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(54) **Titre** : COMPOSITION AQUEUSE GELIFIABLE POUVANT SERVIR A MODIFIER LA PERMEABILITE D'UN RESERVOIR PETROLIFERE

(54) **Title**: AQUEOUS GELLABLE COMPOSITION, USEFUL FOR MODIFYING THE PERMEABILITY OF A PETROLEUM RESERVOIR

(57) **Abrégé/Abstract**:

An aqueous gellable composition having a delayed gelling time is disclosed, which contains a water-soluble polymer crosslinkable with Cr^{3+} and a crosslinking and gel-retarding system containing a Cr^{3+} ion and a salicylic acid ligand, wherein said ligand can be in free form, or in the form of a complex with Cr^{3+}, or partially in free form and partially in complexed from. Such a composition is useful for modifying the permeability in petroleum reservoirs, within a wide range of temperatures, of from about 60°C to 120°C, or higher temperatures.

ABSTRACT

An aqueous gellable composition having a delayed gelling time is disclosed, which contains a water-soluble polymer crosslinkable with Cr^{3+} and a crosslinking and gel-retarding system containing a Cr^{3+} ion and a salicylic acid ligand, wherein said ligand can be in free form, or in the form of a complex with Cr^{3+}, or partially in free form and partially in complexed form. Such a composition is useful for modifying the permeability in petroleum reservoirs, within a wide range of temperatures, of from about 60°C to 120°C, or higher temperatures.

CASE 3395

"AQUEOUS GELLABLE COMPOSITION, FOR MODIFYING THE PERMEABILITY OF A PETROLEUM RESERVOIR"

The present invention relates to an aqueous gellable composition, with delayed gelling time, useful for modifying the permeability of high-permeability regions in petroleum reservoirs, in particular in high-temperature reservoirs.

The invention relates also to a process for reducing the permeability of a reservoir, which process uses said gellable composition.

It is well-known that at the end of the primary step of recovery of petroleum from s petroleum reservoir, in which step the recovery occurs thanks to the natural energy stored in the petroleum reservoir, or with the use of mechanical energy, inside the reservoir still a large amount of petroleum remains. Therefore, in order to increase the amount of petroleum which can be extracted, techniques of secondary recovery are customarily used, which essentially consist in injecting into the reservoir a fluid, generally water or a polymeric solution, or a gas, such as carbon dioxide or steam, which conveys petroleum to the production well.

However, owing to the heterogeneity of the petroleum bearing rock, which is constituted by regions with different permeability, such fluids tend to preferentially flow through the higher-permeability regions. The low-permeability regions remain hence non-fluxed, or only partially fluxed, and this matter of fact prevents the extraction of the therein contained petroleum.

A proposed solution to solve such a problem consists in modifying the permeability of the resevoir by either completely or partially occluding the high-permeability regions, so that the flow of the liquid subsequently injected into the reservoir for the recovery of petroleum can be diverted towards the low-permeability regions.

One among the techniques most widely used for that purpose is based on the injection, into the reservoir, of an aqueous solution of a gellable polymer, which can be gelled by means of a multivalent metal ion, and the generation in_situ of polymeric gels.

Since the regions which one wants to occlude may be very large and/or may be at a long distance from the injection well, it is necesary that the formation of the gel takes place with a delay, so as to enable the gellable solution to reach the desired region and fill it to a complete, or substantially complete, extent.

In particular, the use is known in the art, of gellable compositions having delayed gelling time, which compositions generally consist of a polymer which can be crosslinked by means of a multivalent metal ion, e.g., polyacrylamide, a multivalent metal ion crosslinkg agent and a ligand or sequestering agent for said multivalent metal ion.

So, e.g., in UK patent application 2,187,773, a gellable composition having a delayed gelling time is disclosed, which contains a water-soluble polymer, a crosslinking agent constituted by a complex of Cr^{3+} with a carboxylate ion, in particular acetate ion, and a delaying agent selected from among the carboxy acids, preferably from among the aliphatic monocarboxy acids, in particular acetic acid.

Such a system shows the advantage that low-cost ligand, such as acetic acid, is used, but in case of high-temperature reservoirs, the delay gelling rate which can be obtained is at all insufficient in order to perform the occlusion of large regions and/or regions situated far away from the injection well.

In European patent applications EP 390282 and EP 390279, the use is disclosed of compositions which can be gelled by means of Cr^{3+}, containing as the retardant agent and organic ligand selected from among the aliphatic and aromatic dicarboxy acids, or the α-hydroxyacids or α-aminoacids.

Unfortunately, such compositions did not prove to be satisfactory under all viewpoints; in particular, the proposed ligands are mostly expensive, rendering the process of modification of permeability a burdensome one.

The present Applicant has found now a new aqueous gellable composition having a delayed gelling time, which makes it possible the drawbacks which affect the prior art, as above briefly mentioned, to be overcome.

Therefore, a purpose of the present invention is said aqueous gellable composition with delayed gelling time.

In accordance therewith, according to the present invention, said aqueous gellable composition comprises:

(a) a water-soluble organic polymer crosslikable with Cr^{3+};

(b) a crosslinking and gel-retarding system containing a Cr^{3+} ion and salicylic acid ligand, wherein said ligand can be in free form, or in the form of a complex with Cr^{3+} ion, or partially in free form and partially in complexed form.

The water-soluble organic polymers which can be crosslinked by using Cr^{3+}, useful according to the purposes of the present invention, are generally selected from the group consisting of acrylamide polymers. In particular, there can be used either acrylamide homopolymers, or acrylamide copolymers with one or more copolymerisable unsaturated monomer(s), such as, e.g., acrylic acid, methacrylamide, sodium 2-acrylamido-2-methyl-propane-sulfonate and N-vinyl-2-pyrrolidone. Among the copolymers, the copolymers of acrylamide with sodium 2-acrylamido-2-methyl-propane-sulfonate, the copolymers of acrylamide with N-vinyl-pyrrolidone and the terpolymers of acrylamide with sodium 2-acrylamido-2-methyl-propane-sulfonate and N-vinyl-2-pyrrolidone are preferably used.

Said acrylamide homopolymers and copolymers can be either substantially non-hydrolysed (less than 1% of amidic groups hydrolysed into free carboxy groups), or partially hydrolysed (more than 1% of amidic groups hydrolysed into free carboxy groups). The molecular weight of these acrylamide polymers may generally be comprised within the range of from 100,000 to 20,000,000, and, preferably, within the range of from 200,000 to 12,000,000.

The concentration of the water-soluble organic polymer in the gellable composition according to the present invention can generally range from 1,000 to 80,000 ppm, and preferably is comprised within the range of from 3,000 to 50,000 ppm and, in most preferred form of practical embodiment, is comprised within the range of from 5,000 to 10,000 ppm when fresh water is used, and of from 10,000 to 30,000 ppm when salt water is used (such as, e.g., sea water).

The ligand of Cr^{3+} ion contained in the crosslinking and gel-retarding system according to the present invention is salicylic acid.

Said ligand can be present in the crosslinking/ retardant system in free form, as the acid, or in the form of a complex with Cr^{3+} ion, or partially in free form and partially in complexed form.

According to the preferred form of practical embodiment of the present invention, said ligand is present partially in free form and partially in the form of a complex with Cr^{3+}, because in that way the best results are obtained as regards the gelling rate, in particular at high temperatures, i.e., temperatures equal to, or higher than, 90°C.

In practice, in said preferred form of practical embodiment, the crosslinking and gel-retarding system is constituted by a complex of Cr^{3+} with salicylate ions, in which the molar ratio of salicylate: Cr^{3+} can be comprised within the range of from 1:1 to 3:1, and preferably is 3:1, and salicylic acid, or a soluble salt thereof, in free form, i.e., not bonded in said complex.

The crosslinking and gel-retarding system according to the present invention can additionally contain one or more hydroxy ions and/or neutral molecules, e.g., water, and other monovalent or divalent ionorganic ions suitable for balancing the charge of the same system.

In those forms of practical embodiment of the invention in which the croslinking and gel-retarding system contains an amount of ligand in free form, the molar ratio of said salicylic acid ligand in free form to Cr^{3+} ion can be comprised within the range of from 1:1 to 50:1, and is preferably comprised within the range of from 3:1 to 10:1.

Such a molar ratio is selected as a function of the extent of the delay in gelling time which one wishes to attain, also on considering the temperature of the region of the reservoir, which one wishes to occlude.

The concentration of Cr^{3+} ion in the gellable composition can be comprised within the range of from 10 to 5,000 ppm, and preferably is comprised within the range of from 25 to 800 ppm, with most preferred values being of from 100 to 600 ppm.

The gellable composition of the present invention can additionally contain one or more stabilizer agent(s) for the polymer, as customarily used, e.g., thiourea.

The pH value of the gellable composition according to the present invention can be comprised within the range of from about 2 to about 9, and preferably is of from 4 to 7. Therefore, when either mecessary or desired, the pH value of the composition is adjusted by means of the addition of a mineral acid or base, e.g., hydrochlorid acid, or sodium hydroxide.

The aqueous gellable composition according to the present invention can be prepared by simply blending its components in water, and advantageously aqueous solutions of the same components are used; the sequence of addition of the components is not critic.

However, preferably, an aqueous solution is prepared first, which contains the polymer and the optional stabilizer agent, then an aqueous solution of salicylic acid ligand is added, in case one wishes to operate with a crosslinking and gel-retarding system in which the ligand is totally or partially in non-complexed form, and an aqueous solution is finally added of a complex of Cr^{3+} with salicylate, or an aqueous solution of an aqueous solution of an inorganic Cr^{3+} salt, such as, e.g. nitrate or chloride, is added.

The salicylate complex of Cr^{3+} can be prepared by using known procedures of inorganic chemistry. For example, it can be prepared by reacting chrome hydroxide $Cr(OH)_3$ with sodium salicylate, substantially following the procedure as reported in "Inorganic Syntheses", Vol. 16, pages 80-81.

Water used in the preparation of the gellable composition of the present invention can be free from salts, or it can contain salts and, advantageously, the same water contained in the same reservoir can be used.

A further purpose of the present invention is a process for reducing the permeability in a petroleum reservoir, which process uses the composition disclosed hereinabove.

More particularly, according to the present invention, said process comprises the following steps:

(a) preparing an aqueous gellable composition, as disclosed hereinabove;

(b) injecting said gellable composition into the petroleum reservoir through at least one well;

(c) causing said composition to flow through the reservoir, until it reaches and substantially fills the high-permeability region which has to be treated; and

(d) causing said composition to turn into a gel, with the permeability of the above said region being consequently decreased.

Such a composition is useful for modifying the permeability in a petroleum reservoir, within a wide range of temperatures, of from 60°C up to 120°C, or once more.

Said composition advantageously enables the permeability of high-permeability regions situated deeply in the reservoir or anyway far away from the injection well to be reduced, without that an early gelling occurs.

In general, it was found that delays in gelling rate can be obtained, which can be as long as one week, when one operates at temperatures of the order of 90-120°C.

The low cost of salicylic acid makes it also possible economic advantages to be attained additionally to the above benefits.

The following examples are to be considered as illustrative of the invention, and should not be construed as being limitative of the purview of the same invention.

Example 1

An aqueous solution of a commercial copolymer of acrylamide and sodium 2-methyl-1-propane-sulfonate in a weight ratio of approximately 75:25, with about 4% of hydrolysed amidic groups, is prepared. To the solution of the copolymer, thiourea is added as the stabilizer agent.

An aqueous solution is prepared of Cr(salicylate)$_3$ complex, obtained as follows.

200 ml of an 1.7 M solution of ammonium hydroxide is added, with stirring, to a solution of commercial $CrCl_3.6H_2O$ (13.3 g; 0.05 mol) in 200 ml of water.

The so formed chrome oxide $Cr(OH)_3$ is centrifuged off and then is purified from any chlorine traces, by being repeatedly washed with water and centrifuged, as described in "Inorganic Syntheses", vol. 16, page 31.

To the so obtained $Cr(OH)_3$, 100 ml of a solution at 80°C of sodium salicylate (24 g, 0.15 mol) is added, and the resulting solution is kept with stirring for about 2 hours, always at 80°C.

At the end, the solution is cooled and a solution of diluted hydrochloric acid is added, in order to adjust the pH value at 3.

The Cr(salicylate)$_3$ complex precipitates off and then is filtered off and washed with a solution of diluted hydrochloric acid at pH 3.

The elemental analysis of the obtained product demonstrates that the ratio of chrome:carbon by weight is of 0.21 (theoretical value: 0.20).

Then, samples of gellable composition are prepared by mixing, inside a test tube with screw-threaded cap, the solution of the copolymer and of the stabilizing agent, with solutions containing different concentrations of salicylic acid, and subsequently adding the aqueous solution of Cr(salicylate)$_3$ complex.

All samples so prepared contain 5000 ppm of copolymer, 5000 ppm of thiourea, 200 ppm of Cr^{3+} and concentrations of non-complexed salicylic acid respectively of 0.008 M (molar ratio of salicylic acid:Cr^{3+} = 2.1), 0.024 M (molar ratio of salicylic acid:Cr^{3+} = 6:1) and 0.040 M (molar ratio of salicylic acid:Cr^{3+} = 10:1).

The pH value is adjusted at 5 ±0.1 by means of the addition of sodium hydroxide or hydrochloric acid.

The so prepared samples are finally charged to an oil bath at 120°C for 15 minutes, and then to an oven at the same temperature.

The gelling times of the several samples are reported in Table 1.

Table 1

Molar ratio[(a)] of salicylic acid/Cr(3+)	Gelling time (hours)
2:1	30 ÷ 46
6:1	53 ÷ 118
10:1	150 ÷ 165

(a) The molar ratio relates to the salicylic acid which is not in the complexed form.

Example 2

Example 1 is repeated using sea water for preparing the aqueous gellable compositions.

All samples prepared contain 5000 ppm of copolymer, 5000 ppm of thiourea, 200 ppm of Cr^{3+} [as $Cr(salicylate)_3$] and concentrations of non-complexed salicylic acid, respectively of 0.008 M (molar ratio of salicylic acid:Cr^{3+} = 2.1), 0.024 M (molar ratio of salicylic acid:Cr^{3+} = 6:1) and 0.040 M (molar ratio of salicylic acid:Cr^{3+} = 10:1).

The sample gelling times at 120°C are reported in following table 2.

Table 2

Molar ratio(a) of salicylic acid/Cr(3+)	Gelling time (hours)
2:1	5 ÷ 21.5
6:1	57 ÷ 117
10:1	140

(a) The molar ratio relates to the salicylic acid which is not in the complexed form.

Example 3

By operating as in Example 1, an aqueous gellable composition is prepared, which contains 5000 ppm of copolymer of Example 1, 5000 ppm of thiourea and 200 ppm of Cr^{3+} supplied as $Cr(salicylate)_3$. Furthermore, two gellable compositions are prepared, which contain, besides $Cr(salicylate)_3$ complex, also salicylic acid in non-complexed form, in a molar ratio of salicylic acid to Cr^{3+} respectively of 2:1 and 6:1. The gelling times of the different compositions, at the temperature of 90°C, are reported in following Table 3.

Table 3

Molar ratio(a) of salicylic acid/Cr(3+)	Gelling time (hours)
-	12 - 15(a)
2:1	22 - 46
6:1	166 - 190

(a) This gelling time relates to the gellable composition only containing $Cr(salicylate)_3$.

CLAIMS

1. Aqueous gellable composition having a delayed gelling time, comprising:

(a) a water-soluble organic polymer crosslinkable with Cr^{3+};

(b) crosslinking and gel-retarding system containing a Cr^{3+} ion and a salicylic acid ligand, wherein said ligand can be in free form, or in the form of a complex with Cr^{3+} ion, or partially in free form and partly in complexed form.

2. Composition according to claim 1, characterized in that in the crosslinking and gel retarding system, the molar ratio of the salicylic acid ligand in free form to Cr^{3+} ion is comprised within the range of from 1:1 to 50:1.

3. Composition according to claim 2, characterized in that said molar ratio is comprised within the range of from 3:1 to 10:1.

4. Composition according to claim 1, characterized in that in the crosslinking and gel retarding system the salicylic acid ligand is partially in free form and partially in complexed form.

5. Composition according to claim 1, characterized in that the concentration of the (a) water-soluble organic polymer is comprised within the range of from 1,000 to 50,000 ppm.

6. Composition according to claim 5, characterized in that the concentration of the water-soluble organic polymer is comprised within the range of from 1,000 to 80,000 ppm.

7. Composition according to claim 6, characterized in that the concentration of the water-soluble organic polymer is comprised within the range of from 3,000 to 50,000 ppm when fresh water is used, and of from 10,000 to 30,000 when salt water is used.

8. Composition according to claim 1, characterized in that the concentration of Cr^{3+}ion is comprised within the range of from 10 to 5,000 ppm.

9. Composition according to claim 8, characterized in that the concentration of Cr^{3+} ion is comprised within the range of from 25 to 800 ppm.

10. Composition according to claim 9, characterized in that the concentration of Cr^{3+} ion is comprised within the range of from 100 to 600 ppm.

11. Composition according to claim 1, characterized in that the said water-soluble organic polymer is selected from the group consisting of acrylamide homopolymers and acrylamide copolymers with one or more copolymerisable unsaturated monomer(s), which acrylamide homopolymers or copolymers have a molecular weight comprised within the range of from 100,000 to 20,000,000, said acrylamide homopolymers and copolymers being substantially non-hydrolysed (less than 1% of amidic groups

hydrolysed into free carboxy groups), or partially hydrolysed (more than 1% of amidic groups hydrolysed into free carboxy groups).

12. Composition according to claim 11, characterized in that said acrylamide homopolymers and copolymers have a molecular weight comprised within the range of from 200,000 to 12,000,000.

13. Composition according to claim 11, characterized in that said copolymerisable unsaturated monomers are selected from the group consisting of acrylic acid, methacrylamide, sodium 2-acrylamido-2-methyl-propane-sulfonate and N-vinyl-2-pyrrolidone.

14. Composition according to claim 11, characterized in that said water-soluble organic polymer is selected from the group consisting of the copolymers of acrylamide with sodium 2-acrylamido-2-methyl-propane-sulfonate, the copolymers of acrylamide with N-vinyl-pyrrolidone and the terpolymers of acrylamide with sodium 2-acrylamido-2-methyl-propane-sulfonate and N-vinyl-2-pyrrolidone.

15. Composition according to claim 1, characterized in that said composition additionally contains one or more stabilizer agent(s) for the polymer and, preferably, thiourea.

16. Composition according to claim 1, characterized in that it has a pH value comprised within the range of from about 2 to about 9.

17. Composition according to claim 16, characterized in that it has a pH value comprised within the range of from 4 to 7.

18. Process for reducing the permeability of a petroleum reservoir, which process comprises the following steps:

(a) preparing an aqueous gellable composition as claimed in claim 1;

(b) injecting said gellable composition into the petroleum reservoir through at least one well;

(c) causing said composition to flow through the reservoir, until it reaches and substantially fills the high-permeability region which has to be treated; and

(d) causing said composition to turn into a gel, with the permeability of the above said region being consequently decreased.