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3,276,519

## PARAFFIN CONTROL METHOD

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The present invention relates to new and improved compositions for controlling or inhibiting the deposition of paraffin and the like substances on surfaces of pipes, formations and the like, past which liquid hydrocarbons are conducted, and the methods of using such compositions.

The present invention is particularly adapted to the treating of oil and gas wells and the like.

The present invention is an improvement over the composition and process disclosed in U.S. Patent No. 3,051,653.

Although the slowly soluble solid naphthalenic compounds or mixtures as disclosed in said Patent No. 3,051,653 have been found to be highly effective in most instances of application, there are some well conditions in which a liquid material or a slowly soluble material more compatible with or attuned to such well conditions is required.

It is, therefore, a primary object of the present invention to provide a composition and method for controlling or inhibiting the deposition of paraffin on surfaces past which liquid hydrocarbons are conducted, which may be applied in such variations or combinations to meet various well conditions, that optimum properties of placement can be obtained.

Another object of the present invention is to provide a paraffin control composition which is a liquid under ambient conditions and which will act to prevent paraffin from depositing in surface and down hole equipment where it is desirable to place the product in the system with a chemical pump. This enables a 100% active chemical to be introduced into the system rather than a mixture of an unactive solvent and an active paraffin preventing chemical.

Still another object of the present invention is to provide a new and improved paraffin inhibiting composition which will not freeze under atmospheric conditions and which will also provide a 100% active paraffin preventing chemical.

Yet a further object of the present invention is to provide a new and improved paraffin control composition comprising liquids, readily oil soluble solids, solids which dissolve during placement thereof, as well as slowly soluble solids.

Other objects and advantages will be readily apparent from the description of the invention set forth hereinbelow.

It has been discovered that two or more of certain polycyclic coal tar products and/or their derivatives may be combined in such manner that the compounds with the highest melting points and the lowest solubilities in crude oils, for which treatment for paraffin deposition is proposed, are obtained, thereby providing optimum properties of placement of the compounds.

Some of the classes of compounds and their alkylated and/or hydroxylated derivatives which may be used in carrying out the present invention are naphthalene, an-

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thracene, pyrene, phenanthrene, fluoranthene, fluorene, chrysene, acenaphthene, diphenyl or biphenyl, indene, naphthacene, and naphthanthracene.

Also the acids, nitrogen containing compounds, compounds which are derivations of any combinations of any of the above substituents, and aryl derivatives, of these classes of compounds may be used within the skill of a person skilled in the art.

Some examples of the chemicals are compounds which may be used in the present invention are 1-methyl phenanthrene, phenanthrol, 2-hydroxy phenanthrene, 2-methyl anthracene, anthranol, naphthanthracene, naphthacene, 1,2,5,6 - dibenzanthracene, 1,2 - benzopyrene, 3,4 - benzo-phenanthrene, diphenyl, 4-hydroxy diphenyl (p-phenyl phenol), 1,3,5-triphenyl benzene, 1-methyl naphthalene, 2-methyl naphthalene, 1,6-dimethyl naphthalene, 2,3-dimethyl naphthalene, 2,6-dimethyl naphthalene, 2,7-dimethyl naphthalene, 1-naphthoic acid, 2-naphthoic acid, 1-naphthol, 2-naphthol, abietic acid and 1-methyl 7-isopropyl phenanthrene.

In addition to the specific compounds enumerated above, the following may also be used in the present invention: mono substituted and disubstituted derivatives of phenanthrene; alkylated, hydroxylated and arylated derivatives of phenanthrene; mono substituted and disubstituted derivatives of anthracene; alkylated, hydroxylated and arylated derivatives of anthracene; alkylated and hydroxylated derivatives of chrysene; alkylated and hydroxylated derivatives of pyrene; hydroxy and alkyl derivatives of diphenyl; alkyl and hydroxy derivatives of acenaphthene; alkyl and hydroxy derivatives of fluorene; mono substituted and isomeric disubstituted derivatives of naphthalene; and alkylated and hydroxylated derivatives of naphthalene.

It should be noted, that with the exception of diphenyl and its derivatives, all of the above compounds are fused ring compounds.

By selecting from the above groups, those compounds which are liquid under ambient conditions, it is possible to provide a material which will act to prevent or inhibit paraffin from depositing on surface equipment or down hole equipment, and which can be desirably placed in the system with a chemical pump. This enables a 100% active chemical to be introduced rather than a mixture of an unactive solvent and an active paraffin inhibiting or preventing chemical. An example of this type of chemical is 1-methyl naphthalene which melts at  $-19^{\circ}\text{C}$ .

Some of the above materials having relatively low melting points can be used as solvents for the materials having higher melting points, and thereby provide a product which will not freeze under atmospheric conditions and/or provide a 100% active paraffin deposition prevention chemical.

It should also be noted that the above compounds may be dissolved in a suitable solvent and injected into an oil producing system in a manner which will provide a concentration of from about 1 p.p.m. to about 10,000 p.p.m. in the produced oil to act as a paraffin inhibiting chemical.

In actual field applications, concentrations of paraffin inhibiting composition varying from about 1 p.p.m. (parts per million) to about 20 p.p.m. of well fluids have been found to be satisfactory.

The compounds or mixtures of the present invention may be used in either liquid or solid form, and the solid

form may be particulated, in sticks, balls, or other desired forms without departing from the scope of the invention.

The present invention may be utilized in decreasing or removing paraffin depositions in tank bottoms.

It may also be used in combination with other chemicals, such as corrosion inhibitors, emulsion preventers and others when they are introduced into an oil producing system.

The inventors have authored two papers which relate to the theory they believe explains how these chemicals function as paraffin inhibiting or control agents, and which disclose in detail the various ways in which these chemicals may be used. These papers are entitled "Checking Paraffin Deposition by Crystal Growth Inhibition" and "A New Approach to the Paraffin Problem" and were presented at the 37th Annual Fall Meeting of the Society of Petroleum Engineers of AIME in Los Angeles, California, October 7-10, 1962, and at the Spring Meeting of the Mid-Continent District Division of Production in Amarillo, Texas, March 27-29, 1963, respectively.

The liquid paraffin control compounds and mixtures thereof may also be used in the manner disclosed in co-pending application, Serial No. 278,327, filed May 6, 1963.

In such well treating method, the treating or fracturing fluid containing the paraffin inhibitor is injected or pumped into the well bore at a sufficient pressure and rate to create the horizontal fracture. The treating agent is preferably a high fluid loss fluid and is also introduced into the well bore and fracture in such manner that it is lost to the face of the fracture and into the formation within the first few feet of the fracture.

The treated fluid may be further displaced into the formation by the injection of either additional treated fluid or untreated fluid. The untreated fluid should preferably be of low fluid loss to limit displacement of fluid. The amount of fluid injected into the formations will govern the extent the fluids are extended into the formation, but the flow pattern will exist without regard to the amounts of fluid injected into such formation.

After the fluids have been introduced into the formation and the well has been placed on production, the fluids injected into the well and the natural well fluids will be produced from the formation, through the fracture and into the well bore in a particular pattern.

The treating liquid which has been lost to the formation nearest the well bore will therefore be slowly produced back with the producing fluids. As only a few parts per million are required of most paraffin inhibitors to provide an effective control over the paraffin problems, a continuing control of the paraffin problem is maintained over a long period of time.

The compounds disclosed hereinabove, as well as those disclosed in U.S. Patent No. 3,051,653, and naphthalene can be used in preventing or inhibiting asphalt deposits which are found in many wells in California. These asphalt deposits are different from the ordinary paraffin deposits found in wells throughout most of the United States and the rest of the world, in that they contain little, if any, normal paraffins.

The compounds of the present invention act on the asphalt in a slightly different manner than on the paraffins, actually dissolving them or solvating them so they have little effect on the amount of paraffin which comes out of solution.

These compounds may be used for controlling or removing asphalt in methods similarly to those employed in inhibiting or controlling paraffin, and are particularly suited to be used with a hot oil, well stimulation process. U.S. Patents No. 2,300,348 and 3,014,531 are illustrative of hot oil, well stimulation processes.

A number of field jobs have been successfully performed in the Odessa area of West Texas using a liquid paraffin control material, a mixture of naphthalene and beta naphthol in an aromatic solvent. The use of this

liquid material was particularly successful when used with hydraulic pump installations. The liquid paraffin inhibiting agent was injected into the suction of the power unit with a standard chemical pump. A reduction and a stabilization in the power oil pressure, as well as an increase in production, were reported in most instances.

A laboratory project was conducted to study the effect of various substances on the softening points of asphalt. It is believed that colloidal asphalt plays an important role in paraffin depositions, and a large lowering of the softening point of the asphalt indicates a strong interaction of the additive tested with the asphalt.

Samples of Donna Spears asphalt were obtained from the Kerr-McGee Refining Company located at Wynnewood, Oklahoma. The softening points of these asphalts were determined with a TGA-A.S.T.M. ring and ball tester according to the procedure given in A.S.T.M., Serial D36-26.

Table I shows the softening point lowering obtained by adding 5% by weight of a variety of materials to the asphalt sample.

TABLE I.—EFFECT OF VARIOUS ADDITIVES ON THE SOFTENING POINT OF ASPHALT

Type of Asphalt.....Donna Spears.  
Softening point of asphalt.....111° F.  
Concentration of additives.....5% by wt.

| Additive                     | Melting Point of Additive, ° F. | Softening Point of Mixture, ° F. | Softening Point Lowering, ° F. | Percent Lowering |
|------------------------------|---------------------------------|----------------------------------|--------------------------------|------------------|
| P-126 wax <sup>1</sup> ..... | 126                             | 103                              | -8                             | 7.2              |
| Anthracene.....              | 423                             | 100                              | -11                            | 9.9              |
| Para-phenyl phenol.....      | 329                             | 99                               | -12                            | 10.8             |
| Beta-Naphthol.....           | 252                             | 93                               | -18                            | 16.3             |
| Kerosene.....                | liquid                          | 89                               | -22                            | 19.8             |
| Naphthalene.....             | 176                             | 86                               | -25                            | 22.5             |

<sup>1</sup> A paraffinic wax having a melting point of 126° F.

Naphthalene lowered the softening point considerably more than did the other solids and even a little more than the same weight of liquid kerosene. This indicates a strong interaction between these two substances. The wax had very little effect on the softening point of the asphalt, as expected.

The other three solids all have considerably higher melting points than either the wax or naphthalene and the softening point lowerings obtained with them were greater than with the wax, and less than with naphthalene.

Table II shows the effect of naphthalene concentration on the softening points of several samples of the Donna Spears asphalt and also on several samples of another asphalt identified as Rock Island Tussy. The effect appears to be similar with either type of asphalt.

TABLE II.—EFFECT OF NAPHTHALENE ON SOFTENING POINTS OF ASPHALTS

| Asphalt              | Percent Naphthalene by Weight | Softening Point of Mixture, ° F. | Softening Point Lowering, ° F. | Percent Lowering |
|----------------------|-------------------------------|----------------------------------|--------------------------------|------------------|
| Rock Island Tussy .. | 0                             | 121                              | 0                              | 0                |
| Do.....              | 1                             | 114                              | -7                             | 5.8              |
| Do.....              | 5                             | 94                               | -27                            | 22.3             |
| Donna Spears.....    | 0                             | 111                              | 0                              | 0                |
| Do.....              | 1                             | 104                              | -7                             | 6.3              |
| Do.....              | 5                             | 86                               | -25                            | 22.5             |

Using the testing procedures as disclosed hereinabove, another sample of asphalt, having a softening point of

167° F., and obtained from the Kerr-McGee Refining Company was tested. The results of these tests are shown in Table III, wherein each compound was added to the asphalt sample in the stated percentage thereof and the softening point for each mixture was determined.

TABLE III

| Compound                 | Percent Compound by Weight | Softening Point of Mixture, ° F. |
|--------------------------|----------------------------|----------------------------------|
| Naphthalene              | 1                          | 166.0                            |
|                          | 5                          | 152.5                            |
|                          | 10                         | 106.0                            |
|                          | 20                         | 86.5                             |
| Anthracene               | 1                          | 158.0                            |
|                          | 5                          | 150.0                            |
|                          | 10                         | 159.0                            |
|                          | 1                          | 161.0                            |
| Alpha methyl naphthalene | 5                          | 137.0                            |
|                          | 10                         | 117.0                            |
|                          | 1                          | 158.0                            |
|                          | 5                          | 147.0                            |
| Beta naphthol            | 10                         | 120.0                            |
|                          | 1                          | 160.0                            |
|                          | 5                          | 144.0                            |
|                          | 10                         | 155.0                            |
| Para-phenyl phenol       | 1                          | 157.0                            |
|                          | 5                          | 121.0                            |
|                          | 10                         | 110.0                            |
|                          | 1                          | 162.0                            |
| Xylene bottoms           | 5                          | 134.0                            |
|                          | 10                         | 115.0                            |
| Acintene Dipentene       | 1                          |                                  |
|                          | 5                          |                                  |
|                          | 10                         |                                  |
|                          | 10                         |                                  |

Although there are some wells having paraffin problems which can be helped by the addition thereto of a small amount of a single one of the compounds disclosed hereinabove, it is preferred that the paraffin control material be tailored to the particular well to be treated and that mixtures of two or more of such compounds be used, such as a mixture comprising naphthalene, beta naphthol and an aromatic solvent or a mixture comprising naphthalene, beta naphthol, and xylene bottoms.

Broadly, the present invention relates to a new and improved method of controlling or inhibiting the deposition of paraffin in wells by the treating therewith of certain polycyclic aromatic compounds, principally fused ring compounds, in either liquid or solid form.

What is claimed is:

1. A method of treating oil and gas wells and other equipment for inhibiting the formation of paraffin on surfaces past which liquid hydrocarbons are conducted, comprising the step of introducing into the well or other equipment a treating composition consisting of at least one polycyclic aromatic compound having at least two rings of carbon atoms, said polycyclic aromatic compound selected from the group consisting of pyrene, phenanthrene, fluoranthene, fluorene, chrysene, acenaphthene, indene, naphthacene, naphthanthracene, the alkylated derivatives thereof, the hydroxylated derivatives thereof, the acid derivatives thereof, the nitrogen-containing compounds derived therefrom and the arylated derivatives thereof and said composition having been tailored for the conditions of the well being treated.

2. A method of treating oil and gas wells and other equipment for inhibiting the formation of paraffin on surfaces past which liquid hydrocarbons are conducted, comprising the step of introducing into the well or other equipment a treating composition consisting of a mixture of at least two polycyclic aromatic compounds, said polycyclic aromatic compound selected from the group consisting of pyrene, phenanthrene, fluoranthene, fluorene, chrysene, acenaphthene, indene, naphthacene, naphthanthracene, the alkylated derivatives thereof, the hydroxylated derivatives thereof, the acid derivatives thereof, the nitrogen-containing compound derived therefrom and the arylated derivatives thereof, each of said compounds having at least two rings of carbon atoms, and said composition having been tailored for the conditions of the well being treated.

3. A method of inhibiting or controlling the formation

of paraffin on surfaces past which hydrocarbons flow in a well, over a prolonged period of time, comprising the step of, introducing into the well a relatively high fluid loss paraffin inhibiting liquid, the active ingredient of which is selected from the group of polycyclic aromatic compounds consisting of pyrene, phenanthrene, fluoranthene, fluorene, chrysene, acenaphthene, indene, naphthacene, naphthanthracene, the alkylated derivatives thereof, the hydroxylated derivatives thereof, the acid derivatives thereof, the nitrogen containing compounds derived therefrom, the arylated derivatives thereof and mixtures thereof.

4. The method of claim 3, wherein said paraffin inhibiting liquid is a composition comprising naphthalene, beta naphthol and an aromatic solvent.

5. The method of claim 3, wherein said paraffin inhibiting liquid is a composition comprising naphthalene, beta naphthol and xylene bottoms.

6. A method of hydraulically producing fractures in underground strata penetrated by the bore of a well, comprising the steps of:

(a) introducing into the well a fracturing fluid having a paraffin inhibiting liquid dispersed in at least the spearhead thereof, said paraffin inhibiting liquid being selected from the group of polycyclic aromatic compounds consisting of pyrene, phenanthrene, fluoranthene, fluorene, chrysene, acenaphthene, indene, naphthacene, naphthanthracene, the alkylated derivatives thereof, the hydroxylated derivatives thereof, the acid derivatives thereof, the nitrogen containing compounds derived therefrom, the arylated derivatives thereof and mixtures thereof;

(b) causing said fluid to contact a section of the underground strata to be fractured;

(c) applying sufficient pressure to said fluid to fracture said strata section and inject therein fluid containing said paraffin inhibiting liquid, whereby said paraffin inhibiting liquid is lost to the face of the fracture and into the strata section; and

(d) allowing the paraffin inhibiting liquid to be produced back with the well fluids thereby providing a continuing paraffin inhibiting treatment.

7. The method of claim 6, wherein said paraffin inhibiting liquid is a composition comprising naphthalene, beta naphthol and an aromatic solvent.

8. The method of claim 6, wherein said paraffin inhibiting liquid is a composition comprising naphthalene, beta naphthol and xylene bottoms.

9. A method of treating oil and gas wells and the like for inhibiting the deposition of asphalt on surfaces past which liquid hydrocarbons are conducted, comprising the step of introducing into the well a treating composition consisting of at least one polycyclic aromatic compound having at least two rings of carbon atoms, said polycyclic aromatic compound selected from the group consisting of pyrene, phenanthrene, fluoranthene, fluorene, chrysene, acenaphthene, indene, naphthacene, naphthanthracene, the alkylated derivatives thereof, the hydroxylated derivatives thereof, the acid derivatives thereof, the nitrogen-containing compounds derived therefrom and the arylated derivatives thereof.

10. A method of treating oil and gas wells and the like for inhibiting the deposition of asphalt on surfaces past which liquid hydrocarbons are conducted, comprising the step of introducing into the well a treating composition selected from the group consisting of pyrene, phenanthrene, fluoranthene, fluorene, chrysene, acenaphthene, indene, naphthacene, naphthanthracene, the alkylated derivatives thereof, the hydroxylated derivatives thereof, the acid derivatives thereof, the nitrogen containing compounds derived therefrom, the arylated derivatives thereof and mixtures thereof.

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