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COMPOSITION AND METHOD FOR INHIBITING THE FORMATION OF IN AND REMOVING FROM OIL WELLS AND PIPELINES DEPOSITS OF PARAFFIN AND PARAFFINLIKE DEPOSITS

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12 Claims

ABSTRACT OF THE DISCLOSURE

Compositions for inhibiting and removing paraffin and similar deposits from oil wells and pipelines which compositions contain an alkanol having at least 4 carbon atoms adducted with about 1.5–3.5 moles of ethylene oxide, an oxyethylated-hydrocarbon substituted phenol and water, with or without a lower alkanol or glycol.

This invention relates to a composition of matter and to the use of said composition in a process for preventing, inhibiting and/or removing deposits of solid matter from oil wells, pipelines and the like, and thereby improving their productivity and capacity.

In many oil wells, deposits of paraffin, wax, asphaltic and bituminous organic solids and similar materials accumulate in objectionable quantities on the face of the producing formation, on the screen or liner, or in the pump, the casing or the tubing of the well. Such deposits operate to decrease materially the productivity of the wells in which they occur. Similarly, deposits of the same character are found in some oil flow lines and oil pipelines, where they effectively reduce the capacity of the pipes, sometimes to the point where little or no fluid can be passed through such conduits in the normal manner of operation.

The purpose of removing such deposits is obvious. In some areas, wells decline in productivity at a more or less rapid rate, because of deposition of such deposits on the face of the producing formation. In some cases, the decline is sufficiently rapid that the wells must be serviced in some manner or other at a frequency ranging from several days to several weeks. In some instances, the deposition is so slow that servicing at long intervals is sufficient to maintain the well at a satisfactory level of productivity. The same is true of the various conduits through which the oil travels from the well to the refinery; such as for example through tank batteries, tank farms, pipes, etc.; and periodic servicing of such elements is also required. The capacity of a conduit of circular cross-section is reduced greatly by such deposits, usually well beyond the reduction expected from the ratio of effective cross-sectional areas of the conduit and the fouled conduit. Where organic deposits of the present type occur on formation walls, well productivity may fall substantially to zero, especially in low-pressure fields. Pipe capacities are frequently reduced to a small fraction of their capacities when clean. Ultimately such pipes may be found completely clogged by such deposits. In the case of pipelines, for example, the operator may find himself burdened with the cost of a 6" or 8" line, yet benefiting from a capacity equal to that of a 3" or 4" line. Tank capacities are also reduced by such deposits.

The process which constitutes the present invention consists in subjecting such clogging organic deposits of wax, paraffin, asphaltic or bituminous substances and the like, to the action of a chemical reagent of the char-

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acter described below, to the end that such deposits are removed from the surfaces to which they were originally adherent. By means of the process, the productivity of wells is restored as is the capacity of flow lines, pipelines, traps, tanks, pumps, and other equipment, through which such oil travels from formation to refinery.

It will be obvious that, if the first minute deposit of such organic materials is subjected to our reagent, and if such application of reagent is practised continuously or periodically with sufficient frequency, the operation is a preventive or inhibitive process rather than a corrective process. In addition, it should be noted that our reagent has a more real claim to acting as a preventive, in that surfaces effectively cleaned by its application tend to resist renewed deposition of such materials, and to remain clean and operative for longer periods than if the reagent had not been applied. Therefore, the present process is both a preventive and a corrective one. It may obviously be applied in either sense, and achieve the same ultimate goal, the improvement of efficiency of operation of wells and equipment. Thus, when we have used the word "removing," it should be clearly understood to include the prevention of organic deposits of the present kind.

Our reagent may be applied in a large number of different ways, depending upon the character of the organic material deposit it is desired to remove and on the location of such deposit. If the productivity of a well has declined to undesirably low levels and the clogging deposit is found at the formation, it may be preferable to introduce the reagent, either in undiluted form, or as an aqueous dispersion, into the fluids being produced from the well, and then tie the tubing back into the casing of the well, and circulate the fluids being produced. In this manner chemicalized well fluids are passed over the deposit for a period of from several hours to several days, usually with a striking improvement in well productivity when circulation is stopped and normal production of the well is resumed. In other cases circulation may not be desirable.

Sometimes the deposit is located at some higher or lower level in the tubing. For example, passage of the well fluids past a point in the well which lies opposite a water sand may produce a deposit at that point, because such a water sand commonly represents a point of cooling. In treating tubing deposits, the circulation method above may be practiced. However, in some instances, it is possible to introduce the reagent in undiluted or diluted form into the tubing at the well head by unscrewing the stuffing box. (Usually the tubing does not stand entirely full of fluid, because of slight leakage past the pump.) Where the reagent is introduced with large amounts of water, it will settle relatively slowly down through the oil in the tubing until it reaches the deposit. After introducing the reagent in any desirable manner, it may be allowed to stand in the tubing for any desired period of time before the well is replaced on production. In some instances it may be advisable to pump the well intermittently for very short periods of time, so as to pick up the reagent and lift it above the deposit, letting it settle down past the deposit again during the next idle period. However, one of the advantageous factors of our reagent is that it does not require shutting the well down if one so desires.

Where the organic deposits in question occur in flow lines, the reagent may be introduced and allowed to "soak" the deposit. Thereafter, normal production may be resumed; and the dislodged deposit flushed from the line by the flow of well fluids. In other instances, gas pressure is put on the soaked line, and the deposit flushed out in that manner. Sometimes, introduction of a dilute aqueous solution of the reagent is effected intermittently

and the deposit progressively removed. Or the reagent may be introduced in a continuous fashion, if desired.

In the case of pipelines, the diameter of the pipe and the length of the line make it necessary to apply the reagent in the most economical fashion possible. In such cases we have found that aqueous dilutions thereof are useful. Soaking of the line, i.e., merely introducing the diluted reagent into it and allowing the line to lie idle for a period of time, is practicable. Sometimes we prefer to prepare a relatively large volume of aqueous diluted reagent in a tank at some convenient location at one end of the pipeline, and interrupt the pumping of oil only long enough to switch to the solution tank and pump the volume of reagent dispersion into the line. Then the pumping of oil is resumed, and the liquid cylinder of reagent dispersion is thereby moved across the face of the deposit in the line, over the whole length of line. If desired, the direction of pumping may be reversed when such liquid cylinder of reagent dispersion reaches the opposite end of the line; and a second, or even a third pass or more may be made, of the diluted reagent over the deposit in the line.

Where deposits have been allowed to accumulate over a considerable period of time, they may be of such proportions that application of a normal amount of our reagent would produce sloughing of sufficient of the deposit to plug the conduit further downstream, by forming a bridge with undislodged deposit at that point. In such instances, we prefer to proceed more cautiously, introducing successive small portions of reagent and successively dislodging portions of the deposit which are sufficiently small to pass freely through the limited freeway in the conduit.

Merely introducing our reagent into an area containing a deposit, so the reagent contacts the deposit, is sometimes sufficient to cause the removal of the latter. Sometimes agitation of the reagent at the face of the deposit greatly accelerates removal of the latter. Any suitable agitation means may be employed in such instances.

Application of our reagent upstream in any system, as, for example, into a well, results in an attack on any such organic deposits further downstream. For example, wax or similar deposits, in traps and tanks, are freed and usually flowed out of such vessels in subsequent operation of the system. In the case of tanks we have found that waxy tank bottoms may be removed by introducing the reagent into the tank containing such deposits and allowing the whole to soak for any desired period of time. The deposit is thereby made more free and more readily removable. Removal of deposits of organic matter from oil production equipment, such as traps and tanks and the like, is obviously contemplated by this process.

Because there are so many conditions under which such organic deposits may occur, it is difficult to give any preferred procedure for applying our reagent. The foregoing descriptions have covered instances where such deposits were to be removed from the face of the formation, the well tubing or casing, flow lines, pipelines and tank batteries. They may be taken as preferred methods of operating the process for the respective conditions outlined. All of them are exemplary only. The process may be varied as conditions may require. In all cases, the process consists broadly in the application of the reagent to the organic deposits described above.

The reagent of the present invention is unique. It is characterized by the following components:

(1) An oxyalkylated alkanol having at least 4 carbon atoms (i.e., butanol, isobutanol, sec-butanol, amyl alcohols and isomers, hexyl alcohol and isomers thereof, cyclohexyl alcohol, etc.).

(2) An oxyalkylated substituted phenolic compound such as hydrocarbon-substituted phenols, naphthols, substituted naphthols, etc.

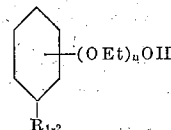
Its activity requires the presence of water. In some instances, it is desirable to have other solvents present.

Examples of suitable solvents are the lower alkanols, for example, methanol, ethanol, propanol, butanol, etc., glycols such as ethylene glycol, etc.

Specifically, the composition contains the following:

(1) An oxyethylated butyl alcohol containing an average of about 1.5–3.5 moles of ethylene oxide.

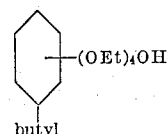
(2) An oxyethylated substituted phenol of the formula



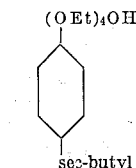
where n is, for example, from about 1 to 12, such as from 2 to 8, but preferably about 3 to 6; and R is a hydrocarbon group such as alkyl, alkenyl, aryl group having from about 2 to 12 carbons, such as from about 4 to 9 carbons, but preferably from about 4 to 6 carbons. In the preferred embodiment the composition contains the following:

(1) Oxyethylated butyl alcohol, for example butyl (OEt)₂OH

(2) Oxyethylated butylphenol, for example (OEt)₄OH



and most preferably



For optimum performance, the specific ratios of the components will vary depending on various factors, such as the particular system, the specific components employed, and the like. We have advantageously employed compositions having the following weight ratios:

Components	Operable Ratios of (1) to (2)	Preferable Ratios of (1) to (2)	Optimum Ratios of (1) to (2)
(1) Oxyalkylated butanol.....	1:5 to 6:1	1:2 to 5:1	1:1 to 4:1
(2) Oxyalkylated alkylphenol.....			

The amount of water employed can vary widely for example from about 0.5 to 20 times the sum of (1) and (2), such as from about 1 to 15 times, for example from about 3 to 12 times, but preferably from about 7 to 10 times.

In addition, solvents can be employed where desirable. For example, where the reagent is dissolved in water, an alcohol such as methanol can be employed as a pour point depressant.

For convenience stock solutions of the reagents are prepared for sale and shipment. The following are examples thereof:

Component	Operable Percent-ages of Total Formulation	Preferable Percent-ages of Total Formulation	Optimum Percent-ages of Total Formulation
(1) Oxyalkylated butanol.....	10 to 70	15 to 50	20 to 40
(2) Oxyalkylated substituted phenol.....	2 to 41	5 to 20	5 to 15
(3) Water.....	10 to 50	20 to 50	40 to 30
(4) Alcohol.....	0 to 45	10 to 40	35 to 15

The following examples are presented for purposes of illustration and not of limitation.

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EXAMPLE 1

A pumping well having a paraffin problem was downhole treated by the batchwise addition of compound A premixed with 2.5 parts water to the casing annulus at a ratio of about 2 gallons of Compound A per 25 BOPD production (2000 p.p.m.) based on daily production. This treatment successfully solved the paraffin problem in the well.

EXAMPLE 2

Continuous downhole treatment was effected by injecting Compound B premixed with 2 parts of water into the casing annulus of a well having a paraffin problem by means of a chemical proportioning pump followed with a production flow line-side stream flash. This treatment successfully solved the paraffin problem in the well.

EXAMPLE 3

A flowing well containing a production packer was treated by adding Compound C premixed with 2 parts of water down into the well by means of tubing. Since the flow line was partially plugged, paraffin was removed in two stages, (1) the flow line was treated first, followed by treatment down tubing. The ratios employed were about 2000 p.p.m. based on daily production. This treatment successfully solved the paraffin problem in the well.

EXAMPLE 4

A flow line having a paraffin problem was cleaned up and controlled by continuous injection with a chemical pump of 2 gallons of Compound D premixed with 2 parts of water.

EXAMPLE 5

A hydraulic subsurface system employing a Kobe pump which had paraffin problem was continuously treated by injecting with a chemical pump. Compound B premixed with 3 parts of water into the suction side of the Triplex pump at the rate of 1 gallon Compound B per 50 bbls. of daily production. In this way the paraffin problem was satisfactorily controlled.

EXAMPLE 6

A gas-lift well having a paraffin problem was treated in the manner employed in the flowing well employing the down tubing batch treatment. The paraffin problem was successfully solved in this way.

EXAMPLE 7

Tank bottoms were successfully cleaned by employing 1-2 gallons of Compound C premixed with 2 parts of water. This premixture was added down the tank thief-hatch and then rolled with the tank bottom by means of gas. Tank bottoms were successfully removed in this manner.

EXAMPLE 8

Compound D was mixed with 3 parts of water and injected into the well. Visual inspection of the flow line prior to starting injection indicated the tubing to be approximately half plugged with paraffin. The water premixed Compound D was injected at the rate of about 4-6 gallons per day of the mixture. After one week, the flow line was visually inspected. It was found that the flow line had the maximum opening with just trace amounts of paraffin being present.

EXAMPLE 9

Six wells in an area were treated with 9 gallons of Compound A premixed in 2 barrels of water. Three wells were circulating and 3 wells were out of production. All 6 wells responded to treatment by cleaning up well heads and flow lines of deposits of iron sulfide and paraffin. In addition 5 gallons of premixed Compound A were dumped down tubing to free rod and pumps before pulling. In 48 hours the well was pulled and rods came out clean with only a small amount of paraffin on the

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pump. The well was already producing 24 hours prior to the pull job.

EXAMPLE 10

A well produced 25 barrels of 38 gravity oil and 5 barrels of water daily for the upper Spraberry zone at a depth of about 7,158 ft. Prior to treatment, inspection of the well head showed a 1/8 inch build-up in the flow line. Three gallons of the Compound A premixed with 5 gallons of water were pumped into the casing. Inspection 48 hours later showed complete paraffin removal.

EXAMPLE 11

A well produced 60 barrels of 38 gravity oil and 23 barrels of water daily from the upper and lower Spraberry zone at a depth of about 7,759 ft. Flow line inspection showed a 1/4 in. build-up of hard paraffin in the flow line. Three gallons of Compound A premixed with 50 gallons of water were pumped into the casing. Inspection after treatment showed only partial removal of paraffin. A second treatment with the same ratio (3 gallons of Compound A in 50 gallons of water) which was pumped into the casing 7 days later removed all paraffin from the flow line.

EXAMPLE 12

A well produced 2-3 barrels of fluid per day, mostly oil. The paraffin was so bad in the well head connectors that only about a 1/2 inch opening in 2 inch connection existed. The fall plug in the end of the tree was packed solid. Twenty-four hours after treatment with Compound D most of the paraffin was removed. After 24 hours the well head connections were completely and absolutely clean down to bright metal.

EXAMPLE 13

A well making 17 barrels of oil and 48 barrels of water per day was treated as in Example 12. Prior to treatment deposition of paraffin in the well head and flow lines were 1/2 inch thick. Four days after treatment 80-90% of the paraffin had been removed.

EXAMPLE 14

A well having the following data:
Production—4 barrels oil/day plus H₂O,
TD—3,689 ft. (St. Andres),
Tubing—3,614 ft.,
Paraffin on top—2,000 ft.,
Well condition—rod hanging, had to slip clutch to move rods.

Well head had a 3/4 in. build-up of paraffin. After treatment with 4 gallons of Compound B in 51 gallons of water the well was pumped continuously for 24 hours. The next day upon inspection the well head was clean and the rod was moving free on release of clutch. Production increased to 40 barrels during first 24 hours. During the next 41 hours 27 barrels of fluid (containing 5% water) was produced.

EXAMPLE 15

A well at 5,200 ft. in San Andres formation had a 5 1/2 inch casing and 2 inch tubing. Before treatment with 4 gallons of Compound C in 40 gallons of water, production was 24 bbls./day. After treatment production increased to 60 barrels per day.

EXAMPLE 16

A well was treated with 3 gallons of Compound B in 5 gallons of water and the casing was flushed down. After 2 days paraffin in the well head became soft and after 4 days nearly all the paraffin was removed.

EXAMPLE 17

Tank bottoms were cleaned up by placing 2 gallons of Compound A in about two feet of oil in tank and circulated for 24 hours. Tank bottoms were bled off.

EXAMPLE 18

A well was inspected by pulling the ball plug off the flow line coming out of the pumping T and found to have about ½ inch of soft paraffin build-up in the line. Two gallons of Compound A premixed with 6 gallons of water were dumped down the annulus and circulated for about 6 hours. Then the well was started back in production. Two days later most of the paraffin was removed with only a thin film of paraffin left in the line.

EXAMPLE 19

A well had rods which would barely fall. Two gallons of Compound A mixed with 4 gallons of water were lubricated down the tubing and then 2 gallons of the mixture was dumped down the annulus and circulation of the well started. In several hours time the rods were falling freely and the well was cleaned up.

EXAMPLE 23

A well having 2 inch well connections swedged to a 3 inch flow line has a depth of 3,300 and produced 37° gravity oil at the rate of 28 BPD, containing 1.78% water. The flow line was plugged with hard built-up paraffin at the time of treatment. The 2 inch well head connection was plugged to a ¾ inch opening. Five gallons of Compound A in a 1 barrel of water was employed in the treatment down the annulus. Inspections of connections indicated that the 2 inch pipe was clear to metal on the lower ¾ of pipe and the top section had ¼ inch of soft paraffin. Prior treatment required the use of steam and every months roustabout crews would break out well head connections and burn them clean.

The compounds employed in the above examples have the following compositions:

	Percent			
	Compound A	Compound B	Compound C	Compound D
n-Butyl-(OCH ₂ CH ₂) ₂ OH.....	30	25		
Iso-butyl-(OHC ₂ CH ₂) ₂ OH.....			30	40
tert-Butyl-  -(OCH ₂ CH ₂) ₄ OH.....	10		15	
Sec-butyl-  -(OCH ₂ CH ₂) ₄ OH.....		10		5
Methanol.....	25	25		
Isopropanol.....			35	
Water.....	35	40	20	5

EXAMPLE 20

A 500 barrel core bottom stock tank had a 14 inch paraffin bottom build-up. The paraffin tank bottom was a hard, dense, immobile mass which is usually physically cleaned by removal of the tank B.S. plate.

This tank bottom was treated with 5 gallons of Compound A in 30 barrels of water which was thoroughly mixed and pumped into the stock tank. The fluid level in the tank was approximately 2 inches with the addition of the chemical-water mixture. The bottom and chemical mixture was then rolled with gas for 6 hours. The tank bottom was completely dispersed and the entire contents bled to the pits. The tank metal was clean and shiny after treatment.

EXAMPLE 21

Paraffin had congealed and accumulated on the internal side walls of the storage tank to a thickness of approximately 1 inch in addition to that contained in the bottom build-up. The stock tank was filled with clean lease crude to which 3 gallons of Compound A was batched through the thief hatch. The tank was then rolled with gas for 36 hours. The tank of crude was then sold to the pipe line. The tank metal (sides and bottom) was clean and shiny after treatment.

EXAMPLE 22

This example illustrates the use of this invention in the treatment of subsurface hydraulics system (Kobe). In this instance paraffin built up in the power oil line and motor end of downhole pump created excessive operating pressure. Three separate Kobe installations were treated, the wells producing 30, 60 and 70 BOPD respectively. Power oil volume in each was 200 BOPD. A mixture of 1 part of Compound A to 4 parts of water was injected into the suction of each triplex continuously at the rate of 4 gallons per day of mix. At the beginning of the test, the triplex operating pressure was 3,500 p.s.i.g. on all three installations. At the end of 4 days, the pump pressure had decreased to 2,700 p.s.i.g. which was normal. The pressure had dropped 800 p.s.i.g. during the test on all three Kobe systems. One of the pumps was pulled after the test revealing a completely clean pump and system.

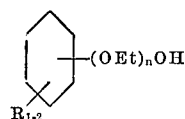
It should be noted that water is essential in the operation of this process. The water in the stock formulation is merely for convenience for in the above examples the stock formulation was further diluted with water. Thus, the amount of water contained in the reagent employed in the process has a wide range. Since water is present in the formulation, the formulation is not a paraffin solvent in the sense that a hydrocarbon would be considered a solvent for paraffin.

Other modes of applying the principle of our invention may be employed instead of those described herein, changes being made as regards the materials and methods disclosed herein, provided the steps or compositions set forth in any of the following claims, or the equivalent of such steps or compositions, are employed or obtained.

Having thus described our invention, what we claim as new and desire to obtain by Letters Patent is:

1. A composition of matter for inhibiting the formation of in and removing from oil wells and pipelines deposits of paraffin and paraffin-like solids consisting essentially of:

- (1) an alkanol selected from the group consisting of butanol, isobutanol, sec-butanol, amyl alcohol and isomers thereof, hexyl alcohol and isomers thereof, and cyclohexyl alcohol, said alkanol being oxyethylated with 1.5-3.5 moles of ethylene oxide,
- (2) an oxyethylated substituted phenolic compound having the formula



where n is an integer of 1-12, and R is a hydrocarbon group having 2-12 carbons atoms, the weight ratio of (1) to (2) being from 1:5 to 6:1,

- (3) water in the amount of 0.5 to 20 times the weight of the sum of (1) and (2), and
- (4) an alcohol selected from the group consisting of methanol, ethanol, propanol, isopropanol, butanol and ethylene glycol, said alcohol being present in an amount sufficient to be a pour point depressant.

2. The composition of claim 1 wherein (1) is an oxyethylated butanol.

3. The composition of claim 1 wherein (1) is an oxyethylated butanol and (2) is an oxyethylated alkylphenol.

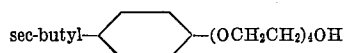
4. The composition of claim 1 wherein (1) is an oxyethylated butanol and (2) is an oxyethylated alkylphenol having 4-6 units of ethylene oxide.

5. The composition of claim 1 wherein (1) is an oxyethylated butanol and (2) is an oxyethylated alkylphenol having 3-12 units of ethylene oxide.

6. The composition of claim 1 wherein (1) is



and (2) is



the weight ratio of (1) to (2) being 2.5:1, and (3) is present in the amount of $1\frac{1}{7}$ times the weight of the sum of (1) and (2), and (4) is methanol in the amount of $\frac{5}{7}$ times the weight of the sum of (1) and (2).

7. A process for inhibiting the formation of in and removing from oil wells and pipelines deposits of paraffin and paraffin-like solids characterized by treating said wells and lines and said deposits with the composition of claim 1.

8. A process for inhibiting the formation of in and removing from oil wells and pipelines deposits of paraffin and paraffin-like solids characterized by treating said wells and lines and said deposits with the composition of claim 2.

9. A process for inhibiting the formation of in and removing from oil wells and pipelines deposits of paraffin and paraffin-like solids characterized by treating said

wells and lines and said deposits with the composition of claim 3.

10. A process for inhibiting the formation of in and removing from oil wells and pipelines deposits of paraffin and paraffin-like solids characterized by treating said wells and lines and said deposits with the composition of claim 4.

11. A process for inhibiting the formation of in and removing from oil wells and pipelines deposits of paraffin and paraffin-like solids characterized by treating said wells and lines and said deposits with the composition of claim 5.

12. A process for inhibiting the formation of in and removing from oil wells and pipelines deposits of paraffin and paraffin-like solids characterized by treating said wells and lines and said deposits with the composition of claim 6.

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