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(56) Documents cited

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(58) Field of search
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C2C
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E1F
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(54) Scale inhibitors

(57) A copolymer of an alkene, preferably a branched chain alkene, and an unsaturated dicarboxylic acid or anhydride, in acidic or neutralised form, is used as a scale inhibitor. The preferred compound is the sodium salt of a copolymer of isobutene and maleic anhydride.

The scale inhibitors may be used in secondary or tertiary oil recovery, desalination of sea water and the softening of boiler feed water.

SPECIFICATION

Scale inhibitors

This invention relates to a method for inhibiting the formation of scale, utilising a copolymer of an alkene and an unsaturated dicarboxylic acid or anhydride in acidic or neutralised form.

A scale inhibitor is a compound or mixture which inhibits crystal growth and thereby reduces the tendency of scale to form.

Scale inhibitors are used in many water treatment processes where there is a risk of inorganic deposits, ie, scale, forming as a result of the presence of certain di- or higher valent metal ions, particularly alkaline earth metal ions.

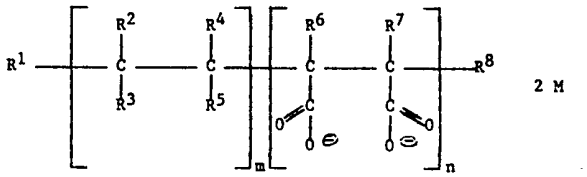
Certain scale inhibitors have the ability to act as threshold agents, that is to say, they are effective at concentrations below those which would be required theoretically to complex completely with multivalent ions present.

Scale inhibitors are used in the oil industry. Water flooding is one of the most successful and extensively used secondary recovery methods. Water is injected under pressure into the reservoir via injection wells and drives the oil through the rock into nearby producing wells. In this type of operation it is most important to ensure that the injection water is free from suspended particles or any chemical or biological substance which might cause blockage of the pore channels in the reservoir rock. The oil in the reservoir is frequently associated with connate water which contains various metal ions, sometimes including barium and strontium. Many oil fields are situated in offshore locations and for them the only source of injection water is the sea. Sea water contains sulphate and carbonate ions which, in the absence of treatment, would react with alkaline earth metal ions in the connate water to precipitate scale. In order to prevent this, scale inhibitors are used. Typical scale inhibitors include sulphonated ethoxylated hydrocarbons, polyacrylates and amine phosphonates.

Another area in which such compounds are employed is in the field of water treatment. Particular aspects include the desalination of sea water and the softening of boiler feed water.

We have now discovered that copolymers of alkenes and unsaturated dicarboxylic acids or anhydrides, in acidic or neutralised form, are useful scale inhibitors.

Thus according to the present invention there is provided a method for inhibiting scale formation which method comprises adding an aqueous solution of a copolymer of an alkene, preferably a branched chain alkene, and an unsaturated dicarboxylic acid or anhydride, in acidic or neutralised form, of formula:



wherein R^1–R^8 are hydrogen atoms or alkyl groups containing 1 to 22 carbon atoms; M^1 is an alkali metal, ammonium or hydrogen ion; and m and n are numbers in the range 3 to 3,000, preferably 10 to 1,000, to an aqueous medium containing potential scale forming constituents.

The preferred branched chain alkene is isobutene, the preferred unsaturated dicarboxylic acid or anhydride is maleic anhydride, and the preferred cation is sodium.

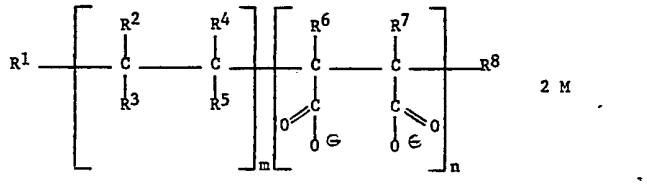
Preferably m and n are equal numbers.

The scale inhibitors are suitably employed in concentrations in the range 1 to 100 ppm.

The scale inhibitors are white, crystalline solids which are soluble in aqueous media and possess good alkaline earth metal complexing characteristics.

They may be used in formulations for use in secondary and tertiary oil recovery or in compositions for use in the desalination of sea water or the softening of boiler feed water.

Thus according to another aspect of the present invention there is provided a method for the recovery of crude oil from a production reservoir which method comprises the steps of injecting into the reservoir through an injection well, an aqueous medium having dissolved therein a scale inhibiting amount of a copolymer of an alkene, preferably a branched chain alkene, and an unsaturated dicarboxylic acid or anhydride, in acidic or neutralised form, of formula:



wherein R^1–R^8, M, m and n are as hereinbefore defined, and recovering crude oil from a production well.

The invention is illustrated with reference to the following Examples.

Examples 1–9

The technique used to evaluate the potential barium scale inhibiting efficiency of the compounds studied was as follows:

Supersaturated, metastable $BaSO_4$ solutions (10^{-4} mol dm^{-3}) were prepared by mixing solutions of Na_2SO_4 and $BaCl_2$ in a small beaker. An electrode was inserted into the solution and the conductance of the solution was monitored using a Wayne Kerr bridge instrument. The potential inhibitor was added to the solution at a known concentration. This often resulted in an initial, temporary increase in the conductance of the solution, reflecting the ionic character of the additive. 0.1g of $BaSO_4$ seed crystals was accurately weighed out and added to the solution which was stirred to ensure that the seed crystals were dispersed throughout the whole volume of the sample.

The subsequent decrease in conductance was monitored as a function of time using a chart recorder. From the resulting trace, values of conductance were taken at specified time intervals, and, where an inhibitor was present, compared with the values when no inhibitor had been present (ie, the blank sample). This was normally done for the conductance values at 20 min; the reason for this being that where the blank was concerned, after 20 min the conductance had almost reached its equilibrium value. Hence, it was concluded that the efficiency of an inhibitor would be reflected in the smaller decrease in conductance after 20 min over the decrease for the blank sample at the same time, ie:–

$$\frac{\Delta T}{\Delta T_o}\ \% = \frac{C_{1,I} - C_{20,I}}{C_{1,B} - C_{20,B}} \times 100$$

where:–

ΔT=the percentage of scale formed, relative to that formed in ΔT_o the blank sample, when a particular inhibitor was present.

$C_{1,I}$=the conductance at 1 min for the inhibitor containing sample.

$C_{20,I}$=the conductance at 20 min for the inhibitor containing sample.

$C_{1,B}$=the conductance at 1 min for the blank sample.

$C_{20,B}$=the conductance at 20 min for the blank sample.

The value of $C_{1,I}$ (and consequently $C_{1,B}$) was chosen because it was often observed that upon addition of the seed crystals there was a marked increase in conductance which decayed away in ca 1 min. Hence, it was only after 1 min that a meaningful comparison could be made.

A number of isobutene-maleic anhydride copolymers in the form of their sodium salts were tested by the above method at various concentration levels.

The results are set out in the following Table.

Table 1

Example	Compound	ppm	% Scale Formation
1	(M_w approx 4,000)	10	71.7
2	"	50	8.0
3	(M_w approx 5.5-6.5 x 10^4)	10	67.8
4	"	20	52.3
5	"	30	31.5
6	"	40	17.3
7	"	50	3.0
8	(M_w approx 16-17 x 10^4)	10	50.4
9	"	50	9.3

Example 10–15

A similar technique was used to evaluate the potential strontium scale inhibiting efficiency of salts of various olefin-maleic anhydride copolymers.

A supersaturated metastable $SrSO_4$ solution was prepared by adding 50 ml of 3×10^{-3} M $SrCl_2$ solution to 50 ml of K_2SO_4 solution of the same molarity, containing the inhibitor being tested. The required molarities were determined from precipitation titration curves. Nitrogen was bubbled through the system to prevent the formation of $SrCO_3$. 0.3 g of $SrSO_4$ seed crystals was added and stirred, and the decrease in conductance was measured using a Wayne-Kerr conductance bridge coupled to a chart recorder. Blank experiments were carried out in the same way, but without the addition of inhibitor.

As before a decrease in conductance occurred on the addition of the seeds as the free ions precipitated out of solution, and this was monitored on a chart recorder. Readings were taken after a 30 min period. The effect of the inhibitors was determined by the percentage scale formation and this was calculated by the fall in conductance in the presence of the inhibitor as a percentage of the fall in conductance of the blank solution, as in the previous examples.

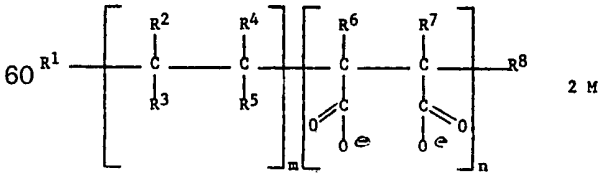
The results set out in the following Table 2 were obtained.

Table 2

Example	Alkene	Molecular Weight	% Scale Formation
10	Isobutene	5 x 10^5	2.6
11	Di-isobutene	5,000-7,000	5
12	Hexene	5,000-7,000	17.9
13	Tetradecene	5,500	64.1
14	Octadecene	1,260	38.5

CLAIMS

1. A method for inhibiting scale formation which method comprises adding an aqueous solution of a copolymer of an alkene and an unsaturated dicarboxylic acid or anhydride, in acidic or neutralised form, of formula:



wherein R^1–R^8 are hydrogen atoms or alkyl groups containing 1 to 22 carbon atoms; M is an

alkali metal, ammonium or hydrogen ion; and m and n are numbers in the range 3 to 3,000, to an aqueous medium containing potential scale forming constituents.

2. A method according to claim 1 wherein the alkene is isobutene.

3. A method according to either of the preceding claims wherein the unsaturated dicarboxylic acid or anhydride is maleic anhydride.

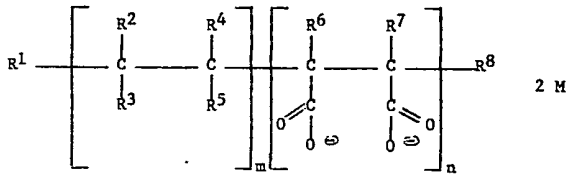
4. A method according to any of the preceding claims wherein M represents a sodium ion.

5. A method according to any of the preceding claims wherein m and n are equal numbers.

6. A method according to any of the preceding claims wherein m and n are numbers in the range 10 to 1,000.

7. A method according to any of the preceding claims wherein the copolymer is employed in concentration in the range 1 to 100 ppm.

8. A method for the recovery of crude oil from a production reservoir which method comprises the steps of injecting into the reservoir through an injection well, an aqueous medium having dissolved therein a scale inhibiting amount of copolymer of an alkene and an unsaturated dicarboxylic acid or anhydride, in acidic or neutralised form, of formula:



wherein R^1–R^8, M, m and n are as hereinbefore defined, and recovering crude oil from a production well.

9. A method for inhibiting scale formation according to claim 1 as hereinbefore described with reference to the Examples.

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