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METHOD AND COMPOSITION FOR REMOVING AND INHIBITING PARAFFIN DEPOSITION

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The present invention relates to methods for treating oil and gas wells to remove and inhibit the deposition and accumulation of wax-like substances on surfaces in contact with crude petroleum containing the wax-like substances, which deposits normally result in plugging of the conduits and passageways for transporting crude petroleum.

The present invention also relates to compositions which can be introduced into oil, and gas wells and which substantially reduce the wax accumulation and inhibit the deposition of wax-like substances on surfaces in contact with crude petroleum, including conduits and other apparatus contained in the passageways through which the crude petroleum is conducted.

One problem in the past that frequently has been encountered in the operation of oil and gas wells for the production of crude petroleum is the deposition and accumulation of wax-like substances, particularly paraffin, on the surfaces of conduits and passageways through which the wax-containing crude petroleum passes on the way to the surface. In addition, the wax-like substances also deposit in the transporting pipe lines and storage tanks and vessels which results in a serious problem of plugging and clogging of this equipment. Deposition and accumulation of waxes may cause malfunctioning of valves and pumps and other apparatus associated with the transporting of the crude petroleum. As the crude petroleum flows from the sub-surface oil-bearing formation to the surface, the wax materials normally tend to precipitate from the oil and accumulate on the interior surface of the tubing and other equipment in the well. The deposition and resulting accumulation of the wax on the surfaces progressively decreases the rate of oil production and requires that extensive cleaning operations be conducted periodically. Constrictions that develop in the pipe lines which conduct the crude oil to the storage tanks result in increased pumping costs and necessitate frequent disassembly and cleaning of the entire pipe line system.

Various attempts have been made to reduce the deposition and accumulation of paraffin within the wells, flow lines, pipe lines, pump equipment and the like, since the clogging of this equipment raises the total cost of operating the wells to maintain the desired production over a long period of time and represents a serious threat to efficiency.

A number of such attempts have taken the form of heating the crude oil to melt the waxes and thereby promote their solution in the crude oil, or employing a solvent to dissolve these materials or both. Attempts to heat the oil and/or heat the solvent are characterized by relative ineffectiveness.

Other methods have introduced solid abrasive material into the pipe line in order to abrade or wear away the waxy deposits, however, these methods are objectionable for obvious reasons including erosion of the pipe line itself and clogging of equipment by the solid abrasive particles. Moreover, such methods do not eliminate the tendency of the wax to continue building up after being worn away by the abrading action. Numerous methods had involved the use of a combination of various solvents including aromatic solvents, but these compositions have been only partially successful. Surfactants have been employed as described in U.S. Patent No. 2,927,078. In order

to be effective, this method requires that relatively large amounts of treating agent be added to the crude oil at frequent intervals. These and other methods and compositions that have been employed in the past have serious disadvantages and drawbacks associated therewith that have prevented them from becoming completely successful.

Accordingly, it is an object of the present invention to remove the accumulated wax deposits and inhibit the deposition of wax on the surfaces of oil well equipment in contact with the crude petroleum containing the wax substances and avoid the disadvantages and drawbacks associated with the prior known methods and compositions for treating oil wells.

It is a further object of this invention to provide compositions that can be introduced into oil and gas wells and which remove the paraffin accumulations and inhibit the formation of paraffin deposits on the surfaces of equipment and apparatus in contact with the crude petroleum oil containing the wax-like substances and which compositions avoid the disadvantages and drawbacks of the prior known compositions for treating oil wells.

It is a further object of the present invention to provide cleaning compositions for injection into conduits, flow passageways and the like, and storage vessels for the crude petroleum oil containing the wax-like substances for removing accumulations of paraffin wax.

It is a further object of this invention to provide compositions which are useful for cleaning metal surfaces that have deposits of accumulated wax thereon.

It is a further object of the present invention to remove wax-like substances and inhibit the deposition and accumulation of wax-like substances on surface in contact with crude oil without requiring heating of the crude oil and which enables a substantial reduction in the amount of treating composition required to maintain the surfaces in a clean condition for a relatively long period of time.

In attaining the above objects, one feature of the present invention resides in a composition containing, as the essential active ingredients, a polyalkylene glycol monoalkylether, an alkylene glycol monoalkylether and a polyoxyalkylene alkylarylether, which in combination, act to substantially completely remove the wax on the surface of the fouled equipment and further act to inhibit the deposition of the wax-like substances from crude oil.

According to another feature of the present invention, the wax accumulations and deposits on the surfaces of various equipment and apparatus in contact with wax-containing crude oil, including oil well tubing, pipe lines, well flow lines, product pipe lines, conduits, storage vessels and the like, can be substantially eliminated and the tendency for deposition of the wax upon the aforementioned surfaces can be inhibited by injecting a treating composition containing a particular combination of active ingredients into the oil well and permitting the treating composition to flow down into the oil-bearing formation and circulate into and around the surfaces of the said equipment and apparatus which serve as conduits and passageways for the wax-containing crude petrolem. The treating composition of the present invention containing the active ingredients functions to substantially completely remove the wax deposits on the surfaces and, further, functions to coat the surfaces with a layer of the treating composition which inhibits the wax particles from attaching to the surfaces and thereby prevents the deposition of the wax.

Other objects, features and advantages of the present invention will become apparent from the following detailed description thereof.

The oil and gas well treating compositions of the present invention comprise as the essential active ingredients, a polyalkylene glycol monalkylether, an alkylene glycol

monoalkylether, and a polyoxyalkylene alkylarylether adduct. Generally, the proportions of the active ingredients; viz: polyalkylene glycol monalkylether:alkylene glycol monalkylether:polyoxyalkylene alkyarylether, can vary from about 1:1:1 to 1:3:2 by weight, although the preferred proportions are about 1:2:1. When combined, the three active ingredients are particularly effective in removing the accumulated deposits of paraffn wax and in inhibiting the deposition of paraffn deposits on the surfaces of equipment employed in oil wells in contact with the crude petroleum.

The polyalkylene glycol monoalkylether component of the treating composition of the present invention can be a normally liquid alkyl ether of a polyalkylene glycol wherein the alkylene portion contains 2 to 5 carbon atoms and includes, for example, the methyl, ethyl, propyl and butyl ethers of diethylene glycol. The alkylene glycol monalkylether component of the treating composition of the present invention includes the lower alkyl ethers such as ethyl, propyl and butyl ethers of alkylene glycols wherein the alkylene portion contains 2 to 5 carbon atoms, for example.

The polyoxyalkylene alkylarylether adduct component of the treating composition of the present invention can be produced from alkylene oxides containing from 2 to 5 carbon atoms and alkylphenols wherein the alkyl group is straight or branched chained and contains 5–12 carbon atoms. Included are nonylphenolethylene oxide adducts wherein the adduct contains from approximately 2 to 10 or more moles of ethylene oxide per mole of nonylphenol. Examples of highly suitable nonylphenol-ethylene oxide ether adduct that can be employed for the purposes of the present invention include adducts containing 4–6 moles of ethylene oxide per mole of alkylphenol and mixtures containing 80% by weight of an adduct wherein the ratio of ethylene oxide is 7 moles per mole of nonylphenol and 20% by weight of an adduct wherein the mole ratio is 4 moles of ethylene oxide per mole of nonylphenol. Other examples of the normally liquid non-ionic adducts include polyoxyethylene-isooctyl phenolether adduct.

Representative of the active ingredients that comprise the treating compositions of the present invention are diethylene glycol monoethyl ether, ethylene glycol monobutyl ether, and polyoxyethylene nonylphenol ether adduct. Particularly effective for treating oil wells to inhibit the deposition and accumulation of paraffn wax is a composition containing the above ingredients in a ratio of 1:2:1 to which is added water to obtain the following formulation:

	Percent
Diethylene glycol monoethyl ether	6.63
Ethylene glycol monobutyl ether	13.26
Polyoxyethylene nonylphenol ether adduct	6.63
Water	73.48

The amount of the oil well treating composition of the present invention that is employed according to the methods of the present invention is a sufficient amount to inhibit the wax deposition. Most conveniently, it can be flushed down the well with water or mixed with water before injection into the well. It has been found, for example, that the relatively small amount of about five gallons of the above mixture per oil well has given particularly effective results which last for a greater period of time, before an additional amount of treating agent is required, than does an equal amount of conventional treating composition or an equal amount of one of the individual components of the present composition.

The particular ingredients of the present invention is particularly active in suspending the paraffn and other wax material, in finely divided form, in the crude oil so as to prevent the deposition of the wax on the surfaces of the equipment. The treating composition penetrates the oil-bearing formations to allow the oil and the gas to flow more freely and thus result in an increase in the productivity of the oil well.

In carrying out the method of the present invention, the oil well treating composition can be injected into the oil well in a number of suitable methods. For example, in a pumping well, the following operations are carried out. With the well pumping, sufficient amount of a carrier liquid is injected down the annulus between the casing and the tube. This carrier liquid can be fresh water, salt water or oil. The well is then placed on vacuum. The quantity of carrier will vary considerably with the type of well that is being treated, however, it has been found that approximately two barrels are sufficient for wells less than 2000 feet deep and approximately fixe barrels have been found to be suitable for wells exceeding 2000 feet in depth. Thereafter, about 1.25 gallons of the treating composition of the present invention together with sufficient water to make up about five gallons are injected into the annulus. Following the injection of the treating composition, a sufficient amount of additional carrier liquid is injected in order to insure that the oil well treating composition flows down and reaches the lower portions of the well. The material is circulated a sufficient length of time at least for the treating composition to flow to the bottom of the well and into the oil-bearing formation to insure adequate mixture and complete contact with all clogged or fouled surfaces. Complete circulation of the oil well treating composition in the lower depthse of the oil well tubing and casing will generally insure greater effectiveness in inhibiting the deposition of the wax on the equipment.

When it is desired to treat flowing wells, the well is first shut in and thereafter approximately five gallons of aqueous solution of the treating composition are injected down the tubing. Following that, sufficient carrier liquid such as water or oil is injected into the tubing to flush down the treating composition. The well is then allowed to remain shut in for a sufficient amount of time to allow the treating composition and water to flow to the bottom of the well. A period of time of about 24 hours has been found to be adequate before the withdrawal of well fluids is commenced.

When used with Kobe or other hydraulic pumps and where the production is returned directly to power-oil tanks it has been found suitable to introduce a small amount, e.g. one gallon, of the treating composition together with enough water to make up about five gallons into the suction line of the pump each month. If the production is returned to a storage tank, a slug treatment at the rate of about 1 to 1.5 gallons of treating composition per month can be injected into the suction line via a chemical pump.

Although previous attempts have been made to employ a nonylphenol-ethylene oxide adduct for treatment of paraffin deposits in petroleum line, as described in U.S. Patent No. 2,927,078, these methods employing a single ingredient have necessitated the use of large amounts of materials. However, the present invention employing the particular ratio of active ingredients identified above substantially reduces the amount of material that is required and eliminates substantial paraffin deposits for periods of time of 45 days and more without injecting a fresh amount of treating composition. The methods of the present invention therefore eliminate the daily addition of dewaxing substances and thereby substantially improve the efficiency of the overall production. Moreover, the treating composition of the present invention is non-corrosive and non-toxic and immediately begins to remove the deposited paraffin.

Results obtained by employing the treating composition of the present invention have been to substantially increase the production of oil and gas wells in the amount of at least 25% and in some cases even higher; for example, oil wells producing seven bbls./day have been raised to a production of 11 to 15 bbls./day.

According to the present invention oil and gas wells can be treated without resorting to the necessity of heating and injecting hot hydrocarbons into the oil wells. Moreover, because of the particular effectiveness of the ingredients of the present composition and their activity, a substantial reduction in the quantity of treating composition can be made and still obetain an excellent increase in the productivity and removal and elimination of all objectionable paraffin wax deposits.

The following example is illustrative of the present invention but is not considered as limiting thereof in any way.

A treating composition of the following formulation was employed where the percent is on a weight basis:

	Percent
Diethylene glycol monoethyl ether	6.63
Ethylene glycol monobutyl ether	13.26
Nonylphenol-ethylene oxide ether adduct	6.63
Water	73.48

5 gallons of the above treating composition were injected into a producing oil well. Approximately an equal amount of water was injected immediately thereafter and the pump was continuously recirculated for the first 24 hours before withdrawal of well fluid was commenced. Thereafter, the oil well was permitted to operate and continued operation for 45 days without requiring injection of a fresh amount of treating composition. The oil well increased production by at least about 25%.

The ether adduct employed above is a mixture of about 80% of an adduct with an ethylene oxide:nonylphenol ratio of 7:1 and 20% by weight of an adduct with an ethylene oxide:nonylphenol ratio of 4:1.

It is not completely understood how the compositions of the present invention assist in inhibiting the deposition and accumulation of paraffin on the equipment in oil wells including conduits, tubing, flow lines and pumping equipment and the like, however, it is believed that the polyoxyethylene monoalkyl ether lowers the surface tension for better penetration of the active ingredients and improves the paraffin carrying ability of the fluid. Moreover, it assists in the reverse flow-back properties of the paraffin in oil and gas producing formulation and acts as a dispersant for the paraffin in the fluid. The second ingredient, the polyalkylene glycol monoalkylether acts as a coupler and a penetrant. The alkylene glycol monoalkylether acts as a coupler to stabilize the entire composition. It is believed that the ingredients provide a thin film of treating composition which coats the various surfaces so as to inhibit deposition of paraffin wax once it has been removed. In such cases where the wax does not deposit in the subsurface equipment of the oil well operation, the treating composition can be injected into the above surface flow lines or storage tanks to prevent the deposition of the paraffin in those areas.

What is claimed is:

1. A method for inhibiting the deposition and accumulation of wax-like substances contained in crude petroleum upon the surfaces in contact with the said crude petroleum which comprises introducing into the said crude petroleum in contact with the said surfaces an inhibiting amount of a treating composition consisting essentially of a dialkylene glycol monoloweralkylether, containing from 2 to 5 carbon atoms in the alkylene group, an alkylene glycol monoloweralkylether containing from 2 to 5 carbon atoms in the alkylene group, and a polyoxyalkylene alkylphenolether wherein the alkylene group contains from 2 to 5 carbon atoms, the alkyl group contains from 5 to 12 carbon atoms, and containing from 2 to 10 moles of alkylene oxide per mole of alkylphenol, in a weight ratio of from about 1:1:1 to about 1:3:2, respectively.

2. A method as defined in claim **1** wherein the wax-like substances contained in crude petroleum is paraffin.

3. A method as defined in claim **1** wherein the treating composition consists essentially of diethylene glycol monoethylether, ethylene glycol monobutyl ether and polyoxyethylene nonylphenol ether, in a weight ratio of from about 1:1:1 to about 1:3:2, respectively.

4. The method as described in claim **1** wherein the treating composition consists essentially of diethylene glycol monoethyl ether, ethylene glycol monobutyl ether and polyoxyethylene-nonylphenol ether adduct in a weight ratio of 1:2:1.

5. A method for inhibiting the deposition and accumulation of wax-like substances contained in crude petroleum upon the surfaces past which the said crude petroleum is conducted which comprises coating said surfaces with an inhibiting amount of a treating composition consisting essentially of dialkylene glycol monoloweralkylether, wherein the alkylene group contains from 2 to 5 carbon atoms, an alkylene glycol monoloweralkylether wherein the alkylene group contains from 2 to 5 carbon atoms, and a polyalkylene alkylphenol ether adduct wherein the alkylene group contains from 2 to 5 carbon atoms, the alkyl group contains from 5 to 12 carbon atoms, and containing from 2 to 10 moles of alkylene oxide per mole of alkylphenol, in a weight ratio of from about 1:1:1 to about 1:3:2, respectively.

6. A method for treating oil and gas wells for inhibiting the deposition and accumulation of wax-like substances upon the surfaces of equipment in contact with the crude petroleum containing said wax-like substances and which comprises injecting into the well and circulating in the sub-surface oil-bearing formation an inhibiting amount of a treating composition consisting essentially of a dialkylene glycol monoloweralkylether, wherein the alkylene group contains from 2 to 5 carbon atoms, alkylene glycol monoloweralkylether wherein the alkylene group contains from 2 to 5 carbon atoms, and a polyoxyalkylene alkylphenol ether adduct, wherein the alkylene group contains from 2 to 5 carbon atoms, and the alkyl group contains from 5 to 12 carbon atoms, and containing from 2 to 10 moles of alkylene oxide per mole of alkylphenol, in a weight ratio of from 1:1:1 to 1:3:2, respectively.

7. The method as defined in claim **6** wherein the wax-like substance is paraffin.

8. The method as defined in claim **6** wherein the treating composition consists essentially of diethylene glycol monoethylether, ethylene glycol monobutylether, and polyoxyethylene nonylphenol ether adduct in a weight ratio of 1:2:1, respectively.

9. A method for treating oil and gas wells for inhibiting the deposition and accumulation of wax-like substances upon the surfaces in contact with the crude petroleum containing the wax-like substances which comprises injecting into the well an inhibiting amount of a treating-composition consisting essentially of a dialkylene glycol monoloweralkylether wherein the alkylene group contains from 2 to 5 carbon atoms, an alkylene glycol monoloweralkylether wherein the alkylene group contains from 2 to 5 carbon atoms and a polyoxyalkylene alkylether adduct wherein the alkylene group contains from 2 to 5 carbon atoms, the alkyl group contains from 5 to 12 carbon atoms, and containing from 2 to 10 moles of alkylene oxide per mole of alkylphenol, in a weight ratio of from about 1:1:1 to about 1:3:2, respectively.

10. The method as defined in claim **9** wherein the treating composition consists essentially of diethylene glycol monoethylether, ethylene glycol monobutylether, and polyoxyethylene nonylphenol ether adduct in a weight ration of 1:2:1, respectively.

11. A method for treating oil and gas wells to inhibit the deposition and accumulation of wax-like substances upon the surfaces of the passageways for conducting the crude petroleum which comprises the steps of injecting into the well a liquid selected from the group consisting of fresh water, salt water and oil, introducing into the well an inhibiting amount of a treating composition consisting essentially of dialkylene glycol monoloweralkyl-

ether wherein the alkylene group contains from 2 to 5 carbon atoms, alkylene glycol monoloweralkylether wherein the alkylene group contains from 2 to 5 carbon atoms and polyoxyalkylene nonylphenol ether adduct wherein the alkylene group contains from 2 to 5 carbon atoms and containing from 2 to 10 moles of alkylene oxide per mole of nonylphenol, in a weight ratio of from 1:1:1 to about 1:3:2, respectively, injecting additional amounts of a liquid selected from the group consisting of fresh water, salt water and oil and thereafter circulating the treating composition in the well a sufficient period of time before withdrawing fluids therefrom.

12. A method for treating oil and gas wells to inhibit the deposition and accumulation of wax-like substances upon the surfaces of the passageways for conducting the crude petroleum which comprises the steps of injecting into the well a treating composition consisting essentially of dialkylene glycol monoloweralkylether, wherein the alkylene group contains from 2 to 5 carbon atoms, alkylene glycol monoloweralkylether, wherein the alkylene group contains from 2 to 5 carbon atoms, and polyoxyalkylene nonylphenol ether adduct, wherein the alkylene group contains from 2 to 5 carbon atoms and containing from 2 to 10 moles of alkylene oxide per mole of nonylphenol, in a weight ratio of from about 1:1:1 to about 1:3:2, respectively, and injecting a sufficient amount of a liquid selected from the group consisting of fresh water, salt water and oil, and permitting the well to stand a sufficient period of time at least for the treating composition to reach the bottom of the well before withdrawal of well fluids therefrom.

13. In the method of treating oil and gas wells wherein the wax-like substances contained in the crude petroleum normally tend to accumulate upon the surfaces of the passageways for conducting the crude petroleum, the improvement whereby the accumulation of the wax-like substances on said surfaces is substantially reduced and the deposition of additional wax is inhibited and which comprises injecting into the well a sufficient amount of a treating composition consisting essentially of dialkylene glycol monoloweralkylether, wherein the alkylene group contains from 2 to 5 carbon atoms, alkylene glycol monoloweralkylether, wherein the alkylene group contains from 2 to 5 carbon atoms and polyoxyalkylene alkylphenol ether adduct wherein the alkylene group contains 2 to 5 carbon atoms, the alkyl group contains from 5 to 12 carbon atoms, and containing from 2 to 10 moles of alkylene oxide per mole of alkylphenol, in a weight ratio of from about 1:1:1 to about 1:3:2, respectively.

14. In the method of claim **13** wherein the treating composition consists essentially of diethylene glycol monoethylether, ethylene glycol monobutylether and polyoxyethylene nonylphenol ether adduct in a weight ratio of from about 1:1:1 to about 1:3:2, respectively.

15. In the method of claim **13** wherein the treating composition consists essentially of diethylene glycol monoethylether, ethylene glycol monobutylether and polyoxyethylene nonylphenol ether adduct in a weight ratio of 1:2:1, respectively.

16. In a method for treating oil wells to remove paraffin deposits on surfaces in contact with wax-containing crude oil, the improvement which comprises injecting into the oil well a composition consisting essentially of dialkylene glycol monoloweralkylether, wherein the alkylene group contains from 2 to 5 carbon atoms, an alkylene glycol monoloweralkylether wherein the alkylene group contains from 2 to 5 carbon atoms, and a polyoxyalkylene alkylphenol ether wherein the alkylene group contains from 2 to 5 carbon atoms, the alkyl group contains from 5 to 12 carbon atoms, and containing from 2 to 10 moles of alkylene oxide per mole of alkylene oxide per mole of alkylphenol, and permitting the composition to flow to the oil bearing sub-surface formation before well fluid is withdrawn therefrom.

17. A composition for treating oil and gas wells for inhibiting the deposition and accumulation of wax-like substances on surfaces that are in contact with crude petroleum containing said wax-like substances and which consists essentially of dialkylene glycol monoloweralkylether, wherein the alkylene group contains from 2 to 5 carbon atoms, alkylene glycol monoloweralkylether, wherein the alkylene group contains from 2 to 5 carbon atoms and polyoxyalkylene alkylphenol ether adduct wherein the alkylene group contains from 2 to 5 carbon atoms, the alkyl group contains from 5 to 12 carbon atoms, and containing from 2 to 10 moles of alkylene oxide per mole of alkylphenol, in a weight ratio of from about 1:1:1 to about 1:3:2, respectively.

18. A composition as defined in claim **17** which consists essentially of diethylene glycol monoethylether, ethylene glycol monobutylether, and polyoxyethylene nonylphenol ether adduct in a weight ratio of from about 1:1:1 to about 1:3:2, respectively.

19. A composition as defined in claim **1** which consists essentially of diethylene glycol monoethylether, ethylene glycol monobutylether, polyoxyethylene nonylphenol ether adduct in a weight ratio of 1:2:1, respectively.

20. An oil and gas well treating composition for controlling the formation of paraffin on surfaces that are in contact with crude petroleum containing paraffin which consists essentially of by weight, 6.63% diethylene glycol monoethylether, 13.26% ethylene glycol monobutylether, 6.63% polyoxyethylene nonylphenol ether adduct and 73.48% water.

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