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(54) **Title**: USE OF TERPOLYMERS AS FLUID LOSS ADDITIVES IN WELL CEMENTING

(57) **Abstract**: What is proposed is the use of a terpolymer comprising 5 -95 mol%of 2-acrylamido-2-methylpropanesulfonic acid, 5 -95 mol%of N,N-dimethylacrylamideand 5 -12 mol%of acrylic acid as a fluid loss additive in well cementing. Acrylsäure als Fluid Loss-Additiv bei der Bohrlochzementierung.

Use of terpolymers as fluid loss additives in well cementing

The present invention relates to the use of terpolymers of 2-acrylamido-2-methylpropanesulfonic acid, acrylic acid and N,N-dimethylacrylamide as fluid loss additives in well cementings.

In the construction chemical sector, various copolymers are frequently used as water retention aids, which are also referred to as "fluid loss additives". A specific field of use in this context is the cementing of wells in the development, exploitation and completion of underground mineral oil and natural gas deposits, and in deep wells.

Water retention aids or fluid loss additives have the task of reducing the release of water from a cement slurry. This is of significance especially in the field of mineral oil and natural gas exploration, since cement slurries consisting essentially of cement and water, in the course of cementing of the wells, are pumped through the ring space between the casing and the well wall. In the course of this, amounts of water can be released from the cement slurry to the underground formation. This is the case especially when the cement slurry flows past porous rock strata in the course of well cementing. The alkalized water originating from the cement slurry can then cause clays in the formations to swell and, with carbon dioxide from the natural gas or mineral oil, form calcium carbonate deposits. These effects reduce the permeability of the deposits, and the production rates are also adversely affected as a result.

Moreover, the cement slurries, as a result of the release of water to the porous underground formations, no longer solidify homogeneously and as a result become pervious to gases and to liquid hydrocarbons and water. This can subsequently lead to escape of the fossil energy carriers through the ring space filled with porous cement.

There have therefore been efforts over a prolonged period to lower such water losses from the cement slurries used to a tolerable minimum.

EP 0 116 671 A1 describes, for example, a cement slurry for deep wells, wherein the content of copolymers is said to reduce water loss. An important constituent of the copolymers used is formed by acrylamides, and especially 2-acrylamido-2-methylpropanesulfonic acid (AMPS®). According to this document, the cement slurries should contain between 0.1 and 3% by weight of the suitable copolymers.

Well cementing and a composition suitable therefor are also addressed by EP 1 375 818 A1. In this case, for fluid loss control, a polymer additive is used which comprises, as well as AMPS®, additional maleic acid, N-vinylcaprolactam and 4-hydroxybutyl vinyl ether.

Likewise based on AMPS® and partially hydrolyzed acrylamide is a copolymer according to US 4,015,991. The copolymer described in this patent is likewise said to improve the water retention capacity in cementitious compositions. The primary field of use mentioned is the cementing of wells.

The use of copolymers of 2-acrylamido-2-methylpropanesulfonic acid and N,N-dimethylacrylamide (DMAA) as a fluid loss additive in well cementing is also described in US 4,515,635. Similar polymers can also be found in US 4,555,269.

The water-soluble copolymers according to US 6,395,853 B1 comprise, inter alia, acrylamides and AMPS®. At the forefront of this property right is a process for reducing water loss in a slurry which is used to obtain mineral oil. In this context, particular mention is made of well cementing and completion, and of the well slurry preceding these process steps.

At the center of US 4,700,780 is a process for reducing water loss in cementitious compositions which also comprise defined salt concentrations. The water retention aid is again a polymer, or polymer salt of AMPS®, and in this case the units of styrene and acrylic acid must also be present.

Terpolymers of 2-acrylamido-2-methylpropanesulfonic acid, acrylic acid and N,N-dimethylacrylamide also form part of the prior art. For instance, US 4,554,081 discusses these terpolymers, preferably in a composition of 16.8 mol% of AMPS®, 73.2 mol% of DMAA and 10 mol% of acrylic acid, and the use thereof as a fluid loss additive in completion fluids, drilling muds and workover fluids with high densities in the field of oil and gas production.

In addition, Plank et al. (J. Appl. Polym. Sci. 106, 3889-3894, 2007 - DOI: 10.1002/app.26897) describe such terpolymers with low proportions of acrylic acid (approx. 1% by weight or approx. 3.6 mol%). In this publication, the efficacy of a copolymer of AMPS® and DMAA as a fluid loss additive in well cementing is compared with said terpolymer. It was found that the efficacy of the copolymer is no different from that of the terpolymer with low proportions of acrylic acid.

These known co- and terpolymers each have a different profile of properties with specific advantages and disadvantages. A general weakness intrinsic to most of these ionic polymers is that their water retention action declines in the presence of high salt concentrations as typically occur in seawater, which is frequently used to make up the cement slurries in offshore oil and gas wells. This is also true especially of salts of divalent cations such as Mg^{2+} and Ca^{2+}.

Over a long period, there have therefore been concerted attempts to provide novel molecules or polymers whose water retention capacity is stable, especially at high salt concentrations, especially in the field of oil and gas exploration and in deep wells.

This object is achieved by the features of the independent claims. The dependent claims relate to preferred embodiments.

It has been found, surprisingly, that terpolymers of 2-acrylamido-2-methylpropanesulfonic acid, N,N-dimethylacrylamide and acrylic acid with an acrylic acid content of about 5 to 12 mol% have distinct advantages with regard to efficacy as a fluid loss additive in well cementing.

The present invention provides for the use of a terpolymer comprising 5 - 95 mol% of 2-acrylamido-2-methylpropanesulfonic acid, 5 - 95 mol% of N,N-dimethylacrylamide and 5 - 12 mol% of acrylic acid as a fluid loss additive in well cementing.

The terpolymer preferably comprises 8 - 12 mol% and more preferably 10 to 11 mol% of acrylic acid.

Although the molar ratio of 2-acrylamido-2-methylpropanesulfonic acid to N,N-dimethylacrylamide is not particularly critical, it is preferred in the context of the present invention that the molar ratio of 2-acrylamido-2-methylpropanesulfonic acid to N,N-dimethylacrylamide is between 50:50 and 80:20, especially between 60:40 and 70:30.

The inventive terpolymer can appropriately be prepared by means of free-radical copolymerization of the abovementioned comonomers. Due to the ionic or hydrophilic character of the comonomers, the copolymerization can appropriately be effected in aqueous solution. It is possible that the 2-acrylamido-2-methylpropanesulfonic acid and the acrylic acid are present fully or partly in the form of salts of alkali metals, alkaline earth metals or mixtures thereof, especially in the form of Na, K, Mg and/or Ca salts. These salts can be used directly for copolymerization. It is likewise possible that these salts are formed only in a subsequent neutralization of the terpolymers formed. Both routes for introduction of said salts into the terpolymer can be taken independently of one another or in combination with one another.

The inventive terpolymer preferably has a molecular weight in the range from 500 000 to 4 000 000 and especially from 1 000 000 to 2 000 000 g/mol.

In the field of mineral oil and natural gas exploration, and in deep wells, as already mentioned at the outset, cement slurries consisting essentially of cement and water, for cementing of the wells, are pumped through the ring space between the casing and the well wall. It is still customary nowadays to use portland cements for this purpose. Accordingly, the inventive use is preferably characterized in that the terpolymer is used as a fluid loss additive in a cement slurry comprising portland cement.

Due to the high salt tolerance of the inventive terpolymers, these terpolymers can advantageously be used as fluid loss additives in cement slurries which comprise seawater or have been made up with seawater.

In the field of mineral oil production, the use of what are called weighting fluids is customary, these generally consisting of concentrated aqueous salt solutions of alkali metal and/or alkaline

earth metals. In the course of well cementing, there may therefore be at least partial mixing of weighting fluids and cement slurries. Due to the high salt tolerance of the inventive terpolymers, the action thereof is not lost even in such cement slurries.

In summary, it can be stated that the inventive terpolymer is appropriately and advantageously used as a fluid loss additive in the cementing of wells in the development, exploitation and completion of underground mineral oil and natural gas deposits, and in deep wells, and is notable especially for tolerance to high salt concentrations which is surprising in view of the prior art.

The present invention is now illustrated in detail by the examples which follow.

Example 1:

A glass reactor with steel stirrer was initially charged with 2200 g of tap water and 158 g of 20% NaOH whilst stirring. Subsequently, 135 g of AMPS® were added while cooling, such that the temperature did not exceed 30°C. Thereafter, 95 g of DMAA and 13.5 g of acrylic acid (which corresponds to approx. 10.6 mol%) were mixed in, and washed in with 100 ml of tap water. In the next step, the pH was adjusted to 7.6 with the aid of NaOH or AMPS®. Within one hour, the reaction mixture was then heated to 62°C under a nitrogen blanket. On attainment of constant temperature, the polymerization was initiated by adding 0.65 g of tetraethylenepentamine (TEPA) and 5 g of $Na_2S_2O_8$, dissolved in approx. 10 ml of H_2O. An exothermic reaction was observed, in the course of which the temperature rose to 70 - 74°C. After the reaction had started, the mixture was stirred for one hour without any further external heating. The end product was a pale yellowish, viscous solution with a pH of 7 – 7.5, a solids content of 10 - 12% by weight and a Brookfield viscosity of 6000 mPa*s.

Example 2:

The liquid loss ("LL") and the rheology of the terpolymer from example 1 were determined in comparison with a commercially available AMPS®/DMAA copolymer (Polytrol® FL 34 from BASF Construction Polymers GmbH) according to API Recommended Practice 10 B at 190°F (88°C) in the following cement slurries with or without addition of salt:

800 g of class G cement (from Dyckerhoff)
352 g of water
0.6% bwoc of fluid loss additive
1.0 g of antifoam (triisobutylphosphate)

The results are reproduced in tables 1 and 2, table 1 relating to Polytrol® FL 34 and table 2 to the terpolymer from example 1. The amount of salt is reported in grams and percent by weight (based on the water content); "bwoc" means percent by weight of cement.

Table 1(Polytrol® FL 34):

Sea Salt		NaCl		Fann 35 - rheology [lbf/100sqft]						LL	Blows out after:
[g]	[%]	[g]	[%]	300	200	100	6	3	600	[ml]	[min:sec]
--	--	--	--	184	138	84	10	8	288	66	
--	--	77.3	18.0	122	90	57	19	18	175	509	06:27
14.7	4.0	--	--	148	115	76	28	24	222	138	
--	--	39.1	10.0	156	122	82	31	28	232	282	21:26

Table 2 (terpolymer):

Sea Salt		NaCl		Fann 35 - rheology [lbf/100sqft]						LL
[g]	[%]	[g]	[%]	300	200	100	6	3	600	[ml]
--	--	--	--	258	200	130	30	24	>300	20
--	--	77.3	18.0	114	80	47	6	4	170	156
14.7	4.0	--	--	>300	228	153	39	36	>300	42
--	--	39.1	10.0	142	165	64	10	8	212	28

It is clearly evident that the terpolymer according to example 1 with the same dosage enables much lower liquid losses than the commercially available Polytrol® FL 34. In addition, the terpolymer according to example 1 is much more salt-tolerant than Polytrol® FL 34, even towards sea salt.

This result is also surprising in that it is stated in the prior art (Plank et al., J. Appl. Polym. Sci. 106, 3889-3894, 2007) that an addition of acrylic acid has no influence on the efficacy of AMPS/DMAA copolymers as a fluid loss additive. It is apparent here that the exact proportion of acrylic acid is crucial.

In addition, it was found that the terpolymer according to example 1, compared to Polytrol® FL 34, exerts only an insignificant retarding effect, if any, on the stiffening time of the cement slurries.

Claims

1. Use of a terpolymer comprising:

   5 - 95 mol% of 2-acrylamido-2-methylpropanesulfonic acid,
   5 - 95 mol% of N,N-dimethylacrylamide and
   5 - 12 mol% of acrylic acid

   as a fluid loss additive in well cementing.

2. Use according to Claim 1, characterized in that the terpolymer comprises 8 - 12 mol% and preferably 10 to 11 mol% of acrylic acid.

3. Use according to Claim 1 or 2, characterized in that the molar ratio of 2-acrylamido-2-methylpropanesulfonic acid to N,N-dimethylacrylamide is between 50:50 and 80:20, preferably between 60:40 and 70:30.

4. Use according to any of Claims 1 to 3, characterized in that the 2-acrylamido-2-methylpropanesulfonic acid and the acrylic acid are present fully or partly in the form of salts of alkali metals, alkaline earth metals or mixtures thereof, especially in the form of Na, K, Mg and/or Ca salts.

5. Use according to any of Claims 1 to 4, characterized in that the terpolymer has a molecular weight in the range from 500 000 to 4 000 000 and especially 1 000 000 to 2 000 000 g/mol.

6. Use according to any of Claims 1 to 5, characterized in that the terpolymer is used as a fluid loss additive in a cement slurry comprising portland cement.

7. Use according to any of Claims 1 to 6, characterized in that the terpolymer is used as a fluid loss additive in a cement slurry comprising seawater.

8. Use according to any of Claims 1 to 7, characterized in that the terpolymer is used as a fluid loss additive in the cementing of wells in the development, exploitation and completion of underground mineral oil and natural gas deposits, and in deep wells.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2013/050275

A. CLASSIFICATION OF SUBJECT MATTER
INV. C09K8/487 C09K8/12
ADD.

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)
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 of data base and, where practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 554 081 A (BORCHARDT JOHN K [US] ET AL) 19 November 1985 (1985-11-19) cited in the application column 9, lines 57-64; examples I (1, 2, 3, 5); table 1	1-8
A	PLANK ET AL.: J. APPL. POLYM. SCI., vol. 106, 2007, pages 3889-3894, XP002693166, cited in the application the whole document	1-8
A	US 2005/034864 A1 (CAVENY WILLIAM J [US] ET AL) 17 February 2005 (2005-02-17) claims 1,2 the whole document	1-8

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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

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Date of the actual completion of the international search	Date of mailing of the international search report
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Name and mailing address of the ISA/	Authorized officer
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INTERNATIONAL SEARCH REPORT

International application No
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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 640 942 A (BROTHERS LANCE E [US]) 3 February 1987 (1987-02-03) claims 1,2,6 the whole document	1-8
A	US 2011/308800 A1 (SARAP GIRISH DINKAR [IN] ET AL) 22 December 2011 (2011-12-22) claim 1 the whole document	1-8
A	US 2011/263749 A1 (REICHENBACH-KLINKE ROLAND [DE] ET AL) 27 October 2011 (2011-10-27) example 1 the whole document	1-8

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2013/050275

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