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RESEARCH AND DEVELOPMENT LIMITED; P.O.
Box 71, Craigmuir Chambers, Road Town, Tortola (VG).

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(72) Inventors; and

(75) Inventors/Applicants (*for US only*): **CHEN, Yiyao**
[CN/FR]; Schlumberger Technology Corporation, 110
Schlumberger Drive, MD-1, Sugar Land, TX 77478 (US).
LEE, Jesse [US/US]; Etudes et Productions Schlumberger,
1, rue Becquerel, BP 202, F-92142 Clamart Cedex (FR).
DROCHON, Bruno [FR/US]; Schlumberger Technology
Corporation, 110 Schlumberger Drive, MD-1, Sugar Land,
TX 77478 (US).

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(74) Agent: **ETUDES ET PRODUCTIONS SCHLUM-
BERGER**; 1, rue Henri Becquerel, BP 202, F-92142
Clamart Cedex (FR).

(71) Applicant (*for FR only*): **SERVICES PETROLIERS
SCHLUMBERGER** [FR/FR]; 42, Rue Saint Dominique,
F-75007 Paris (FR).

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(71) Applicant (*for AE, AL, AU, AZ, BG, CO, CZ, DE, DK,
GR, HU, ID, IE, IL, IT, KP, KR, KZ, LT, MX, MY, NO,
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ZA only*): **SCHLUMBERGER TECHNOLOGY B.V.**
[NL/NL]; Parkstraat 83-89, NL-2514 JG The Hague (NL).

(71) Applicant (*for GB, JP, NL only*): **SCHLUMBERGER
HOLDING LIMITED**; P.O. Box 71, Craigmuir Cham-
bers, Road Town - Tortola (VG).

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(71) Applicant (*for CA only*): **SCHLUMBERGER CANADA
LIMITED** [CA/CA]; 525-3rd Ave S.W., Calgary, Alberta,
T2P 0G4 (CA).

(71) Applicant (*for all designated States except AE, AL, AU,
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(54) Title: VISCO-ELASTIC SURFACTANT SPACERS

(57) Abstract: A spacer for use in an oil well cementing operation comprises an aqueous solution of a visco-elastic surfactant. A method of treating a well in a cementing operation, comprises pumping the spacer into a well ahead of a cement slurry for cementing the well.

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Description

Visco-Elastic Surfactant Spacers

Technical field

[0001] This invention relates to spacers such as are used in cementing operations in oil and gas wells and the like. In particular, the invention relates to the use of visco-elastic surfactants.

Background art

[0002] When wells such as oil and gas wells are drilled, a drilling fluid, commonly known as 'mud' is circulated through the well to assist in removing drilled material, to stabilise the wall of the well and to balance the pressure of fluids in the formation through which the well. At various points during the drilling of the well, and once the well drilling is completed, casings are typically cemented in the well. This is achieved by positioning the casing in the well and pumping a cement slurry down the casing from the surface and back up the annulus between the casing and the wall of the well where it is allowed to set to support the casing and provide zonal isolation.

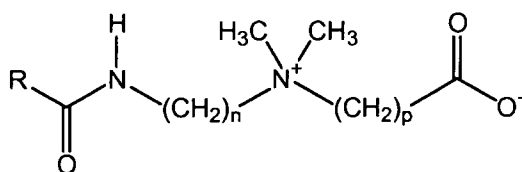
[0003] In cementing operations, drilling mud remaining in the well needs to be cleaned up before pumping cement to improve the bonding of cement to casing and wellbore. The cleanup is typically done by pumping a chemical wash with surfactant solutions through the well. Following this a spacer is pumped through the well to displace the mud ahead of the cement slurry. The spacer needs to have a proper rheology profile to displace the mud and chemical wash fluid and carry particles remaining in the well. Since the spacer comes into contact with both the mud and cement, it needs to have some compatibility with both materials. For the mud side, the spacer fluid should be compatible with the mud particles, brine and solvents. For cement side, the fluid should be able to tolerate high pH, calcium and other cementing additives. By itself, the spacer also needs to be able to be weighted with brines or solid weighting agents to maintain the hydrostatic pressure in the well.

[0004] Visco-elastic surfactants (VES) have previously been proposed for well treatment fluids, particularly in the field of fracturing. They have also been proposed for other uses involving the controlled transport of particulate

materials. Examples of such proposed uses can be found in US6435277; US6482866; WO 2005/014975 and WO 2007/119211. Further aspects of the use of visco-elastic surfactants can be found in 'Expanding Applications for Viscoelastic Surfactants', Oilfield Review Winter 2004/2005.

Disclosure of the invention

- [0005] A first aspect of this invention provides a spacer for use in an oil well cementing operation, comprising an aqueous solution of a visco-elastic surfactant.
- [0006] The visco-elastic surfactant can comprise a zwitterionic surfactant that is typically present in an amount of less than 5%. In a preferred embodiment, the zwitterionic surfactant has the betaine structure



wherein R is a hydrocarbon group that may be branched or straight chained, aromatic, aliphatic or olefinic and has from 14 to 26 carbon atoms and, optionally contains an amine; $n = 2$ to 4 ; and $p = 1$ to 5 ; and mixtures thereof.

- [0007] The visco-elastic surfactant can also comprise an amphiphilic polymer as a rheology enhancer. The rheology enhancer can comprises a block copolymer of polypropylene glycol and polyethylene glycol; and a polynaphthalene sulphonate. The rheology enhancer is typically present in an amount of less than 0.02%.
- [0008] Further components can be added for controlling the density of the spacer to a predetermined level, for example heavy brine such as calcium bromide and/or calcium chloride.
- [0009] The spacer can further comprise a co-surfactant.
- [0010] A second aspect of the invention, provides a method of treating a well in a cementing operation, comprising pumping a spacer according to the first aspect of the invention into a well ahead of a cement slurry for cementing the well.

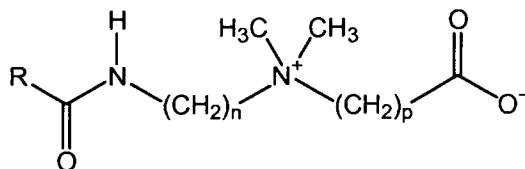
- [0011] The spacer can either be preceded by a chemical wash or can be pumped into the well with no chemical wash preceding the spacer.
- [0012] Preferably, the cement slurry immediately follows the spacer.
- [0013] The spacer can be batch mixed or mixed on the fly and may be foamed or unfoamed.
- [0014] Further aspects of the invention will be apparent from the following description.

Brief description of the drawings

- [0015] Figure 1 shows a plot of viscosity vs temperature for an embodiment of the invention alone and in the presence of a density regulator; and Figure 2 shows a plot of viscosity vs temperature for an embodiment of the invention at different pH.

Mode(s) for carrying out the invention

- [0016] One particularly preferred embodiment of the invention can be based on a current VES fracturing formulations using a zwitterionic surfactant and an amphiphilic polymer. The zwitterionic surfactant can comprise a betaine structure



wherein R is a hydrocarbon group that may be branched or straight chained, aromatic, aliphatic or olefinic and has from 14 to 26 carbon atoms and, optionally contains an amine; $n = 2$ to 4 ; and $p = 1$ to 5 ; and mixtures thereof. Particularly preferred forms of such betaines are $\text{R}=\text{C}_{17}\text{H}_{33}$, $n=3$, and $p=1$ (BET-O-30); and $\text{R}=\text{C}_{21}\text{H}_{41}$, $n=3$, and $p=1$ (BET-E-40).

- [0017] The amphiphilic polymer acts as a rheology enhancer and can comprise a first component of a block copolymer of polypropylene glycol and polyethylene glycol; and a second component as a polynaphthalene sulphonate.
- [0018] This formulation can provide a VES fluid which can be used as cementing spacer fluid. This fluid formulation can be used to gel heavy brines and so meets the requirement for pressure control in the well and other density

requirements. Figure 1 shows a plot of viscosity vs temperature for two applications for a formulation according to an embodiment of the invention. In both cases, the formulation comprises a solution of 4.5% of zwitterionic surfactant and 0.015% of amphiphilic polymer. Line A shows the viscosity behaviour on changing temperature. Line B shows the corresponding plot to line A in a 13ppg solution that includes calcium bromide and calcium chloride as density regulators. As shown can be seen from Figure 1, the fluid has good rheology in heavy brine. This formulation is also stable in a basic environment (high pH), as shown in Figure 2 in which line C shows viscosity vs temperature behaviour at pH10 and line D the corresponding behaviour at pH 12. This provides the opportunity to retain the gel strength in the spacer when in contact with cement. The formulation is also tolerant to a certain concentration of cementing dispersant such as Daxad.

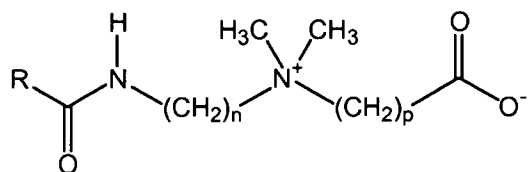
- [0019] Addition of the amphiphilic polymer allows the fluid to have good shear recovery even at very low surfactant concentrations (in the examples given above, the surfactant is present at a level of less than 5%). This gives the opportunity to use the spacer fluid at low surfactant concentration and so provide a lower cost solution over a range of temperatures.
- [0020] As well as the properties that allow the formulation of the invention to be used as spacer, the presence of the surfactant fluid means that it can also be formulated to provide a chemical wash function to clean up the surface of the wellbore and casing to achieve better bonding. One embodiment of the invention comprises a single fluid doing the job of both the chemical wash and the spacer to simplify job operation and further save cost.
- [0021] Unlike cationic or anionic surfactants, the zwitterionic surfactant also provides increased oil tolerance. This oil tolerance can be enhanced by the use of co-surfactants which allows the spacer to maintain viscosity while in contact with oil based mud.
- [0022] In use, the spacer can be prepared at the surface by batch mixing followed by pumping downhole, or by on the fly mixing as it is pumped downhole. It

can be prepared in a foamed or unfoamed forma according to requirements.

[0023] Other changes within the scope of the invention will be apparent.

Claims

1. A spacer for use in an oil well cementing operation, comprising an aqueous solution of a visco-elastic surfactant.
2. A spacer as claimed in claim 1, wherein the visco-elastic surfactant comprises a zwitterionic surfactant.
3. A spacer as claimed in claim 2, wherein the zwitterionic surfactant is present in an amount of less than 5%.
4. A spacer as claimed in claim 2 or 3, wherein the zwitterionic surfactant has the betaine structure



wherein R is a hydrocarbon group that may be branched or straight chained, aromatic, aliphatic or olefinic and has from 14 to 26 carbon atoms and, optionally contains an amine; $n = 2$ to 4 ; and $p = 1$ to 5 ; and mixtures thereof.

5. A spacer as claimed in any preceding claim, wherein the visco-elastic surfactant comprises an amphiphilic polymer as a rheology enhancer.
6. A spacer as claimed in claim 5, wherein the rheology enhancer comprises a block copolymer of polypropylene glycol and polyethylene glycol.
7. A spacer as claimed in claim 5 or 6 wherein the rheology enhancer comprises a polynaphthalene sulphonate.
8. A spacer as claimed in claim 5, 6 or 7, wherein the rheology enhancer is present in an amount of less than 0.02%.
9. A spacer as claimed in any preceding claim, comprising further components for controlling the density of the spacer to a predetermined level.
10. A spacer as claimed in claim 9, wherein the further components comprise heavy brine.
11. A spacer as claimed in claim 10, wherein the heavy brine comprises calcium bromide and/or calcium chloride.
12. A spacer as claimed in any preceding claim, further comprising a co-surfactant.

13. A method of treating a well in a cementing operation, comprising pumping a spacer as claimed in any preceding claim into a well ahead of a cement slurry for cementing the well.
14. A method as claimed in claim 13, wherein the spacer is preceded by a chemical wash.
15. A method as claimed in claim 13, wherein there is no chemical wash preceding the spacer.
16. A method as claimed in claim 13, 14 or 15, wherein the cement slurry immediately follows the spacer.
17. A method as claimed in any of claims 13-16, wherein the spacer is batch mixed prior to pumping into the well, or mixed on the fly during pumping into the well.
18. A method as claimed in any of claims 13-17, wherein the spacer is foamed or unfoamed.

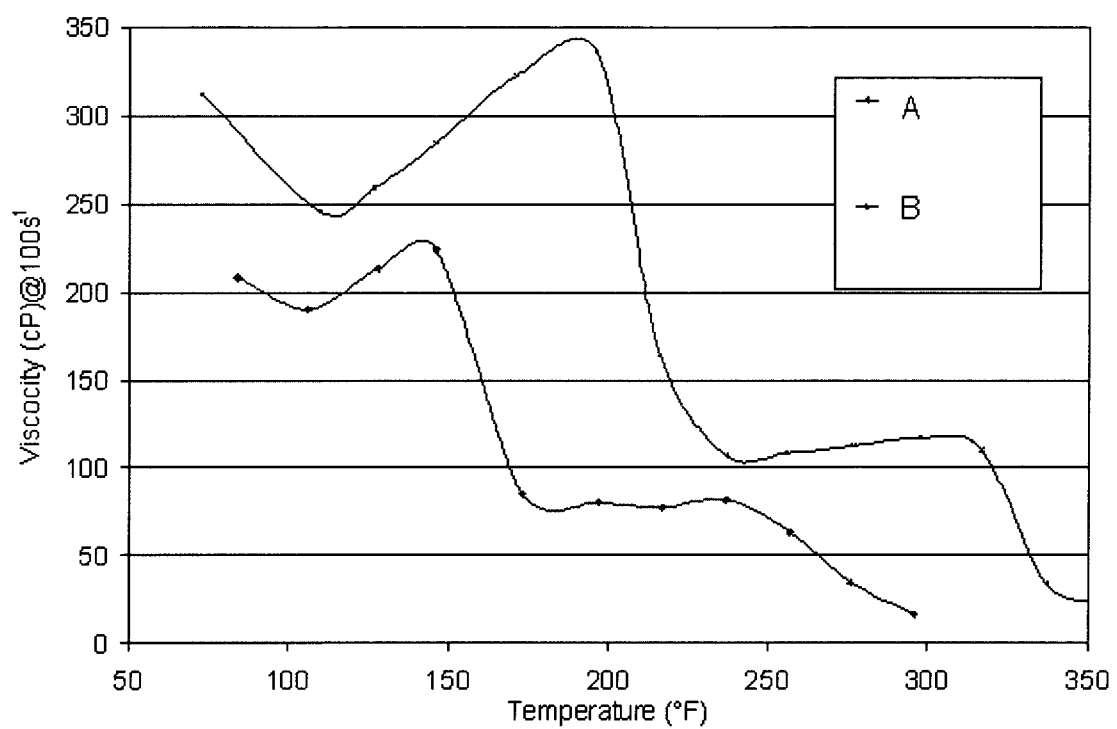


Figure 1

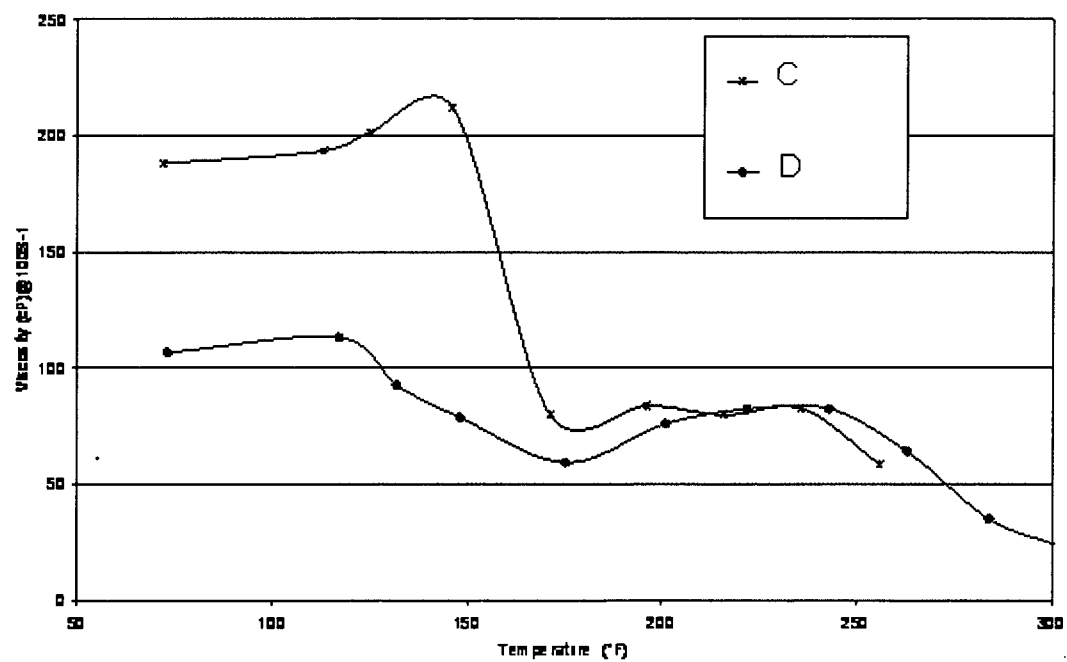


Figure 2

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2008/011090

A. CLASSIFICATION OF SUBJECT MATTER
INV. C09K8/40 C09K8/42

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 practical, 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	WO 2007/119211 A (SCHLUMBERGER CA LTD [CA]; SCHLUMBERGER SERVICES PETROL [FR]; SCHLUMBER) 25 October 2007 (2007-10-25) cited in the application paragraphs [0001], [0005], [0018], [0048], [0037]; figure 1; example 1	1-11
X	WO 2004/057155 A (SCHLUMBERGER CA LTD [CA]; SCHLUMBERGER SERVICES PETROL [FR]; SCHLUMBER) 8 July 2004 (2004-07-08) claims 1,5,7	1,2,5-7
X	US 2003/221832 A1 (REDDY B RAGHVA [US] ET AL REDDY B RAGHAVA [US] ET AL) 4 December 2003 (2003-12-04) paragraph [0017]; example 1	1,2,4,9, 12-18

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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Name and mailing address of the ISA/
European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

Authorized officer

Redecker, Michael

INTERNATIONAL SEARCH REPORT

Information on patent family members

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