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3,661,785

INHIBITION OF DEPOSITION OF WATER INSOLUBLE COMPOUNDS IN AQUEOUS SYSTEMS

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No Drawing. Original application Apr. 4, 1968, Ser. No. 718,913, now Patent No. 3,557,164, dated Jan. 19, 1971. Divided and this application Apr. 27, 1970, Ser. No. 43,259

U.S. Cl. 252—8.55 B Int. Cl. C02b 5/06

4 Claims

ABSTRACT OF THE DISCLOSURE

Deposition of water insoluble compounds from aqueous systems containing them is inhibited by adding to the aqueous system, which may be a subsurface formation water or brine, a small but effective amount of a phosphate ester of ethoxylated esterified triol or the alkali metal or ammonium salts thereof.

CROSS-REFERENCE TO RELATED INVENTION

This application is a division of SN 718,913 filed Apr. 4, 1968, and now U.S. 3,557,164.

BACKGROUND OF THE INVENTION

(1) Field of the invention

The present invention is directed to phosphate esters of ethoxylated esterified triol and the alkali metal and ammonium salts thereof. More particularly, the invention is concerned with inhibition of deposition of water insoluble salts or compounds from aqueous systems containing them by adding to such systems a phosphate ester of ethoxylated esterified triol and the alkali metal and ammonium salts thereof. In its more specific aspects, the invention is concerned with inhibition of deposition of water insoluble compounds in wells, flow lines, and in other equipment containing or through which aqueous media are flowed to prevent fouling by deposition of water insoluble compounds.

(2) Description of the prior art

Heretofore it has been known to use certain compounds in aqueous systems to alleviate or prevent deposition of water insoluble compounds therefrom such as in wells, well flow lines, conduits, and the like. The same has been true with respect to boiler feed water and other systems. However, such prior art methods and compounds have not been entirely satisfactory since, especially in oil wells, it is necessary that the inhibitor have the characteristics of being adsorbed on the surface rock formation to a sufficient extent to provide a sufficient amount of inhibitor to be effective yet it must also be desorbed into the produced water or brine such that the produced water or brine contains a sufficient amount of the inhibitor to be effective. Additionally, the inhibitor must also be susceptible to injection into subsurface rock formations under pressure.

It is also important from an economic standpoint that the inhibitor be effective in small quantities and be producible from readily available chemicals without complicated and expensive methods.

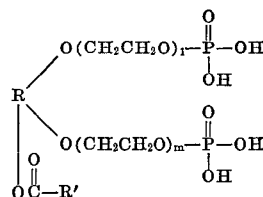
The present invention is quite advantageous and useful in these respects.

Specific prior art considered with respect to this invention include the following listed U.S. Patents: 2,128,161; 3,213,017; 3,258,071; 3,258,428; 3,271,306; 3,283,817; 3,288,217; 3,304,349; 3,308,161 and 3,336,221.

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SUMMARY OF THE INVENTION

The present invention may be briefly described and summarized as involving new compounds useful as inhibitors of aqueous systems from deposition of water insoluble compounds and involve phosphate esters of ethoxylated esterified triols having the following formula:



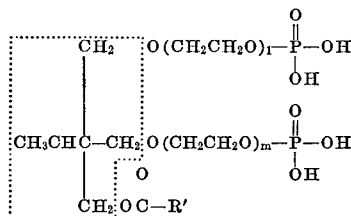
where

R is a hydrocarbon radical having 3 to 50 carbon atoms derived from a triol $\text{R}(\text{OH})_3$;

R' is a long chain organic radical having from 6 to 20 carbon atoms; and

$1 + m = n$ and n is the total number of moles of ethylene oxide incorporated in the molecule in the range from 2 to 30 and the alkali metal and ammonium salts thereof.

As an example of specific compound of the present invention without restricting the invention thereto, the following structure is given:



In this particular case, the radical R is enclosed in dotted lines and is derived from trimethylol propane. Equally, it may be derived from other triols.

The invention may also be summarized as involving adding or introducing into aqueous systems containing water insoluble compounds phosphate esters of the type given above and the alkali metal and ammonium salts thereof. The aqueous systems may desirably be water or brine produced from a subsurface earth formation or the inhibitor may be injected into the subsurface formation containing interstitial water or brine to be adsorbed on and desorbed from the rock into the water.

INVENTION VARIABLES

In the practice of the present invention, tall oil acid or other fatty or rosin acids are used to esterify triols. As examples of organic acids which may be used are those having from 6 to 20 carbon atoms in the long chain. Specific acids include by way of illustration and not by way of limitation: the rosin acids such as abietic, neoabietic, dehydroabietic, levopimaric, palustic, pimaric, isopimaric, unsaturated fatty acids such as oleic, linoleic, linolenic saturated fatty acids such as stearic, palmitic, myristic and the like.

The triols useful in the present invention include, trimethylol propane, glycerine, 1,2,4-butane triol, 1,2,6-trihydroxyhexane, $\alpha^1, \alpha^3, \alpha^5$ - trihydroxyhexamethylbenzene, and the like, and may contain from 3 to 15 carbon atoms.

The inhibitor of the present invention preferably contains from 2 to 30 moles of ethylene oxide and more preferably 4 to 12 moles for best results.

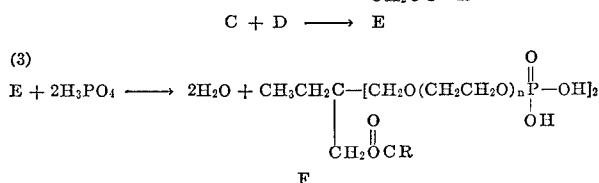
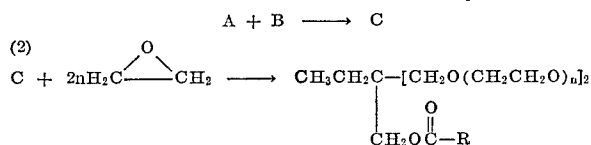
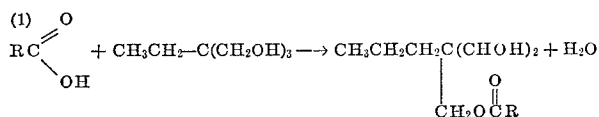
Good results are obtained with the inhibitor present in the aqueous system in an amount within the range from

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about 0.1 to about 50 p.p.m. with best results from about 1 to 20 p.p.m. The amount of the inhibitor used may depend on the particular water insoluble compound in the aqueous system and should be selected to give best results.

The water insoluble compounds and/or salts commonly encountered in aqueous systems and water and/or brines from oil and/or water wells and the like include calcium sulfate, commonly referred to as "gyp," barium sulfate, strontium sulfate, calcium carbonate, magnesium carbonate, strontium carbonate, iron carbonate, iron oxide and the like.

The inhibitors of the present invention may be prepared in accordance with the following equations:



The organic acid A is a long chain fatty acid such as a tall oil acid. The amount of ethylene oxide may range from 2 to 30 moles, but is preferably 4 to 12 moles. In the several equations, n is an integer from 1 to 15 and R is a chain having 6 to 20 carbon atoms.

EXAMPLES

(1) Esterification: 3.91 moles of tall oil fatty acid (A) was used to esterify 3.91 moles of trimethylolpropane (B). Toluene sulfonic acid was used as the catalyst and 3.9 moles of water were recovered from the reaction mixture during the esterification reaction.

(2) Ethoxylation: 3.87 moles of the ester C was ethoxylated with 15.4 moles of ethylene oxide. Sodium hydroxide was used as the catalyst. The ethoxylation was carried out in a temperature range of 240–300° F. and a pressure range of 60–80 p.s.i. The product is represented by E in Equation 2.

(3) Phosphorylation: The phosphate ester, F, was prepared by the reaction of 0.348 mole E with 1.39 moles of 115% polyphosphoric acid. The reaction was carried out at 110° C. for three hours.

The product F was tested as an inhibitor for calcium sulfate scale. It was found that 10 p.p.m. of the inhibitor, F, prepared as indicated above would inhibit the precipitation of calcium sulfate from a solution which was supersaturated to the extent of 0.06 mole/l. for a period of over 60 24 hours.

In this example, glycerine was employed instead of trimethylol propane and an inhibitor in accordance with the present invention was produced and tested as follows:

(1) Esterification: 3.53 moles tall oil acids was used to esterify 3.86 moles of glycerine. The reaction was carried out for six hours at 200° F. in the presence of 300 g. of toluene added as a reflux solvent. 3.5 moles of water were collected. After distillation of the toluene, 3.52 moles of product were recovered.

(2) Ethoxylation: 3.52 moles of the tall oil ester of glycerine was ethoxylated with 21.2 moles of ethylene oxide with 5 grams of NaOH used as the catalyst. The temperature was 240–300° F., and the pressure was 60–80 p.s.i.

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(3) Phosphorylation: 0.5 mole of the foregoing ethoxylated tall oil ester of glycerine was reacted with 2.0 moles of 115% phosphoric acid. The reaction was carried out two hours at 110° C. to give the phosphate ester (G) of the present invention.

This product G was tested as an inhibitor for calcium sulfate scale. It was found that 10 p.p.m. of the inhibitor prepared as indicated above would prevent for 24 hours the precipitation of calcium sulfate from a solution which was supersaturated in CaSO_4 to the extent of 0.06 moles/l.

The compounds or inhibitors of the present invention may be used as the mono- or di-alkyl metal or ammonium salts. Particularly, the mono- and di-sodium and potassium salts are quite effective and useful.

Compound F was used to inhibit deposition of CaCO_3 from a CaCO_3 solution which deposited scale. In this case, 20 p.p.m. of compound F gave 58% inhibition.

Compound F. was further used in inhibiting CaSO_4 deposition from an aqueous system which deposited scale with the following results:

Concentration of inhibitor, p.p.m.:	Percent inhibition
25 -----	96
10 -----	100
Blank -----	0
Fresh solution -----	-----
10 -----	62
Mono K salt of F, 10 -----	72
Di K salt of F, 10 -----	26
Di Na salt of F, 10 -----	86
Blank -----	0

The inhibitor G formed from glycerine as the triol in the present invention is also effective against calcium sulfate deposition as shown by the following:

Concentration of inhibitor, p.p.m.:	Percent inhibition
25 -----	100
10 -----	100
Blank -----	0

Inhibitor or Compound G was also used as an inhibitor of calcium carbonate deposite with the following results:

Concentration of inhibitor, p.p.m.:	Percent inhibition
20 -----	44.0
Blank -----	0

The effectiveness of Compound G on barium sulfate deposition from a solution containing 500 p.p.m. BaSO₄ in 5% NaCl brine was determined as follows:

Concentration of

30—very slight precipitate after 30 min.¹

10—slight precipitate after 15 min.
Blank—heavy precipitate on mixing.

¹ Precipitate very light after 2 hours.

It will be apparent from the foregoing examples that the present invention is quite important and useful.

The following test was used to determine calcium sulfate scale inhibition.

Two solutions were made up:

Solution 1: 200 g. NaCl, AR grade; 43.8 g. $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, USP grade; 20.3 g. $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, AR grade. Dissolve in distilled water, dilute to 2 liters.

Solution 2: 177.5 Na₂SO₄, AR grade (anhydrous). Dissolve in distilled water, dilute to 1 liter.

Place 50 ml. of Solution 1 in a 6-oz. prescription bottle. Add the desired amount of inhibitor (normally, 5, 10, 20 and 40 p.p.m.) and mix well. Then add 5.0 ml. of Solution 2 to the bottle. Mix well by shaking.

Allow the bottles to stand 24 hours, then titrate the residual hardness in a 2 ml. aliquot. The hardness titration is carried out using ethylene diamine tetra acetic acid solution and hardness indicator.

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Calculate the percent inhibition by the following formula:

$$\text{Percent inhibition} = \frac{\text{ml. to titrate sample} - \text{blank}}{\text{fresh blank} - \text{blank}} \times 100$$

The severity of the test can be increased by placing the bottles in an oven maintained at an elevated temperature such as 150° F. for several hours.

Static tests for calcium carbonate inhibition were carried out using a synthetic brine. The tests were done in 6-ounce prescription bottles. The samples on test were heated in an air oven at 160° F. for 20 hours in order to increase the severity of the test. At the end of the heating period, an aliquot from the test solution was titrated for hardness using the standard ethylene diamine tetra acetic acid hardness titration. The percent inhibition was calculated by the following formula:

$$\text{Percent inhibition} = \frac{\text{sample hardness} - \text{blank hardness}}{\text{fresh blank hardness} - \text{blank hardness}} \times 100$$

The test solutions which were used were made up as follows:

Solution A: 160 grams (2.74 moles) NaCl; 2.0 grams (0.027 mole) CaCl₂ (anhydrous); 1.32 grams (0.0044 mole) MgCl₂·6H₂O. These salts were dissolved in water and diluted to 1 liter.

Solution B: 2.0 grams (0.024 mole) NaHCO₃. The sodium bicarbonate was dissolved in water and diluted to 1 liter.

In carrying out a test, 50 ml. of Solution A was placed in a 6-ounce prescription bottle along with the desired amount of inhibitor. Fifty milliliters of Solution B was then added to the bottle, the bottle shaken well and placed in an oven maintained at 160° F. for 20 hours. At the end of this period, the residual hardness was determined using an aliquot and the percent inhibition calculated by comparing the performance of the inhibited sample with the performance of an uninhibited sample.

The hardness was determined by the EDTA hardness titration procedure.

Tests for barium sulfate scale inhibition were carried out using the following procedure.

Two test solutions were made up as follows:

Solution 1: 50 g. NaCl; 0.99 g. BaCl₂·2H₂O to 1 liter in H₂O.

Solution 2: 50 g. NaCl; 1.27 g. Na₂SO₄·10H₂O to 1 liter in H₂O.

The inhibitor to be tested was added to 50 ml. of Solution 1 in a 6-ounce prescription bottle. Then 50 ml. of Solution 2 were added to the bottle and the contents mixed by vigorous shaking.

The degree of inhibition was determined by measuring the length of time required for a precipitate of BaSO₄ to become visible in the bottle.

In practicing the present invention to prevent deposition of water insoluble salts or compounds in oil well conduits, tubing strings, pumps, and flow lines, the inhibitor as an aqueous solution may be forced or squeezed into a subsurface formation under a pressure sufficient to inject the inhibitor out into the formation but preferably insufficient to fracture the formation unless the formation has become plugged with deposits such as "gyp." If the formation has become plugged, it may be desirable to fracture the formation to open up a passage or to treat the formation to open a passage for the inhibitor. After the inhibitor has been adsorbed in and on the rock formation for a suffi-

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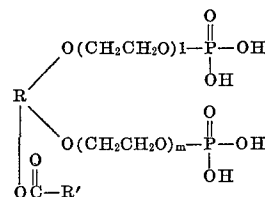
cient period of time, the well may be placed on production to allow the inhibitor to be desorbed into the produced water to prevent deposition of "gyp."

The inhibitors may also be added to other water handling systems where scale deposition is a problem.

The nature and objects of the present invention having been completely described and illustrated and the best mode contemplated set forth, what I wish to claim as new and useful and secure by Letters Patent is:

1. A method for inhibiting deposition of water insoluble compound selected from the group consisting of calcium sulfate, barium sulfate, strontium sulfate, calcium carbonate, magnesium carbonate, strontium carbonate, iron carbonate and iron oxide from an aqueous system containing same which comprises:

adding to said system a small but effective amount of an inhibitor selected from the group consisting of the phosphate esters of ethoxylated esterified triols having the following formula:



where

R is a hydrocarbon radical having 3 to 50 carbon atoms derived from a triol R(OH)₃;

R' is a long chain hydrocarbon radical having 6 to 20 carbon atoms obtained from fatty or rosin acids; and

1+m+n is the total number of moles of ethylene oxide incorporated in the molecule and is within the range from 2 to 30 and the alkali metal and ammonium salts thereof.

2. A method in accordance with claim 1 in which the amount of inhibitor added is within the range from about 2 to about 50 p.p.m. based on said aqueous system.

3. A method in accordance with claim 1 in which the aqueous system is water in a subsurface earth formation and the inhibitor is introduced into said subsurface earth formation and thereby added to said water.

4. A method in accordance with claim 1 in which:

(a) the amount of the inhibitor added is within the range from about 2 to about 50 p.p.m. based on the aqueous system;

(b) the aqueous system is water in a subsurface earth formation and the inhibitor is introduced into said subsurface earth formation and thereby added to said water; and

(c) the triol is trimethylol propane.

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HERBERT B. GUYNN, Primary Examiner

U.S. Cl. X.R.

210—58; 252—180; 260—403