness of oil well drilling muds.

[0029] The preferred shale inhibitor of the invention maintains the solubility and rheological characteristics of the carboxymethyl cellulose which has been used to prepare it.

[0030] According to an advantageous aspect the shale inhibitor of the invention has a very low tendency to dusting and this feature simplifies its handling and the preparation of its solutions.

[0031] According to a preferred embodiment of the invention, for the preparation of the solid shale inhibitor, carboxymethyl cellulose in the form of powder
is mixed to homogeneity in a granulating conventional apparatus or in a high shear mixer with the organic amine in the form of a 50 wt% aqueous solution.

[0032] The thus obtained solid shale inhibitor is a white powder having a content of water of about 2-10 wt%.

[0033] In another aspect the present invention is a method for inhibiting hydration of shales in drilling operations comprising the step of

[0034] A. preparing a solid shale inhibitor in the form of powder by mixing to homogeneity 80 to 99.5 pbw, preferably 92 to 99 pbw, of carboxymethyl cellulose in the form of powder having DS from 0.8 to 1.3 with 0.5 to 20 pbw, preferably from 1 to 8 pbw, of an organic amine selected from: diamines with a saturated C2-C8 alkyl chain, such as 1,6-hexamethylenediamine, 1,2-ethylenediamine, 1,3-propylenediamine, 1,4-butanediamine, 1,5-pentanedi­amine; 1,2-diaminocyclohexane; 2-(dimethylamino) ethanol; diethylene triamine; triethylene tetramine; polyalkoxy diamine represented by the general formula

$$\text{NH}_2-R-[\text{OR'}]_x\text{OR}-\text{NH}_2 \quad (I)$$

in which x has a value from about 1 to about 20, preferably from 2 to 3 and R and R' are alkylene groups having 1 to 6 carbon atoms, preferably CH₂CH(CH₃);

[0035] B. preparing the drilling fluid by dissolving into the fluid the solid shale inhibitor in the form of powder in an amount of about 1 wt% to about 2 wt% of the fluid;

[0036] C. introducing the drilling fluid to the wellbore at a pressure sufficient to treat the subterranean formation.

[0037] The drilling fluid contains water or brine and the normally used additives, well known by the people skilled in the art; the order in which the additives and the product of the invention are added into the well fluid is not critical.

[0038] In yet another aspect the present invention is an aqueous based drilling fluid comprising the solid shale inhibitor of the invention.

[0039] The adducts according to the present invention are particularly suitable for the shale inhibition, as described in the examples which follow.

[0040]

[0041]
Example 1.

Preparation of a solid shale inhibitor according to the invention

100g of a low viscosity PAC from Lamberti SpA (carboxymethyl cellulose having DS 1 and Brookfield viscosity at 20°C, 60 rpm and 2 wt% of 14 mPa*s) are charged in a high shear mixing with 7.5 g of an organic amine represented by the formula (I), in which x has an average value from 2 to 3, R and R' are the alkylene group -CH₂CH(CH₃) and having molecular weight of 230, previously dissolved in water at a concentration of 50 wt% mixing for 10 minutes at 25°C.

The obtained product is dried on a fluid bed dryer for 20 minutes at 80°C

A solid shale inhibitor is form of powder is obtained, having the following characteristics:

% wt of amine = 7 wt%

Brookfield viscosity (2 wt%) = 12.5 mPa*s

Colour =

Content of water = 5.8 wt%

pH at 2% = 9.2

Smell = light

Examples 2-4.

Solid shale inhibitors are prepared as described in Example 1, varying only the amount of amine used as reported in Table 1. Their characteristics are also summarised in Table 1.

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[^1]: Brookfield viscosity
[^2]: pH of a 2 wt% solution
[^3]: Colour
[^4]: Smell
[^5]: Content of water (wt%)
Shale inhibiting tests.

The Cuttings Recovery Test, sometimes referred to as the Hot Roll Dispersion Test, was conducted to evaluate the shale inhibition performance of the shale inhibitors prepared in Example 1-4.

It is a commonly used procedure for the optimization of the composition of drilling fluids for reactive shale formations.

Procedure:

Condition the shales to constant humidity and grind them coarsely.

Sieve the shales on ASTM E 11-01 mesh screens and recover for the subsequent tests the fraction collected between 5 and 10 mesh size screens.

Prepare the test drilling fluid (a Carbonate Mud) as per the following formulation, by means of an Hamilton Beach mixer:

- Fresh water: 1 bbl
- Bentonite (conf. to API Spec. 13A, 16th ed. feb 2004, § 9): 2.8 ppb
- Xanthan Gum: 1 ppb
- Shale inhibitor: 3.5 ppb
- K$_2$CO$_3$: 21 ppb
- Polyalkyleneglycol: 10.5 ppb

Place the fluid in a hot rolling cell.

Weigh accurately 30 grams of the shales and add to the fluid in the hot rolling cell.

Seal and roll the cell for 16 hours in a preheated oven @176°F (80°C).

After the rolling period is completed, remove from the oven and cool the cell to room temperature in a cold water-bath.

Open the cell, pour the content onto a ASTM E 11-01 10 mesh size screen and carefully wash any adhering material from the shales by using a solution with the same brine phase composition of the mud.

Remove and dry the cuttings to constant weight in an oven set to 158°F (70°C).

The higher the percentage of shales recovered (% of recovery), the better the performance of the shale inhibitor.
Comparative tests (Ex. 5-8) were also performed dosing separately in the fluid, as shale inhibitor, the low viscosity PAC and the organic amine used to prepare the shale inhibitors of Ex. 1-4; the percentage of amine on the total amount of shale inhibitor added is reported in Table 2.

The results of the shale inhibiting tests are also reported in Table 2 together with the rheological properties of the drilling muds used in the tests (measured with a 35 Fann viscometer immediately after the preparation).

Table 2

<table>
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<th>% amine</th>
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* comparison Example
CLAIMS

1. Solid shale hydration inhibitor in the form of powder consisting of the addition product of 80 to 99.5 parts by weight (pbw) of carboxymethyl cellulose having DS from 0.8 to 1.3 with 0.5 to 20 pbw of an organic amine selected from: diamines with a saturated C₂-C₈ alkyl chain, such as 1,6-hexamethylene diamine, 1,2-ethylenediamine, 1,3-propylenediamine, 1,4-butanediamine, 1,5-pentanedi amine, 1,2-diaminocyclohexane; 2-(dimethylamino) ethanol; diethylene triamine; triethylene tetramine; polyalkoxy diamine represented by the general formula
\[\text{NH}_2\text{-R-}[\text{OR'}]_x\text{-OR-NH}_2\] (I)
in which x has a value from about 1 to about 20 and R and R' are alkylene groups having 1 to 6 carbon atoms.

2. Solid shale hydration inhibitor in the form of powder according to claim 1., wherein the organic amine is a polyalkoxy diamine represented by the general formula (I) in which x has a value from 2 to 3, and R and R' are CH₂CH(CH₃).

3. Solid shale hydration inhibitor in the form of powder according to claim 2., consisting of the addition product of 92 to 99 pbw of carboxymethyl cellulose having Brookfield viscosity at 20 °C, 2 % by weight and 60 rpm comprised between 10 and 200 mPa*s with 1 to 8 pbw of the organic amine.

4. Method for the preparation of a solid shale inhibitor in the form of powder by mixing to homogeneity 80 to 99.5 pbw of carboxymethyl cellulose in the form of powder having DS from 0.8 to 1.3 with 0.5 to 20 of an organic amine selected from: diamines with a saturated C₂-C₈ alkyl chain, such as 1,6-hexamethylene diamine, 1,2-ethylenediamine, 1,3-propylenediamine, 1,4-butanediamine, 1,5-pentanedi amine, 1,2-diaminocyclohexane; 2-(dimethylamino) ethanol; diethylene triamine; triethylene tetramine; polyalkoxy diamine represented by the general formula
\[\text{NH}_2\text{-R-}[\text{OR'}]_x\text{-OR-NH}_2\] (I)
in which x has a value from about 1 to about 20 and R and R' are alkylene groups having 1 to 6 carbon atoms.

5. Method for the preparation of a solid shale inhibitor in the form of powder according to claim 4., wherein the organic amine is a polyalkoxy diamine represented by the general formula (I) in which x has a value from 2 to 3, and R and R' are CH₂CH(CH₃).
6. Method for the preparation of a solid shale inhibitor in the form of powder according to claim 5., wherein 92 to 99 pbw of carboxymethyl cellulose having Brookfield viscosity at 20 °C, 2 % by weight, and 60 rpm comprised between 10 and 200 mPa*s are mixed to homogeneity with 1 to 8 pbw of the organic amine.

7. Method for inhibiting hydration of shales in drilling operations comprising the step of:
   A. preparing a solid shale inhibitor in the form of powder by mixing to homogeneity 80 to 99.5 pbw of carboxymethyl cellulose in the form of powder having DS from 0.8 to 1.3 with 0.5 to 20 pbw of an organic amine selected from: diamines with a saturated C2-C8 alkyl chain, such as 1,6-hexamethylenediamine, 1,2-ethylendiamine, 1,3-propylenediamine, 1,4-butenediamine, 1,5-pentanediame; 1,2-diaminocyclohexane; 2-(dimethylamino) ethanol; diethylene triamine; triethylene tetramine; polyealkoxy diamine represented by the general formula
   \[ \text{NH}_2-R-\left[\text{OR'}\right]_x\text{OR-NH}_2 \] (I)
   in which x has a value from about 1 to about 20 and R and R' are alkylene groups having 1 to 6 carbon atoms;
   B. preparing the drilling fluid by dissolving into the fluid the solid shale inhibitor in the form of powder in an amount of about 1 wt% to about 2 wt% of the fluid;
   C. introducing the drilling fluid to the wellbore at a pressure sufficient to treat the subterranean formation.

8. Method for inhibiting hydration of shales in drilling operations according to claim 7., wherein in step A. the organic amine is a polyealkoxy diamine represented by the general formula (I) in which x has a value from 2 to 3, and R and R' are CH₂CH(CH₃) and wherein 92 to 99 pbw of carboxymethyl cellulose having Brookfield viscosity at 20 °C, 2 % by weight, and 60 rpm comprised between 10 and 200 mPa*s are mixed to homogeneity with 1 to 8 pbw of the organic amine.
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C09K7/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C09K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name or data base and, where practical, search terms used)

EPO-Internal, PAJ, WPI Data, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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<td>EP 1 188 772 A (NOVIANT OY) 20 March 2002 (2002-03-20) claim 1</td>
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Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

* Special categories of cited documents:
  *A* document defining the general state of the art which is not considered to be of particular relevance
  *E* earlier document but published on or after the international filing date
  *L* document which may throw doubt on priority claim(s) or which is cited to establish the publication date of another document or other special reason (as specified)
  *X* document referring to an oral disclosure, use, exhibition or other means
  *P* document published prior to the international filing date but later than the priority date claimed

*Y* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

*Z* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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Date of the actual completion of the international search 27 April 2005

Date of mailing of the international search report 06/05/2005

Name and mailing address of the ISA

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Tel. (+31-70) 340-2040, Tx. 51 651 epo ml, Fax: (+31-70) 340-6016

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Pollio, M
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