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(21) International Application Number: PCT/EP99/01302 (22) International Filing Date: 25 February 1999 (25.02.99) (30) Priority Data: 98 02586 4 March 1998 (04.03.98) FR (71) Applicant (for all designated States except CA FR US): SOF-ITECH N.V. [BE/BE]; Rue de Stalle 142, B-1180 Brussels (BE). (71) Applicant (for CA only): SCHLUMBERGER CANADA LIMITED [CA/CA]; 24th floor, Monenco Place, 801 6th Avenue, S.W., Calgary, Alberta T2P 3W2 (CA). (71) Applicant (for FR only): COMPAGNIE DES SERVICES DOWELL SCHLUMBERGER [FR/FR]; 50, avenue Jean-Jaurès, F-92541 Montrouge (FR). (71) Applicant (for all designated States except US): NILSSON, Frederik [SE/FR]; 18, rue Tiphaine, F-75015 Paris (FR). (72) Inventors; and (75) Inventors/Applicants (for US only): BARLET-GOUEDARD, Véronique [FR/FR]; Résidence La Baleine, 2, impasse du Cachalot, F-92290 Châtenay Malabry (FR). BRAND,		Fabien [FR/GB]; Schlumberger Evaluation & Production Services (UK) Limited, Fluids Chemistry St. Austell, Par Moor Road-Par, Cornwall PL24 2SQ (GB). MAROY, Pierre [FR/FR]; 2, allée Charles Nicolle, F-78530 Buc (FR). (74) Agent: MENES, Catherine; Etudes et Productions Schlumberger, Division Dowell, 26, rue de la Cavée, Boîte postale 202, F-92142 Clamart Cedex (FR). (81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: RETARDING SYSTEMS AND APPLICATION TO OIL WELL CEMENTING		
(57) Abstract The present invention relates to systems for retarding setting in an oilfield well cement slurry constituted by a solution of a phosphonate selected from methylene phosphonic acid derivatives and a phosphate, in particular selected from the following salts or the corresponding acids: mono-phosphates (ortho-phosphates PO_4^{2-}, meta-phosphates PO_3^-), acyclic poly-phosphates (pyrophosphates $\text{P}_2\text{O}_7^{4-}$, tripolyphosphates $\text{P}_3\text{O}_{10}^{5-}$) or cyclic poly-phosphates. The system preferably may also comprise a retarder booster and is more particularly applicable to cementing at low or medium temperatures.		

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RETARDING SYSTEMS AND APPLICATION TO OIL WELL CEMENTING

The present invention relates to drilling techniques for oil, gas, water, geothermal or analogous wells. More precisely, the invention relates to an additive, and to compositions including the additive, for cement slurries, more particularly for cementing a casing in an oil well or the like.

- 5 After drilling an oil well or the like, a casing or a coiled tubing is lowered into the well and cemented over all or a portion of its length. Cementing can in particular prevent fluids being exchanged between the different formation layers through which the well passes, it can prevent gas from rising via the annular space surrounding the casing, or it can limit the ingress of water into the production well. Of course, it also has the principal aim of consolidating the well and protecting the casing.
- 10 While a cement slurry is being prepared, then injected into the well, and finally positioned in the zone to be cemented, it must have relatively low viscosity and practically constant rheological properties. In contrast, once it is in position, an ideal cement would rapidly develop high compressive strength so as to enable other work in the well under construction to be resumed, in particular to enable drilling to be continued.
- 15 In practice, practically all cementing slurries are formulated with an additive which retards setting of the cement, normally known as a retarder. The most widely used retarders are lignosulphates, hydroxycarboxylic acids such as citric acid, glucoheptonic acid or gluconic acid, saccharides or polysaccharides such as carboxymethylhydroxyethyl cellulose, and organophosphates.
- In practice, selecting a retarder depends on the temperature at the well bottom, the cement slurry
20 circulation temperature, and the presence or absence of other additives with which the retarders may be incompatible. The majority of known retarders are effective only in a relatively narrow temperature range, a fact which is more critical as the temperatures to which the cement slurries are subjected are not always precisely known. A further difficulty is high sensitivity to variations in concentrations of retarder or of other additives, and occasionally also to the cements used.
- 25 Under such conditions, formulating a cement slurry which is suitable for every eventuality remains a particularly difficult art, all the more so since oil well cements are, by their very definition, used on sites which are usually far from the facilities of an industrial laboratory and which generally do not have access to the complete range of available additives.

- 30 The present invention aims to provide a novel retarding system which is suitable for low/medium temperature applications, namely typically 70°C to 140°C, and which is compatible with additives which are currently used for oilfield cements such as latexes, chemically cross-linked polyvinyl alcohol type fluid loss control agents (in particular those described in United States patent US-A-5 594 050) and

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for which the effect on a cement slurry is readily predictable, and in particular which has low sensitivity to variations in cement quality.

This aim is satisfied in the present invention by a system constituted by a solution of a phosphonate selected from derivatives of methylene phosphonic acid, and a phosphate.

- 5 The phosphates may be mono-phosphates (ortho-phosphates PO_4^- , meta-phosphates PO_3^-) or acyclic poly-phosphates (pyrophosphates $\text{P}_2\text{O}_7^{4-}$, tripolyphosphates $\text{P}_3\text{O}_{10}^{5-}$), or cyclic poly-phosphates. Salts can also be used, for example, preferably sodium or potassium salts, or the acids (if they exist) of the following compounds: orthophosphoric acid H_3PO_4 , sodium dihydrogen phosphate NaH_2PO_4 , sodium monohydrogen phosphate Na_2HPO_4 , trisodium phosphate Na_3PO_4 , pyrophosphoric acid $\text{H}_4\text{P}_2\text{O}_7$, sodium tripolyphosphate $\text{Na}_5\text{P}_3\text{O}_{10}$, and sodium cyclotrimetaphosphate $\text{Na}_3\text{P}_3\text{O}_9$.

The preferred retarding system of the invention is obtained with a calcium and sodium salt of ethylenediamine-N,N,N',N'-tetrakis(methylene) phosphonic acid or the pentasodium salt of ethylenediamine tetra(methylenephosphonic) acid, associated with an orthophosphate.

- 15 The phosphonate to phosphate weight ratio is preferably in the range 2 to 4, more preferably in the range 3 to 3.5.

- The retarding system of the invention is suitable for applications between 50°C and about 140°C. In a variation of the invention, the retarding system also comprises a retarder booster which can extend the range of application of the retarder of the invention to medium temperatures. For reasons of increased compatibility with other additives, and in particular fluid loss control additives, it is preferable to use as
20 a retarder booster a mixture of lignosulphates and hydroxycarboxylic acids (such as gluconates), but other conventional hydroxycarboxylic acid-based retarder boosters or lignosulphates can also be used. It should be noted that these retarder boosters are themselves retarders but of quite low efficiency and thus are usually used in combination with other retarders. In this optimised variation of the invention, the retarding system is constituted by 40% to 45% of orthophosphoric acid, 10% to 15% of the calcium and
25 sodium salt of ethylenediamine-N,N,N',N'-tetrakis(methylene)phosphonic acid and 40% to 50% of retarder booster, the percentages being by weight.

The retarding system of the invention can also contain a biopolymer which can improve the rheology of the cement slurry by minimising settling problems for systems with a high concentration of the retarding system.

- 30 In contrast to the numerous conventional retarders, the retarding system of the invention is advantageously compatible with different types of fluid loss control agents or gas migration agents, in particular with latexes, and can be used in slurries in which seawater is used as the mixing water.

The following examples illustrate the invention without limiting its scope.

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Except where otherwise indicated, the tests were carried out using a system comprising a calcium/sodium salt of ethylenediamine tetramethylene phosphonic acid comprising (2.5 calcium per 3 sodium per mole) which is commercially available from MONSANTO under the trade name DEQUEST 2047 (the "phosphonate") and an orthophosphoric acid from PROLABO (the phosphate or H_3PO_4) with a purity of 99.999%, in 85% solution in water. The cement used was a class G oilfield cement (Dickerhoff North G).

Example 1

60 ml of a cement slurry was prepared with a density of 1.893 g/cm^3 , and with a water/cement volume ratio of 0.44. The phosphonate and phosphate were added to the mixing water before the cement. After stirring for 35 seconds at 4000 revolutions per minute, 3.5 g of slurry was weighed out and introduced into a calorimeter at 85°C . The time between introduction into the calorimeter and the maximum hydration peak was measured as a function of the percentage (calculated from the weight of cement) of phosphonate and orthophosphoric acid and is shown in Table 1.

Table I N°	% phosphonate	% H_3PO_4	Time
1	0	0	3:20
2	0.05	0	5:00
3	0.075	0	3:45
4	0.05	0.1	11:00
5	0.05	0.15	4:10
6	0.05	0.05	5:20
7	0	0.15	3:45
8	0	1.2	1:15

While the calorimetric tests only indirectly reflect cement setting, it can be seen that in the absence of phosphonate, the orthophosphate acts as an accelerator or a very slight retarder depending on the concentration and temperature.

The phosphonate alone acts as a retarder up to a certain threshold but there is clearly a synergistic effect when the phosphonate is used in combination with the orthophosphate. This table also shows the need for optimisation of the phosphonate/phosphate ratio.

Example 2

The same protocol was used, this time using mixtures of phosphonate and pyrophosphoric acid for setting at 85°C.

Table II				
N°	% phosphonate	% H ₄ P ₂ O ₇	Time (hh:min)	Intensity (mW)
9	0	0	3:30	175
10	0.1	0	11:40	105
11	0.1	0.0004	16:00	80
12	0.1	0.0006	11:30	90
13	0.1	0.0012	13:10	85

In similar fashion to orthophosphoric acid, Table II above shows that there is a critical ratio at which a synergistic effect exists between the retarding effect of the phosphonate and the retarding effect of the phosphate.

Example 3

The tests were repeated at 111°C (231°F) and by adding 35% (by weight of cement) of silica flour as is usual from such temperatures to prevent retrogression of the compressive strength and an increase in the permeability of the set cement. The water to cement ratio was kept at 0.44, the slurry density was 1.797 g/cm³. The same protocol as that described above was used except that the silica flour was mixed with water for 15 seconds before cement addition was commenced.

In Table III below, a * after the time indicates the presence of two hydration peaks, the maximum peak reported here corresponding to the second hydration peak. A stark reduction in peak intensity (of the order of 50% or more) could be associated with setting spread over a long period, which is not desirable for a good retarding system.

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Table III Test	% phosphonate	% H ₃ PO ₄	Time (hh:min)	Intensity (mW)
14	0	0	2:05	125
15	0.05	0	3:20	105
16	0.075	0	4:10	100
17	0.2	0	6:40*	70
18	0.4	0	10:00	2
19	0	0.1	2:30*	105
20	0	1.2	1:10*	95
21	0.05	0.05	2:30*	110
22	0.05	0.15	2:30*	90
23	0.05	1.2	1:25*	100
24	0.2	0.008	5:30*	90

It can be seen that the orthophosphate retained a very strong accelerating effect, even at relatively low concentrations. As the phosphonate concentration increased, the intensity of the principal hydration peak strongly diminished until it practically disappeared, i.e., the cement no longer set but behaved as a gel.

These calorimeter cell tests have thus shown that a synergistic effect exists for the retarding effect when the phosphonate/phosphate ratio equals a certain value. They also show that there is a critical threshold for the concentration of phosphonate in the cement slurry, above which threshold cement setting is affected.

Example 4

Following the calorimetric tests, the authors of the present invention sought to optimise a three-component retarding system: a phosphonate (the calcium/sodium salt of ethylenediamine tetramethylene phosphonic acid used in the preceding examples), orthophosphoric acid and a retarder booster comprising 11.5% (by weight) of sodium gluconate, 76% of modified sodium lignosulphonate and 6.5% of tartaric acid.

These tests were carried out in 3 temperature ranges: between 68°C and 91°C (low temperature range); between 91°C and 113°C (medium temperature range) and between 113°C and 138°C (high temperature range).

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It should be noted that these temperatures correspond to temperatures at a well bottom of a slurry pumped from the surface. It should also be noted that this temperature is normally lower than the temperature at which cement setting occurs such that in practice, the compressive strengths of the set cement in the well are higher than the values measured during these tests. These temperature ranges are encountered in low or medium temperature wells.

The experimental data are shown in Tables IV, V and VI below in which the concentration of retarder (active matter) is given with respect to the weight of cement. The proportions by weight of orthophosphoric acid and phosphonate were varied between 10% and 62% and 1% and 31% respectively (the percentage by weight of retarder booster, being the complement to 100% not being shown in these tables). For all of the test slurries, the quantity of water was adjusted to obtain a fixed density of 1.89 g/cm³.

For the low temperature tests, 0.03% (with respect to the weight of cement) of a biopolymer and 0.1 gallons per sack of cement of a normal dispersing agent, in this case an aqueous solution of polynaphthalene sulphonate (PNS), were added, (i.e., 0.1 US gallons (3.78 litres) per 42 kilogram sack, 0.1 gps = 9 cm³/kg of cement).

The medium and high temperature tests were carried out without adding polynaphthalene sulphonate but with 0.065% of biopolymer (such as "BIOZAN" produced by the Kelco Oilfield Group), acting as an anti-settling agent. Further, compositions comprising 35% (with respect to the weight of cement) of silica flour were used for these tests.

The slurries were prepared and the measurements carried out using protocols recommended by the API (American Petroleum Institute), using the following order for adding the additives: preparing the mixing water by successive addition of phosphonate, orthophosphoric acid, if necessary an antifoam agent and the dispersing agent, then adding a premixed dry solid material mixture (cement, biopolymer and silica flour).

The thickening time corresponded to the production of a consistency of 100 BC, measured in standardised BC units. The transition time corresponded to passing from a consistency of 30 BC to a consistency of 100 BC.

The time required to attain a compressive strength of 50 psi (pounds force per square inch) (i.e., 345 kPascals) and 500 psi (3450 kPascals) was also measured for each slurry. Further, the compressive strength after 24 hours was measured (1 psi = 6.894 kPascals). A value of the order of 2000 psi (13.8 Mpascals) after 24 hours is generally judged to be satisfactory for the envisaged applications.

A further series of measurements was made on the slurry rheology, at the mixing temperature and at the circulation temperature T in the well for temperatures below 85°C or at 85°C for higher temperatures. The data measured in this instance were the plastic viscosity (in milliPascals second or centiPoises) and

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the yield point (expressed, as is customary in this art, in $\text{lbf}/100\text{ft}^2 = 0.4787$ Pascals). Compositions with low viscosity and low yield point are desirable.

Measurements were also carried out on the gel strength developed when the composition was left to rest for 10 minutes (in $\text{lbf}/100\text{ft}^2$). These measurements were carried out at the temperature of slurry circulation at the well bottom. Because the formulations in Tables VI and VII contained no dispersing agent, the relatively high gel values obtained after 10 minutes of rest are not significant. Further, the gel was easily broken up as shown by the results after one minute's stirring at 3 revolutions per minute (gel + 1 minute).

Finally, the last column shows the volume of free water (indicating settling in certain phases of the slurry) formed for 250 ml of slurry (values approaching zero were desirable).

These tests enabled a preferred ternary retarding system to be selected which comprised between 39% and 45% of orthophosphoric acid, 10% to 15% of phosphonate and 40% to 51% of retarder booster (modified sodium lignosulphonate/sodium gluconate). With this optimum composition, the retarding effect on cement setting was good, with a relatively monotonic response depending on the concentration of the retarder added, and relatively low sensitivity to temperature variations; low sensitivity to shear (characterized by a short time between the time to obtain 100 BC and that to obtain 50 psi) and rapid development of compressive strength (rapid passage from 50 to 500 psi) and good compressive strength after 24 hours.

For the medium temperature range, an optimum was discerned for compositions comprising 40.5% of orthophosphoric acid, 12.25% of phosphonate and 47.25% of retarder booster.

For improved slurry stability, in particular at the highest temperatures, the preferred retarding system of the invention also contains at least 2%, preferably 3% (with respect to the weight of dry retarder) of biopolymers.

The retarder was prepared in the form of an aqueous solution, preferably relatively concentrated, a concentration by weight in the range 15% to 25% being a good compromise to obtain both a relatively low retarder viscosity (in particular to facilitate on-site mixing) and the possibility of using only relatively low concentrations. In the following, the concentration of retarder in the aqueous solution was fixed at 16.9%, corresponding to a density of 1.07 g/ml.

30 Example 5

Table VII below shows the performance of the retarder selected following the experiments described in Example 4, namely a solution containing 16.9% of a mixture constituted by 40.5% of orthophosphoric acid, 12.25% of phosphonate and 47.25% (percentage by weight) of a retarder booster based on sodium

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gluconate and modified sodium lignosulphonate and adding 3% of biopolymers (with respect to the weight of retarder active matter).

For these tests, an antifoam agent was systematically used and, for low temperatures, a polynaphthalene sulphonate type dispersing agent. For tests carried out at over 100°C, the slurries were formulated with

5 35% of silica (percentage per weight of cement BWOC).

Table VII									
Temperature T (° C)	68.3	76.7	85	90.6	101.7	110	115.6	126.7	137.8
Density (g/cm ³)	1.893	1.893	1.893	1.893	1.893	1.893	1.893	1.893	1.893
Retarder (cm ³ /kg)	9.9	10.8	22.5	40.5	68.7	81.4	87.3	119.7	137.7
Dispersing agent (cm ³ /kg)	5.85	4.5	5.4	3.6	-	-	-	-	-
Antifoam agent (cm ³ /kg)	2.7	2.7	2.7	2.7	2.7	2.7	2.7	2.7	2.7
silica (% BWOC)	-	-	-	-	35	35	35	35	35
Rheology at 20 °C Viscosity (mPa.s)	24	26	28	34	63	77	87	109	116
Ty (lbf/100ft ²)	0.5	1.8	2.5	1.6	8.3	10	11	16	26
Rheology at T Viscosity (mPa.s)	14	14	16	35	36	40	45	62	59
Ty (lbf/100ft ²)	3.6	9.5	5.9	3.7	5.9	4.5	7.3	11	10
gel After 10 min.	25	29	45	20	10	8	12	13	10
+ 1 min at 3 rpm	7	10	5	4	5.5	3	6	5.5	4
Free water (ml)	0.7	2	0.1	0	0.2	0.05	0.05	0.05	0.05
Time to 100 BC (hrs:min)	6:09	3:53	5:29	5:47	6:05	5:00	5:17	7:41	8:43
Transition 30 → 100 BC (min)	25	17	14	35	29	5	5	5	5
50 psi (hrs:min)	11:18	9:19	8:41	7:55	8:37	7:36	7:25	12:11	14:13
500 psi (hrs:min)	12:53	10:22	10:02	9:16	9:52	9:01	8:59	14:47	16:46
CS 24hrs (psi)	2350	2587	2783	3287	2334	1948	1999	1369	1665

It can be seen that the performance obtained was highly satisfactory over the entire range of test temperatures. In particular, a very short transition time was noted between a consistency of 30 BC and 100 BC with a time period between the time to obtain 50 psi and 500 psi generally of the order of 60-90 minutes.

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Example 6

On site, it is very difficult to adhere precisely to the prescribed additive concentrations. The usual retarders are sometimes extremely sensitive to small differences in concentration as is shown in Table VIII below, where a variation in retarder concentration of the order of only 0.2 litres per sack of cement can cause a variation in the thickening time (arbitrarily defined as the time to obtain a consistency of 100 BC) of more than 4 hours, or even more than 16 hours with certain retarders.

Further, certain conventional retarders are highly sensitive to temperature variations. As the tests carried out with a 38% refined lignosulphonate solution show, a temperature difference of the order of 10°C can cause a variation in thickening time by a factor of 2.

By comparison, the retarder of the invention has a lower sensitivity to variations in concentrations and temperatures.

Table VIII T (°C)	Retarder	Concentration (cm ³ /kg)	Time to 100 BC (hrs:min)
85	50% solution of partially modified calcium and sodium lignosulphonate	3.5 7	4 :10 22:46
85	38% refined lignosulphonate solution	3.5 7	2:26 8:23
96.1	38% refined lignosulphonate solution	7.7	3:34
96.1	18% calcium glucoheptonate solution	2.8 6.3	4:00 >10:00
85	Retarder of invention	10.6 14.1	4:20 6:00
96.1	Retarder of invention	40.8 44.3	3:30 6:00
101.5	Retarder of invention	50 53.5	3:30 6:00
107.2	Retarder of invention	58.4 61.9	4:30 6:00

Example 7

A further constraint is due to supplies from cement works and compositional variations which are encountered between cements from different sources.

Some conventional retarders are highly sensitive to these differences which is absolutely not the case with the retarding system of the invention, as shown in Table IX. For these tests, the temperature was

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fixed at 101.7°C, the slurry density at 1.89 g/cm³ and the concentration of retarder at 53.7 cm³ per kilo of cement. The slurries also contained 2.1 cm³ of antifoam agent per kilogram of cement and 35% (with respect to the weight of cement) of silica flour.

Table IX			
Cement type :	Dyckerhoff North	LoneStar	Saudi
Rheology at 20°C Viscosity (mPa.s)	75	71	76
Ty (lbf/100ft ²)	10	8.5	15
Rheology at 85°C Viscosity (mPa.s)	37	33	30
Ty (lbf/100ft ²)	6.2	6.5	8.5
gel After 10 min.	11.5	15	29
+ 1 min (at 3 rpm).	5.5	8	11
Free water (ml)	traces	traces	traces
Time to 100 BC (hrs:min)	6:05	6:20	5:14
Transition 30 → 100 BC (min)	29	8	33
50 psi (hrs:min)	8:37	8:41	6:59
500 psi (hrs:min)	9:52	9:59	9:52
C.S. 24hrs (psi)	2334	2080	2334

5 Example 8

This example ascertains the possibility of using a hydroxycarboxylic acid as a retarder. The preceding tests enabled the orthophosphoric acid: phosphonate: retarder booster ratio to be optimised at 60:18:22, the quantity of biopolymers remaining fixed at 3% of the quantity of dry matter in the retarder solution. Slurries were used with a density of 1.89 g/cm³, adding 2.1 cm³ of antifoam agent per kilogram of cement. For the low temperature test, a 40% polynaphthalene sulphonate solution was used as the dispersing agent.

Table X, in which the concentrations of retarder are concentrations by weight with respect to the weight of cement, shows that the hydroxycarboxylic acid is perfectly suitable as a retarder booster and sometimes even produced superior results, however gelling problems were encountered with certain fluid loss control agents.

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Table X		Temperature :	68.3°C	101.7°C	137.8°C
Retarder (%)			0.07	0.7	1
Dispersing agent (polynaphtalene sulphonate) (cm ³ /kg)			5.6	-	-
Silica flour (% BWOC)			-	35	35
Rheology at 20 °C	Viscosity(mPa.s)		22	62	70
	Ty (lbf/100ft ²)		1.6	9	12
Rheology at T °C	Viscosity (mPa.s)		14	34	31
	Ty (lbf/100ft ²)		6.1	10	14
gel	After 10 min.		15	20	18
	+ 1 min (at 3 rpm).		4	11	6
Free water	(ml)		2	0.6	0.35
Time to 100 BC (hrs:min)			5:38	6:01	5:23
Transition 30 → 100 BC (min)			17	30	9
50 psi (hrs:min)			10:28	8:48	8:56
500 psi (hrs:min)			11:45	10:02	10:37
C.S. 24hrs (psi)			2471	2472	3152

Example 9

5 This example ascertains that a mixture of a hydroxycarboxylic acid and a lignosulphonate can be used as a retarding agent. All of the tests were carried out at 137.8°C, with a slurry with a density of 1.89 g/cm³, adding 2.1 cm³ of antifoam agent per kilogram of cement and 35% of silica flour (BWOC). The performance obtained (Table XI) was again very satisfactory.

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Table XI	60/18/22	60/18/22	40.5/12.5/47.2	40.5/12.5/47.2
H ₃ PO ₄ /Phosphonate/retarder booster:				
Retarder (%)	1	2	0.7	1
Rheology at 20°C Viscosity(mPa.s)	83	123	72	84
Ty (lbf/100ft ²)	19	33	14	12
Rheology at 85°C Viscosity (mPa.s)	43	58	36	40
Ty (lbf/100ft ²)	19	25	12	13
gel After 10 min.	49	23	17	15
+ 1 min (at 3 rpm)	12	19	11	9
Free water (ml)	2.5	0	1.2	0.5
Time to 100 BC (hrs:min)	1:03	3:19	3:24	9:17
Transition 30 → 100 BC (min)	3	4	5	6
50 psi (hrs:min)	not	7:43	not measured	11:20
500 psi (hrs:min)	measured	8:55		13:20
C.S. 24hrs (psi)		4115		2972

Example 10

Since the optimised retarding system of Example 5 was particularly optimised for low temperatures, it was ascertained that it could also be used with a slurry containing plaster, more particularly used for deepwater drilling at very low temperature. The slurries, tested at 20°C, had a density of 1.89 g/cm³, contained 5.3 cm³ of antifoam agent per kilolgram of cement, 7 cm³ (per kilo of cement) of dispersing agent (polynaphthalene sulphonate in 40% solution) and 150% of plaster (with respect to the weight of cement).

Table XII			
Retarder concentration (cm ³ per kilo of cement) :	28.1	42.2	28.1
Rheology after mixing at 20°C Viscosity (mPa.s)	99	119	99
Yield point Ty (lbf/100ft ²)	6.0	11.0	6.0
Rheology after completion at 20 °C Viscosity (mPa.s)	113	134	149
Yield point Ty (lbf/100ft ²)	6.0	8.0	7.1
gel After 10 min.	13	19	16
+ 1 min (at 3 rpm)	9	10	9
Free water (ml)	0	0	0
Time to 100 BC (hrs:min)	2:05	4:30	2:18
Transition 30 → 100 BC (min))	30	56	15
Compressive strength (psi) After 5h	-	830	889
After 8h	-	735	-
After 2 days	-	1079	822
After 3 days	-	1517	983
After 7 days	-	1982	1783

The retarding system of the invention enabled a compressive strength of more than 500 psi to be obtained after only 5 hours, with a thickening time of 4:30 at 20°C and 2:18 at only 10°C. This shows good development of compressive strength.

5 Example 11

This retarding system was also tested at 20°C for systems based exclusively on plaster (Table XIII). The system density was 1.8 g/cm³, comprised 2.1 cm³ of antifoam agent per kilogram of plaster and 3.5 cm³ of retarder per kilo of plaster.

Table XIII	
Rheology after mixing at 20°C Viscosity (mPa.s)	84
Yield point Ty (lbf/100ft ²)	22
Rheology after completion at 20°C Viscosity (mPa.s)	61
Yield point Ty (lbf/100ft ²)	14
gel After 10 min.	14
+ 1 min (at 3 rpm).	8
Free water (ml)	0
Time to 100 BC (hrs:min)	3:40
Transition 30 → 100 BC (min))	5

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It can be seen that the retarding system of the invention is also capable of retarding a system based exclusively on plaster.

Example 12

- 5 The Dequest 2047 system was replaced by the pentasodium salt of ethylenediamine tetra(methylenephosphonic) acid, commercially available from Monsanto under the trade name Dequest 2046. The retarder was constituted by a 17.5% solution of a mixture of 38.8% of orthophosphate, 15.97% of phosphonate and 45.25% of retarder booster (percentages by weight) and 2.87% of biopolymers (with respect to the weight of retarder active matter). The slurry density was 1.893 g/cm³,
10 comprising 35% (by weight of cement) of silica flour and containing 3 cm³ of antifoam agent per kilogram of cement, the concentration of retarding agent being 68.4 cm³ per kilogram of cement. The measurements were carried out at 101.7°C.

- The performances indicated in Table XIV are remarkable; the very long thickening time should in particular be noted, but the transition time was only 36 minutes and the compressive strength developed
15 very rapidly. The absence of calcium thus appears to have a favorable effect.

Table XIV		
Rheology after mixing at 20°C	Viscosity (mPa.s)	89
	Yield pointTy (lbf/100ft ²)	9
Rheology at 85°C	Viscosity (mPa.s)	47
	Yield pointTy (lbf/100ft ²)	6
Gel	After 10 min / + 1 min at 3 rpm.	7 / 2.5
	Free water (ml)	0.05
	Time to 100 BC (hrs:min)	14:26
	Transition 30 → 100 BC (min))	36
	Time to 50 psi (hrs:min)	14:33
	Time to 500 psi (hrs :min)	15:54
	CS after 24 hours	21.07 MPa (3057 psi)

Example 13

- Based on example 12, the retarding system constituted by the pentasodium salt of ethylenediamine
20 N,N,N',N4 tetramethylene phosphonic acid (EDTMP) and phosphoric acid has been further studied.

-15-

Cement slurries have been prepared following the API procedure using a cement from Dyckerhoff (North, Black Label), a dispersing agent (0.03 gal/sk, 2.66 ml/kg of cement), an anti-foam agent (0.03 gal/sk, 2.66 ml/kg of cement), 35% of silica flour (BWOC) and the retarding system EDTMP acid/phosphoric acid (0.2gal/sk, 17,77 ml/kg of cement for the tests reported table XV and 0.4 gal/sk, 35,51ml/kg of cement for the tests reported table XVI below).

A water solution of pentasodium EDTMPS salt is used and has an active material content of 25 wt.%. The phosphoric acid is a 85% solution. The different ratios for EDTMP acid/phosphoric acid that have been tested are based on a 30 wt. % retarder concentration in water solution. The ratios have been calculated using the mathematical system below:

$$\left\{ \begin{array}{l} \frac{0.25x}{0.85y} = z \\ x + y = 30 \end{array} \right.$$

where x is the concentration of EDTMP acid in wt. %, y is the concentration of the phosphoric acid in wt. % and z the desired ratio EDTMP acid/phosphoric acid.

TABLE XV						
z	0.4	0.50	0.59	0.70	0.8	0.9
Mixing rheology						
Pv (mPa.s)	47	42	38	40	39	43
Ty lbf/100sqft	13	6	5	6	6	6
10"gel (lbf/100sqft)	10	5	5	6	6	6
API rheology @ 85°C						
PV(mPa.s)	32	37	32	28	41	39
Ty	18	26	37	32	23	25
10" gel	9	11	12	14	11	12
10'gel/1'stirring	18/13	12/9	14/13	12/7	10/7	11/8
API Free water (ml)	6.7	3.0	4.3	3.6	3.2	2.6
Thickening Time @85°C	1:56	8:52	8:44	11:33	15:38	>15.5 h
Time to 100 BC (hrs:min)	0:22	0:35	0:53	0:58	1:06	-
Transition 30→ 100 (hrs:min)						
Thickening Time @104.4°C						
Time to 100 BC (hrs:min)	1:00	1:37	2:30	3:40	3:54	5:51
Transition 30→ 100 (hrs:min)	0:15	0:16	0:23	0:25	0:30	0:45

TABLE XVI					
z	0.50	0.59	0.70	0.8	0.9
Mixing rheology					
Pv (mPa.s)	41	42	39	43	42
Ty lbf/100sqft	3	4	4	4	6
10"gel (lbf/100sqft)	4	4		5	6
API rheology @ 85°C					
PV(mPa.s)	23	27	27	24	26
Ty	13	18	19	19	19
10" gel	7	8	8	10	10
10'gel/1'stirring	13/9	15/13	16/11	10/8	12/10
API Free water (ml)	18	8	7.5	5.3	6
Thickening Time @104.4°C					
Time to 100 BC (hrs:min)	7:11	9:30	10:43	12:04	13:22
Transition 30→ 100 (hrs:min)	0:20	0:23	0:27	0:22	2:57

From table XV and XVI, trends can be observed. First, as the ratio of EDTMP acid increases from 0.4 to 0.9, the thickening time increases. Second, the free water decreases with increasing EDTMP acid ratio. Third, the absolute transition time from 30 bc to 100 bc increases as the EDTMP acid ratio increases. However, if the transition time is calculated as a percentage of the thickening time a decrease is observed with increasing EDTMP acid ratio in the range from 0.4 to 0.8.

At an EDTMP acid ratio of 0.9 at 220 °F and 0.4 gal/sk, the cement set is poor with a low strength. The set cement at this condition could be broken with the force of the hands. An important observation is that all other samples have shown a "true" and hard set that was difficult to clean out from the consistometer test cell.

Best results are obtained with a ratio ranging between 0.6 and 0.8, preferably of about 0.7, a good compromise between the thickening time and the amount of produced free water, and a ratio which also assure that the retarder is efficient event at high concentration without 'killing' the cement.

Table IV

Test No	Concentration %	T (°C)	Phosphate %	H ₃ PO ₄ %	Thickening time hrs:min	Transition time min.	50 psi hrs:min	500 psi hrs:min	Strength after 24 hours psi	Rheology mixing PV	Rheology on Ty	Rheology circulation temperature PV	Rheology at Ty	Gel at 10min	+ 1min	Free water ml
1	0.5	79.5	16	36	20:54	45	23:10	27:19	0	57	2.2	34	4.1	21	6	0
2	0	79.5	16	36	3:41	31	8:33	10:06	1825	57	3.1	31	6.9	37	10	0
3	0.375	90.5	16	36	3:23	50	7:20	8:39	2483	59	2.6	38	6.3	52	15	0
4	0.125	68.3	16	36	10:56	30	20:28	23:23	510	57	3.5	37	4.8	19	7	0
5	0.375	68.3	16	36	29:15	26	41:02	45:25	0	58	3	32	3.6	14	3	0
6	0.125	90.5	16	36	2:30	45	7:33	8:56	2497	48	1.5	26	16	98	27	0
7	0.375	83	31	36	9:41	17	15:12	19:10	1348	36	3.3	33	6.4	31	13	0
8	0.125	75.8	1	36	13:03	26	22:19	24:44	0	62	3.6	37	5.3	26	8.5	0
9	0.375	75.8	1	36	34:56	56	35:24	41:00	0	60	3.4	35	6.2	12	5.5	0
10	0.250	86.7	1	36	12:34	32	8:06	9:31	2931	62	2.6	38	18	112	36	0
11	0.125	83	31	36	9:32	78	10:25	12:13	2062	51	2.2	51	6.6	65	14	0
12	0.250	72	31	36	25:50	60	30:58	34:49	0	54	5.6	37	5.9	20	8.5	0
13	0.375	83	19.75	62	3:27	24	8:24	10:12	2300	58	4.7	42	16	64	29	0
14	0.125	75.8	12.25	10	18:00	34	33:34	36:41	0	56	2.3	34	6.2	26	9.5	0
15	0.375	75.8	12.25	10	64:40	60	>8 days	>8 days	0	62	2.4	42	5.8	34	11	0
16	0.250	86.7	12.25	10	35:43	60	26:10	32:36	32	56	3	49	25	144	50	0
17	0.250	79.5	27.25	10	54:38	60	>8 days	>8 days	0	58	4	36	6.3	29	9	0
18	0.125	83	19.75	62	2:10	54	8:26	10:06	2142	53	2.2	34	13	101	24	0
19	0.250	72	19.75	62	7:02	33	9:49	12:15	1650	55	6.5	41	7.4	39	13	0
20	0.250	79.5	4.75	62	5:14	41	10:33	12:33	2010	58	1.5	35	6.1	28	11	0
21	0.250	79.5	16	36	12:18	34	21:47	25:38	480	47	5.3	39	8.7	27	12	0
22	0.250	79.5	16	36	12:26	24	16:10	18:36	1344	60	2.1	37	6.6	39	13	0
23	0.250	79.5	16	36	12:24	23	19:18	22:27	824	49	3.6	33	5.7	27	10	0

Table V

Test No	Concentration %	T (°C)	Phospho-nate %	H ₃ PO ₄ %	Thickening time hrs:min	Transition time min.	50 psi hrs:min	500 psi hrs:min	Strength after 24 hours psi	Rheology on mixing PV Ty	Rheology at circulation temperature PV Ty	Gel At 10min + 1min	Free water ml
1	1.5	101.7	16	36	16:53	60	17:01	19:26	1144	112 10	69 9	14 7.5	0.05
2	0.7	101.7	16	36	2:54	28	7:22	8:21	2769	103 23	53 23	58 34	0.2
3	1.3	112.8	16	36	3:26	20	8:00	9:44	2676	96 15	61 11	11.5 6	0.05
4	0.9	42.2	16	36	15:27	36	12:45	14:48	1927	100 18	57 21	6 9.5	0
5	1.3	42.2	16	36	35:43	22	37:00	39:00	2	101 17	56 13	15 10	0.1
6	0.9	112.8	16	36	1:42	15	5:50	7:04	2941	100 19	69 33	27.5 7.5	0.1
7	1.3	105.6	31	36	9:04	18	14:01	17:00	1750	82 14	51 14	19 10	0.05
8	0.9	97.8	1	36	8:39	40	13:47	15:13	2005	101 16	54 13	15 9	0.5
9	1.3	97.8	1	36	33:11	50	37:23	40:11	20	109 15	60 10	8 5	0.05
10	1.1	108.9	1	36	5:30	21	11:12	13:05	2323	95 13	57 9	9 4	0.1
11	0.9	105.6	31	36	5:37	200	6:45	8:23	2249	95 20	45 30	85 17	0.05
12	1.1	94.4	31	36	26:06	100	33:56	39:00	0	90 12	60 22	44 22	0
13	1.3	105.6	19.75	54	2:19	21	5:29	6:32	2400	95 20	60 15	24 12	0
14	0.9	97.8	12.25	18	20:37	120	38:32	42:16	0	102 15	60 12	15 7	0
15	1.3	97.8	12.25	18	26:28	180	80:43	87:30	0	103 9	58 5	5 4.5	0.5
16	1.1	108.9	12.25	18	4:10	4	18:34	21:28	0	100 9.5	55 6	9 5	0
17	1.1	101.7	27.25	18	30:18	22	42:10	49:13	0	98 12	64 9	20 9	0
18	0.9	105.6	19.75	54	1:46	13	4:35	5:51	2700	100 25	57 21	31 15	0
19	1.1	94.4	19.75	54	4:12	25	8:26	10:07	2200	101 23	57 24	60 14	0
20	1.1	101.7	4.75	54	3:10	24	5:45	6:54	2468	89 19	61 16	15 9	0
21	1.1	101.7	16	36	6:31	37	8:26	9:32	2652	93 12	54 10	18 8	0
22	1.1	101.7	16	36	5:58	33	10:12	11:33	2300	103 16	56 14	17 14	0.2
23	1.1	101.7	16	36	5:27	47	10:05	11:36	2180	94 16	55 13	13 10	0.2

Table VI

Test No	Concentration %	T (°C)	Phospho-nate %	H ₃ PO ₄ %	Thickening time hrs:min	Transition time min.	50 psi hrs:min	500 psi hrs:min	Strength after 24 hours psi	Rheology mixing PV	Rheology on Ty	Rheology circulation temperature PV	Rheology at 10min	Gel at 10min	Free water ml
1	3	126.7	16	36	18:38	24	24:38	27:47	50	134	18	69	7.3	2	0.05
2	1.5	126.7	16	36	3:07	4	5:31	6:50	2399	112	14	73	12	5	0.05
3	2.625	137.8	16	36	6:55	13	9:47	12:11	2150	129	11	72	6.6	2.5	0.1
4	1.875	115.6	16	36	9:58	15	10:11	11:50	2563	101	13	61	8	3	0.3
5	2.625	115.6	16	36	30:52	45	23:11	27:32	50	129	11	72	6.6	2.5	0.1
6	1.875	137.8	16	36	2:15	18	5:56	7:32	2550	93	14	49	10	1	0.05
7	2.625	130.6	31	36	4:12	21	10:21	15:04	2572	119	16	56	11	2	0.1
8	1.875	122.8	1	36	6:58	4	11:11	13:18	2640	92	12	48	7.6	1	0.5
9	2.625	122.8	1	36	29:18	25	32:14	38:51	0	106	15	52	7.6	1	0.1
10	2.250	133.9	1	36	7:09	5	7:02	8:18	3484	103	14	54	8.5	1.5	0.1
11	1.875	130.6	31	36	4:35	40	6:44	9:15	2393	103	13	63	9.7	7	0
12	2.25	119.4	31	36	7:00	40	14:02	18:23	1042	125	18	70	13	7	0
13	2.625	130.6	19.75	46	2:57	20	6:41	7:53	1100	111	22	67	10	5	0
14	1.875	122.8	12.25	26	11:42	6	13:47	16:37	2052	106	13	58	4.6	2	0.5
15	2.625	122.8	12.25	26	22:24	5	42:41	47:39	0	97	13	45	8	6	0.05
16	2.250	133.9	12.25	26	7:18	21	11:12	13:27	1813	101	14	44	9.8	1.5	0.05
17	2.250	126.7	27.25	26	11:39	42	16:29	24:18	490	93	11	54	6	2	0.05
18	1.875	130.6	19.75	46	2:05	17	5:50	7:08	2891	122	17	73	13	1.6	0.05
19	2.250	119.4	19.75	46	5:00	23	8:23	9:59	2733	117	24	73	12	5	0
20	2.250	126.7	4.75	46	11:01	17	13:49	15:33	2213	135	19	61	1.7	2	0.6
21	2.250	126.7	16	36	6:37	18	9:59	12:16	2521	94	11	54	6	2	0
22	2.250	126.7	16	36	5:07	22	11:28	13:38	2161	103	12	61	5	2	0.05
23	2.250	126.7	16	36	7:53	20	14:55	17:21	1794	101	17	51	9	1	0.05

5

CLAIMS

1. A system for retarding setting in a cement slurry for an oil well or the like, the system being constituted by a solution of a phosphonate selected from methylene phosphonic acid derivatives and a phosphate.
2. A retarding system according to claim 1, characterized in that said phosphate is selected from the following salts or corresponding acids: mono-phosphates (ortho-phosphates PO_4^{2-} , meta-phosphates PO_3^-), acyclic poly-phosphates (pyrophosphates $\text{P}_2\text{O}_7^{4-}$, tripolyphosphates $\text{P}_3\text{O}_{10}^{5-}$), and cyclic poly-phosphates.
3. A retarding system according to claim 2, characterized in that said phosphate is selected from salts, preferably sodium or potassium salts, or from acids (when they exist) of the following compounds: orthophosphoric acid H_3PO_4 , sodium dihydrogen phosphate NaH_2PO_4 , sodium monohydrogen phosphate Na_2HPO_4 , trisodium phosphate Na_3PO_4 , pyrophosphoric acid $\text{H}_4\text{P}_2\text{O}_7$, sodium tripolyphosphate $\text{Na}_5\text{P}_3\text{O}_{10}$, and sodium cyclotrimetaphosphate $\text{Na}_3\text{P}_3\text{O}_9$.
4. A retarding system according to any preceding claim, characterized in that said methylene phosphonic acid derivative is a calcium and sodium salt of ethylenediamine-N,N,N',N'-tetrakis(methylene) phosphonic acid, or the pentasodium salt of ethylenediamine tetra(methylenephosphonic) acid.
5. A retarding system according to claim 4, characterized in that said phosphate is orthophosphoric acid H_3PO_4 .
6. A retarding system according to any preceding claim, characterized in that the phosphonate to phosphate ratio is in the range 2 to 4 by weight, preferably in the range 3 to 3.5 by weight.
7. A retarding system according to any preceding claim, characterized in that it further comprises a retarder booster selected from lignosulphonates, hydroxycarboxylic acids, or mixtures of lignosulphonates and hydroxycarboxylic acids.
8. A retarding system according to any preceding claim, characterized in that it further comprises a biopolymer.
9. A retarding system according to any preceding claim, characterized in that it is constituted by 40% to 45% of orthophosphoric acid, 10% to 15% of the calcium and sodium salt of ethylenediamine-N,N,N',N'-tetrakis(methylene)phosphonic acid, and 40% to 50% of retarder booster, the percentages being percentages by weight.
10. A retarding system according to any preceding claim, characterized in that it is constituted by the pentasodium salt of ethylenediamine N,N,N',N4 tetramethylene phosphonic acid (EDTMP) and phosphoric acid.

- 5 11. A retarding system according to claim 10, wherein the weight ratio EDTMP/phosphoric acid is between 0.6 and 0.8 and preferably of about 0.7.
12. The use of a retarding system according to any one of claims 1 to 9 in cementing a well with a Portland cement based slurry at a setting temperature in the range 50°C to 140°C.
13. The use of a retarding system according to any one of claims 1 to 9 in plaster-based systems.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 99/01302

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C04B28/02 C04B22/16 C04B24/00 //(C04B28/02,22:16,24:00),
C04B103:22

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 C04B

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.
X	GB 2 240 334 A (SANDOZ LTD) 31 July 1991 (1991-07-31) page 2, paragraph 3 page 3, line 10 page 4, line 3 - line 22; claims 1,6,8,9 ---	1-4,7
A	DATABASE WPI Section Ch, Week 9309 Derwent Publications Ltd., London, GB; Class D15, AN 93-071351 XP002083231 & JP 05 017770 A (KUMAGI GUMI CO LTD), 26 January 1993 (1993-01-26) abstract ---	1-4
A	US 4 734 134 A (PADTBERG RUEDIGER O ET AL) 29 March 1988 (1988-03-29) column 2, line 32 - line 53; claims --- -/--	1-3,12



Further documents are listed in the continuation of box C.



Patent family members are listed in 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, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Theodoridou, E

INTERNATIONAL SEARCH REPORT

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PCT/EP 99/01302

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 614 859 A (PUMPTech NV) 14 September 1994 (1994-09-14) page 2, line 53 - page 3, line 25 ---	1,4,12
A	FR 1 164 344 A (SOCIÉTÉ DES APPLICATIONS CHIMIQUES DANS L'INDUSTRIE) 8 October 1958 (1958-10-08) the whole document ---	1,13
A	EP 0 572 261 A (HALLIBURTON CO) 1 December 1993 (1993-12-01) page 7, line 59 - page 8, line 15 page 8, line 47 - line 48; claims -----	1,4,10, 12

INTERNATIONAL SEARCH REPORT

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International Application No

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