PCT WORLD INTELLECTUAL PROPERT International Burea

INTERNATIONAL APPLICATION PUBLISHED UNDER T

WO 9607710A1

(51) International Patent Classification 6 : C09K 7/06 — A1

(11) International Publication Number: **WO 96/07710**

(43) International Publication Date: 14 March 1996 (14.03.96)

(21) International Application Number: PCT/GB95/02034

(22) International Filing Date: 30 August 1995 (30.08.95)

(30) Priority Data:
9417974.4 7 September 1994 (07.09.94) GB

(71) Applicant *(for all designated States except CA FR US)*: SOFITECH N.V. [BE/BE]; Rue de Stalle 140, B-1180 Brussels (BE).

(71) Applicant *(for FR only)*: COMPAGNIE DES SERVICES DOWELL SCHLUMBERGER S.A. [FR/FR]; 50, avenue Jean-Jaurès, F-92541 Montrouge (FR).

(71) Applicant *(for CA only)*: SCHLUMBERGER CANADA LIMITED [CA/CA]; 24th floor, Monenco Place, 801 6th Avenue S.W., Calgary, Alberta T2P 3W2 (CA).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: SMITH, Philip, Stephen [GB/CO]; Edificio Alpino, Calle 85, 10-41 Santafe de Bogota (CO). HIBBERT, Julie, Ann [GB/AE]; Dr. A. P. Hibbert, Adma Opco, W3, P.O. Box 303, Abu Dhabi (AE).

(74) Agent: HOOPER, John, Peter, Lindesay; Schlumberger Cambridge Research Limited, High Cross, Madingley Road, Cambridge CB3 0EL (GB).

(81) Designated States: AM, AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TT, UA, UG, US, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG), ARIPO patent (KE, MW, SD, SZ, UG).

Published
With international search report.
Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(54) Title: STABILISING EMULSIONS

(57) Abstract

Drilling muds are employed when drilling an oil well, primarily to carry rock cuttings up to the surface and out of the wellbore. Both water-based and oil-based muds are used, but the latter possess many operational advantages. However, conventional oil-based muds do suffer from a number of undesirable characteristics - the oil may be retained on the drill cuttings, and the presence of large amounts of the essential emulsifiers and other oil wetting agents can alter the wettability of oil-holding reservoir formations through which the borehole passes, thereby reducing their permeability to oil, and so making it more difficult to extract the oil therefrom. The present invention seeks to provide an alternative way of preparing water-in-oil emulsions so that in such emulsions high water levels and high stability can still be achieved but with the use of minimal levels of surfactant. More specifically, the invention suggests that the stability of water-in-oil emulsions may be significantly enhanced by using as a stabilising agent a particular type of silane - thus, first there is formed a water-in-oil emulsion with a fine dispersed aqueous phase in the continuous oil phase, and then there is added to this a silane having bonds which hydrolyse and condense to form a cross-linked polymer at the water-oil interface.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	**GB**	United Kingdom	**MR**	Mauritania
AU	Australia	**GE**	Georgia	**MW**	Malawi
BB	Barbados	**GN**	Guinea	**NE**	Niger
BE	Belgium	**GR**	Greece	**NL**	Netherlands
BF	Burkina Faso	**HU**	Hungary	**NO**	Norway
BG	Bulgaria	**IE**	Ireland	**NZ**	New Zealand
BJ	Benin	**IT**	Italy	**PL**	Poland
BR	Brazil	**JP**	Japan	**PT**	Portugal
BY	Belarus	**KE**	Kenya	**RO**	Romania
CA	Canada	**KG**	Kyrgystan	**RU**	Russian Federation
CF	Central African Republic	**KP**	Democratic People's Republic of Korea	**SD**	Sudan
CG	Congo			**SE**	Sweden
CH	Switzerland	**KR**	Republic of Korea	**SI**	Slovenia
CI	Côte d'Ivoire	**KZ**	Kazakhstan	**SK**	Slovakia
CM	Cameroon	**LI**	Liechtenstein	**SN**	Senegal
CN	China	**LK**	Sri Lanka	**TD**	Chad
CS	Czechoslovakia	**LU**	Luxembourg	**TG**	Togo
CZ	Czech Republic	**LV**	Latvia	**TJ**	Tajikistan
DE	Germany	**MC**	Monaco	**TT**	Trinidad and Tobago
DK	Denmark	**MD**	Republic of Moldova	**UA**	Ukraine
ES	Spain	**MG**	Madagascar	**US**	United States of America
FI	Finland	**ML**	Mali	**UZ**	Uzbekistan
FR	France	**MN**	Mongolia	**VN**	Viet Nam
GA	Gabon				

STABILISING EMULSIONS

The present invention relates to stabilising emulsions, and concerns in particular a method for stabilising water-in-oil emulsions suitable for use in oil-based drilling muds.

When drilling a well, specifically an oil well, a drilling mud is employed primarily to carry rock cuttings up to the surface and out of the wellbore. Other functions of the mud are to cool and lubricate the drill bit, to protect against blowouts by counteracting downhole formation pressure, to maintain a stable borehole, and to prevent loss of fluids to the formations being drilled. Both water-based and oil-based muds are used as drilling muds. Water-based muds (WBMs) are generally cheaper than oil-based muds (OBMs), but the latter possess many operational advantages, particularly for the drilling of high angle, long reach and high pressure/high temperature wells. However, conventional oil-based muds do suffer from a number of undesirable characteristics. For example. the oil may be retained on the drill cuttings, which has unfortunate environmental implications. In addition, the presence of emulsifiers and other oil wetting agents, which are essential components of conventional OBMs (these are usually emulsions of water in oil, and the emulsifiers and wetting agents keep the emulsions stable and useful), can alter the wettability of oil-holding reservoir formations through which the borehole passes, thereby reducing their permeability to oil, and so making it more difficult to extract the oil therefrom.

Emulsifiers and oil wetting agents are added to conventional OBMs to emulsify the water phase in the oil phase, and to ensure that all of the solids in the mud are wetted by the oil. Surfactants, solids at the interface, or polymers can be used to stabilise such emulsions, and high levels of water can be stabilised in such muds, whilst maintaining all the other properties required of an oil-based mud, provided that sufficient surfactant is present. Now, the amount of oil in the mud

and the oil wetting characteristics of the mud are important parameters affecting the concentration of oil retained on drilling cuttings, and unfortunately the high levels of surfactant often required result in undesirably strong oil wetting characteristics. The present invention seeks to provide an alternative way of preparing water-in-oil emulsions so that in such emulsions high water levels and high stability can still be achieved but with the use of minimal levels of surfactant. More specifically, the invention suggests that the stability of water-in-oil emulsions may be significantly enhanced by using as a stabilising agent a particular type of silane - thus, first there is formed a water-in-oil emulsion with a fine dispersed aqueous phase in the continuous oil phase, and then there is added to this a silane having bonds which hydrolyse and condense to form a cross-linked polymer at the water-oil interface.

Thus, according to the present invention there is provided a method for enhancing the stability of a water-in-oil emulsion, in which method there is added to the emulsion a silane having bonds which are capable of hydrolysing and condensing whereby a cross-linked silicone is formed at the interface between the oil and the water, thereby encapsulating the water droplets and so stabilising the emulsion.

In a second aspect, the invention provides a method for forming a stable water-in-oil emulsion, in which method:

a) first there is formed a fine dispersed aqueous phase within a continuous oil phase, this being the desired water-in-oil emulsion; and then

b) there is added to the emulsion a silane having bonds which are capable of hydrolysing and condensing whereby a cross-linked silicone is formed at the interface between the oil and the water, thereby encapsulating the water droplets and so stabilising the emulsion.

The water-in-oil emulsion can be prepared in any convenient way suitable

for making a fine dispersion of an aqueous phase in a continuous oil phase, but preferably it is prepared by strong physical agitation of the aqueous and oil components in the presence of a suitable water-in-oil emulsifier.

Suitable emulsifiers include fatty acid soaps such as calcium dioleate, fatty amides such as the reaction products of oleic acid and diethylamine thiamine, a variety of polymeric emulsifiers containing alcohol or carboxylic acid groups or organophilic clays, and certain organic-silicone-based polymers. Such polymers can be the cross-linked organosilicone polymers disclosed in EP 0,298,402, but the preferred emulsifiers are silicone copolymers having a silicone backbone with pendant hydrophobic alkyl chains and pendant ethylene oxide/propylene oxide chains, as typified by that material known as TEGOPREN 7006 supplied by Th. Goldschmidt. This is believed to be an alkyl - and polyether-modified siloxane.

Naturally, the emulsifiers should be present at low concentrations; 0.5-50g/l of emulsion seems acceptable.

Suitable silanes for use in the method of the present invention are those of the General Formula:

$$R_{4-n} - Si - X_n \qquad (I)$$

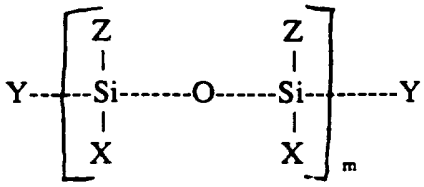
(wherein R represents a straight- or branched-chain alkyl group containing from 1 to 18 carbon atoms, or an aryl group,

X represents a R'O-, R'COO-, R'NH-, R'_2N-, R'=NO- or HO- group, or a halogen atom, and

R' represents a straight- or branched-chain alkyl group containing from 1 to 8 carbon atoms, or an aryl group), and

n is 1-3);

or of the General Formula:



(II)

(wherein Y and Z represent R, R' or X, as just defined, and
m is 0-100).

A particularly preferred silane is methyl-trimethoxy-silane (a compound of General Formula I wherein R is the methyl group, n is 3, and each X is a methoxy group).

These silanes may be used at any convenient concentration; one in the range from 0.5 to 20g/l of emulsion seems most suitable.

The silane employed is one that hydrolyses and condenses in use. If required, a suitable catalyst - for example, an alkali such as sodium hydroxide - may be present in the aqueous phase during the addition of the silane, or alternatively an appropriate catalyst - such as an organometallic catalyst, or a metal, or metal halide, such as tin, or zinc chloride - may be present in the oil phase.

The method of the present invention is particularly suitable for stabilising emulsions which have a high water content - for example, those with an oil/water creation of up to 40/60.

By means of the methods of the present invention water droplets may be encapsulated by the cross-linked silicone, thereby isolating the water from the oil and so reducing the tendency for droplet coalescence which can lead to emulsion instability.s

Although discussed here in relation to the drilling of oil well boreholes, the methods of the present invention are suitable for enhancing the stability of any water-in-oil emulsion, and other examples of these are those for use in cosmetics,

in paints or in the oil-refining industry. However, the methods are particularly suitable for use in the preparation of oil-based drilling muds - OBMs - which show non-oil-wetting characteristics and acceptable rheological properties.

The present invention is further illustrated by reference to the following Example, which describes the preparation of a stabilised emulsion having an oil/brine ratio of 50:50.

Example

1 g of TEGOPREN 7006 (supplied by Th. Goldschmidt) was dissolved in 175 ml kerosene (BP 83 HF, from BP Chemicals), with minimal mixing. 175 ml of calcium chloride brine was then emulsified into the kerosene using either a Hamilton Beach mixer or a Ystral high shear blender, and the resultant emulsion allowed to cool to room temperature.

After cooling, 3 g of methyl-trimethoxy-silane was added in a short but vigorous mixing procedure, and the resultant emulsion was left for approximately 30 mins to allow cross-linking to take place.

The final emulsion this formed was stable, and suitable for use as a drilling fluid.

CLAIMS:

1. A method for enhancing the stability of a water-in-oil emulsion, in which method there is added to the emulsion a silane having bonds which are capable of hydrolysing and condensing whereby a cross-linked silicone is formed at the interface between the oil and the water, thereby encapsulating the water droplets and so stabilising the emulsion.

2. A method for forming a stable water-in-oil emulsion, in which method:

a) first there is formed a fine dispersed aqueous phase within a continuous oil phase, this being the desired water-in-oil emulsion; and then

b) there is added to the emulsion a silane having bonds which are capable of hydrolysing and condensing whereby a cross-linked silicone is formed at the interface between the oil and the water, thereby encapsulating the water droplets and so stabilising the emulsion.

3. A method as claimed in either of the preceding Claims, in which the water-in-oil emulsion is prepared by strong physical agitation of the aqueous and oil components in the presence of a suitable water-in-oil emulsifier.

4. A method as claimed in Claim 3, in which the emulsifier is a silicone copolymer having a silicone backbone with pendant hydrophobic alkyl chains and pendant ethylene oxide/propylene oxide chains.

5. A method as claimed in either of Claims 3 and 4, in which the emulsifier is present at a concentration of from 0.5 to 50g/l of emulsion.

6. A method as claimed in any of the preceding Claims, in which the silane is of the General Formula:

$$R_{4-n} - Si - X_n \qquad (I)$$

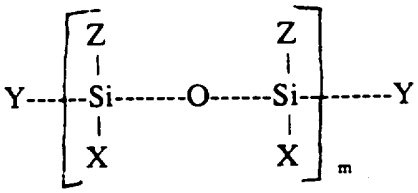
(wherein R represents a straight- or branched-chain alkyl group containing from 1 to 18 carbon atoms, or an aryl group,

X represents a R'O-, R'COO-, R'NH-, R'_2N-, R'=NO- or HO- group, or a halogen atom, and

R' represents a straight- or branched-chain alkyl group containing from 1 to 8 carbon atoms, or an aryl group), and

n is 1-3);

or of the General Formula:



(II)

(wherein Y and Z represent R, R' or X, as just defined, and

m is 0-100).

7. A method as claimed in Claim 6, in which the silane is methyl-trimethoxy-silane.

8. A method as claimed in any of the preceding Claims, in which the silane is used at a concentration of from 0.5 to 20g/l of emulsion.

9. A method of stability enhancement or water-in-oil emulsion formation as claimed in any of the preceding Claims and substantially as described hereinbefore.

INTERNATIONAL SEARCH REPORT

Interna al Application No
PCT/GB 95/02034

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C09K7/06

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 6 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)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP,A,0 059 037 (DOW CORNING CORPORATION) 1 September 1982 see page 3, line 19 - page 4, line 21 see page 6, line 18 - line 22 see page 12, line 9 - page 13, line 17 see page 18, line 6 - page 19, line 25 ---	1-4,6,9
Y	EP,A,0 298 402 (DOW CORNING) 11 January 1989 cited in the application see page 2, line 19 - line 25 see page 3, line 1 - page 5, line 2 ---	1-4,6,9
Y	GB,A,2 113 236 (DOW CORNING) 3 August 1983 see page 1, line 38 - page 2, line 56	1-4,6,9
A	see page 3, line 36 - page 4, line 42 ---	7
	-/--	

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

[X] 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 doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" 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

"T" 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

"X" 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

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

1

Date of the actual completion of the international search
19 December 1995

Date of mailing of the international search report
29. 12. 95

Name and mailing address of the ISA
European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax (+31-70) 340-3016

Authorized officer
Boulon, A

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Internal Application No
PCT/GB 95/02034

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	DATABASE WPI Derwent Publications Ltd., London, GB; AN 94-008112 & CA,A,2 093 505 (DOW CORNING CORP) see abstract ---	1-4,6,9
A	DATABASE WPI Derwent Publications Ltd., London, GB; AN 88-188763[27] & SU,A,1 357 421 (KIEV POLY) , 7 February 1987 see abstract ---	1-9
A	DATABASE WPI Derwent Publications Ltd., London, GB; AN 82-74050E[35] & SU,A,876 697 (SIBE PETRO IND RES) see abstract -----	1-9

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

Internal Application No
PCT/GB 95/02034

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
EP-A-59037	01-09-82	US-A-	4381241	26-04-83
		AU-B-	8080582	14-09-82
		CA-A-	1177634	13-11-84
		WO-A-	8202898	02-09-82
EP-A-298402	11-01-89	US-A-	4853474	01-08-89
		DE-A-	3874825	29-10-92
		JP-A-	1030633	01-02-89
GB-A-2113236	03-08-83	US-A-	4421656	20-12-83
		CA-A-	1188955	18-06-85
		DE-A-	3237630	07-07-83