Maintenance of Oil Production and Refining Equipment

The present invention relates to the removal of deposits in oil production and refining equipment and in particular to the removal of deposits of asphaltene and/or petroleum waxes from such equipment.

Crude petroleum is a mixture of many components which varies depending on the source. Typically, it will include relatively low molecular weight components, mostly hydrocarbons including aliphatic and aromatic compounds. Relatively low molecular weight products such as naphtha, gasoline, diesel or light fuel oil, benzene and toluene are obtained mainly from these components. Usually crude petroleum also includes materials having much higher molecular weights including those known as asphaltenes and petroleum waxes. Asphaltenes vary depending on the source of the oil, but are typically polycyclic, usually aromatic or partly aromatic, compounds, including heterocyclic especially N and S atoms, and typically with multiple aliphatic substituent chains. Asphaltenes are probably not truly soluble in most crude oils, but are present as fine particles or platelets. Their dispersion in the oil is aided by the presence of resinous materials usually called maltenes and the relatively high temperatures of most oil producing formations. Petroleum waxes are long chain, typically C_{15} to C_{100}, usually mainly open chain aliphatic compounds. They are often described as paraffins and may be straight or branched chain materials. Usually they are soluble in crude oil, particularly at the temperatures of most oil producing formations.

In refining, the normal fate of these materials is to be cracked into lower molecular weight compounds that then form part of useful fractions in the products e.g. petroleum waxes can be converted into useful shorter chain alkanes or alkenes, or to end up as still bottoms e.g. as part of bitumenic products.

During production and processing, and in particular at temperatures below those of the oil producing formation, asphaltenes and petroleum waxes may separate from the bulk of the oil and may become solidified as deposits on surfaces with which they are in contact. These deposits can block the well or other pipes through which the oil passes, or be deposits at the bottom of separation vessels or storage tanks during production and the early stages of refinery operations. It is important to remove such deposits to avoid blockage of pipes and reduction in the capacity of vessels.

Conventionally, aromatic solvent, such as xylene, sometimes in combination with dispersants are used to remove both asphaltenes and petroleum waxes from pipes and vessels. Such aromatic materials are good solvents, but environmental considerations are leading to pressure to reduce the proportion of such volatile aromatic compounds used in industrial applications.

The present invention is based on the discovery that certain, particularly alkyl, esters of aromatic carboxylic acids, particularly benzoic acid, are very effective solvents for materials deposited in oil

recovery and refining equipment, particularly asphaltenes and petroleum waxes and are environmentally much less objectionable than the xylenic solvents currently used for such purposes.

The present invention accordingly provides a method of removing from or preventing or inhibiting the deposition in a well pipe or vessel of asphaltenes and/or petroleum waxes which comprises contacting the asphaltene and/or petroleum wax or the well pipe or vessel adjacent a location where deposition of asphaltene and/or petroleum wax is expected, with a solvent including at least one compound of the formula (I):

$$R^1 - (AO)_n - OOC - (CH_2)_m - Ph - (R^2)_p \qquad (I)$$

where

R^1 is a C_1 to C_{20} hydrocarbyl group, particularly a C_3 to C_{18} alkyl or alkenyl group;

AO is an alkyleneoxy group, particularly an ethyleneoxy or a propyleneoxy group, and may vary along the (poly)alkyleneoxy chain;

n 0 or from 1 to 100, desirably 0;

m is 0, 1 or 2, desirably 0; and

Ph is a phenyl group, which may be substituted with groups $(R^2)_p$; where each R^2 is independently a C_1 to C_4 alkyl or alkoxy group; and p is 0, 1 or 2, desirably 0;

and subsequently removing the solvent with softened, dissolved or dispersed asphaltenes and/or petroleum waxes from the well, pipe or vessel.

In the compound of the formula (I) used in the invention R^1 can be an alkyl or alkenyl group. Alkyl groups have the advantage that they are more stable, particularly to oxidation than alkenyl groups, but alkenyl esters generally remain fluid at lower temperatures than alkyl esters, especially for longer chain materials. Desirably, an alkenyl group includes only a single double bond as multiple unsaturation generally gives poor stability. In removing asphaltenes, R^1 is particularly a relatively short chain, such as a C_2 to C_{10} chain, for example a C_3 to C_6, alkyl group. Desirably R^1 is branched e.g. it is an *iso*-propyl (prop-2-yl), *sec*-butyl (but-2-yl), *iso*-butyl (2-methyl-prop1-yl), *tert*-butyl and/or 2-ethyl hexyl group, to reduce the ease with which the ester can be hydrolysed. Esters with secondary alcohols are particularly useful in this regard and R^1 is thus especially a C_3 to C_5 secondary alkyl group and very desirably an *iso*-propyl group. Other relatively short chain alkyl esters that can be used include ethyl, nonyl, and other straight chain alkyl benzoates such as propyl, butyl, pentyl and hexyl benzoates. A benefit of relatively short chain esters is that they have low viscosity. In removing petroleum waxes, longer chain esters may be desirable to improve the low temperature solubility of the waxes in the solvent. Thus, R^1 can be a C_6 to C_{20}, particularly a C_8 to C_{18} alkyl or alkenyl group which may be straight chain e.g. as in mixed esters such as (mixed C_{12}/C_{13} alkyl) benzoate, or branched e.g. as in 2-ethylhexyl or *iso*-nonyl or branched chain C_{18} alkyl as in so-called *iso*-stearyl (actually a mixture of

mainly branched C_{14} to C_{22} alkyl with an average chain length close to C_{18}). Unsaturated longer chain groups include oleyl. Where longer chain length groups are used, particularly longer than C_{12}, it is desirable that they are or include branching and/or unsaturation and/or that mixtures of such esters are used, as these promote liquid esters where straight chain saturated ester compounds may be solid and thus more difficult to use.

Although the carboxylic acid used in the ester can be a dihydrocinnamic acid or a phenylacetic acid, it is very desirably a benzoic acid i.e. desirably m is 0. Similarly, although the phenyl ring of the acid may be substituted, it is desirable that it is unsubstituted i.e. desirably p is 0. The esters used in the invention may include a (poly)alkyleneoxy chain, $(AO)_n$ in formula (I), between the carboxyl group and the group R^1. When present the (poly)alkyleneoxy chain is desirably a (poly)ethyleneoxy, a (poly)propyleneoxy chain or a chain including both ethyleneoxy and propyleneoxy residues. Generally, it is desirable not to include such a chain in the ester i.e. desirably n is 0.

Particularly for dissolving asphaltenes, an especially useful ester is *iso*-propyl benzoate and the invention specifically includes a method of the invention in which the solvent is or includes *iso*-propyl benzoate. *Iso*-propyl benzoate has a combination of properties that make it exceptionally useful in the solvent role. As a pure material, it has a wide liquid range having a high boiling point (BP ca 219°C) and remaining fluid at temperatures below normally expected environmental temperatures (pour point < -60°C); it has a flash point (ca 99°C) so that it is classified as non-flammable and under normal use conditions it has a low vapour pressure; it has a density similar to that of water (1.008 $kg.l^{-1}$ at 25°C); and a low viscosity (2.32 cSt at 25°C; measured by the U tube method, equivalent to 2.34 mPa.s).

By comparison other alkyl benzoates have viscosities (at 25°C) as follows:

ethyl benzoate: 1.9 cSt; 2-ethyl hexyl benzoate: 6.1cSt; nonyl benzoate: 7.5cSt; (mixed C_{12}/C_{13} alkyl) benzoate: 14cSt; and *iso*-stearyl benzoate: 30cSt.

To provide a balance of solubility for both asphaltene and petroleum wax, mixed esters, having a variety of groups R^1, or blends of compounds of the formula (I), may be advantageous by providing a combination of solvency properties matching combinations of asphaltene and waxes. Such mixed esters of blends can have the additional benefit that they are more liquid than pure, especially linear saturated compounds of similar overall R^1 carbon number.

The solvent used in the method of the invention can be wholly of one or more compounds of the formula (I), or it may contain other solvents in admixture. Although xylenes can be included it is unlikely that xylenes or other solvent including a substantial proportion of aromatic hydrocarbons will be used as a major component of any such mixed carrier fluid, because of its adverse environmental impact. Mixtures with paraffinic liquid solvents may improve the solubility of petroleum waxes, but are

likely to reduce the solubility of asphaltenes. Other solvents such as water soluble alcohols may be included either as carriers for additives (see below) or to improve compatibility with aqueous materials in use. In such mixed solvents, the proportions used will thus depend on the particular nature of material deposited in the pipe or vessel, and probably on the balance and detailed composition of asphaltenes and waxes. When mixtures are used, compounds of the formula (I) will typically be present in at least 25%, usually at least 40%, more usually at least 50%, desirably at least 60%, and particularly at least 75%, by weight of the total carrier fluid used. When present, other solvent components will desirably be used at level typically of from 1 to 75, usually 1 to 40%, more desirably 2 to 25, and particularly 5 to 15% by weight of the total carrier fluid used.

To aid in dispersing the asphaltene and/or petroleum wax, the solvent may include dispersants, particularly non-ionic surfactants and dispersants such as alcohol alkoxylates; reaction products between poly-*iso*-butylene succinic anhydrides (PIBSA's) and alcohol alkoxylates, particularly C_{10} to C_{18} e.g. C_{13} to C_{15} alcohol ethoxylates; reaction products between PIBSA's and alkanolamines such as di- and tri-ethanolamine; and sorbitan fatty acid esters, especially mono esters and particularly esters of unsaturated fatty acids e.g. sorbitan mono-oleate; sulphonic acid dispersants such as alkyl aryl sulphonic acids; or resinous dispersants such as phenol formaldehyde resin dispersants and ethylene vinyl acetate co-polymers. When used dispersants will typically be included as from 1 to 40%, more usually 1 to 30% and desirably from 1 to 20%, by weight of the solvent formulation.

Further additives such as fluid loss agents particularly such as synthetic polymers such as polyacrylamides, polyacrylates, polyamides and similar polymers (some of which can also function as viscosity improving agents); corrosion inhibitors; demulsifiers; scale inhibitors; oxygen scavengers; and other similar additive materials, can be included in the solvent formulation used in the invention. Particularly when such other additives are used, one or more co-solvents may be used e.g. a water soluble alcohol, such as propanol, particularly for use in systems operating in the presence of water, and/or a dispersant for the additive may be included.

Generally, in production wells, the temperatures of the oil bearing formation and the crude oil are often superambient typically within the range 50 to 150°C, particularly 60 to 120°C. Asphaltene and/or waxes tend to be deposited at temperatures below those of the formation, but generally within or somewhat below the ranges given above, particularly in the range 40 to 110°C. The compounds of the formula (I), particularly *iso*-propyl benzoate, are better solvents for such materials at such moderately elevated temperatures. Thus it may be advantageous to operate at superambient temperature e.g. by heating the solvent, either deliberately or e.g. in an oil well by contact with rock formations at elevated temperatures, to improve solvent performance. The temperature of pipes, tanks and refinery

equipment will generally be determined by the desired operating temperatures (often linked to the feed temperature).

The equipment treated can be pipes such as pipes in oil well structures, including the interior bore of well casings, pipelines, including well head pipes, undersea pipes and pipework in refineries; or vessels such as oil separators (to separate gas, oil water and resinous phases); storage tanks, particularly near the well head and at or near refineries; and refinery equipment. The removal of deposits of asphaltenes and/or waxes can be by way of introducing a body of solvent into contact with the deposit, if necessary providing circulation or agitation of the solvent, and removal of the softened, dissolved or dispersed deposit from the equipment. In storage tanks and other refinery process locations, the use of solvents to remove tank bottoms has the advantage of not needing to open the tank for mechanical cleaning. The tank contents, tank bottoms and/or solvent can be heated to aid solubilisation and the tarry solid tank bottoms dispersed into the solvent and usually added to a crude oil stream for further refinery processing.

The invention includes a method of treating an oil storage tank, vessel, or oil refinery pipework to remove deposits of asphaltenes and/or petroleum waxes, in which a treatment material including a compound of the formula (I) as defined above is introduced into the tank, vessel or pipework at or adjacent the location of a deposit of asphaltene and/or petroleum wax, and subsequently softened dispersed or dissolved asphaltene and/or petroleum wax is removed from the tank, vessel or pipework.

Particularly in oil wells, conventional techniques include preventative application of solvents optionally including dispersants with the aim of preventing flocculation and deposition of asphaltenes and/or waxes. These methods generally involve continuous treatment by pumping the treatment material down the well e.g. using capillary tubing, or by a slip stream. This lays down a thin layer of treatment material in the area where deposition is considered likely and can effectively prevent flocculation and deposition in the tubing and flow lines. They are less effective in preventing deposition in the near wellbore area e.g. within the production formation itself. In such cases the treatment material needs to be placed in the formation where it can inhibit solid deposition e.g. by squeezing the treatment material into the formation.

The invention accordingly includes a method of treating an oil well to remove a deposit of asphaltenes and/or petroleum waxes, in which a solvent including a compound of the formula (I) as defined above is introduced into the oil well in or adjacent to a deposit on a surface or in a rock formation.

The invention further includes a method of treating an oil well to inhibit or prevent the deposition of asphaltenes and/or petroleum waxes, in which a stream of a treatment material including a compound of the formula (I) as defined above is introduced into the oil well in a location, particularly onto a

surface or into a rock formation, where deposition is expected thereby carrying away asphaltenes and/or petroleum waxes before they are deposited on the surface or in the formation.

The following Examples illustrate the invention. All parts and percentages are by weight unless otherwise specified.

Example 1

Scampton C4 crude oil was added to hexane to precipitate asphaltene (the hexane dissolves asphaltene stabilising resins), the upper solvent layer was removed and residual hexane allowed to evaporate to give asphaltene as a viscous liquid residue. 5.2 g *iso*-propyl benzoate solvent was added to 0.048 g of asphaltene and after a few minutes at ambient temperature virtually all the asphaltene had dissolved (a few very small particles of asphaltene remained visible in the solution). The estimated (minimum) solubility was calculated as ca 0.85% by weight.

Example 1a

In a separate experiment, asphaltene was made as described in Example 1and its solubility was assessed in the various solvents as decribed in Example 1. The solvents were ethyl benzoate, *iso*-propyl benzoate, 2-ethyl hexyl benzoate, nonyl benzoate, 3:1 by weight mixture of *iso*-propyl benzoate and nonyl benzoate, (mixed C12/C13 alkyl) benzoate and *iso*-stearyl benzoate. In each case the majority of the asphaltene dissolved but a few very small particles remained visible in the solution.

Example 2

About 0.025 g asphaltene (obtained as described in Example 1) was smeared onto a weighed 5 cm x 1 cm rectangular mild steel coupon and placed inside a weighed glass jar which was then reweighed to give the amount of asphaltene by difference. About 2 ml solvent (weighed accurately) was added, the jar sealed and the sealed jar placed on moving rollers, so that the metal coupon was constantly covered with solvent at ambient temperature, for about half an hour. The asphaltene was removed completely from the metal coupon, indicating an effective minimum solubility of asphaltene in the solvent of 1.3%. Similar results were obtained using xylene as the solvent.

Example 2a

In a separate experiment, Example 2 was repeated using the solvents listed in Example 1a. In each case, the solvent removed all of the asphaltene from the metal coupon.

Example 3

Example 2 was repeated using about 0.18 g asphaltene and about 0.5 ml *iso*-propyl benzoate. Again the solvent removed all the asphaltene from the metal coupon.

Example 3a

In a separate experiment, Example 3 was repeated using different quantities: 0.4 g of asphaltene and 1 ml solvent, and the solvents listed in Example 1a. In each case, at the end of the rolling most of the asphaltene was removed, but small traces were left adhering to the metal surface. The residues could not be measured quantitatively, but visual inspection of the metal coupons suggested that the ranking of the solvents in this test was (from best to worst):

ethyl benzoate > nonyl benzoate > 2-ethyl hexyl benzoate > 3:1 by weight mixture of *iso*-propyl benzoate and nonyl benzoate > *iso*-propyl benzoate > (mixed C12/C13 alkyl) benzoate > *iso*-stearyl benzoate.

Example 4

The solubility of soft white paraffin wax [mp 49 to 59°C] in *iso*-propyl benzoate was measured. At ambient temperature, the wax solubility was low (less than 1%), but on warming to 50 to 60°C more than 60% by weight (on solvent) of the wax could be dissolved.

Example 4a

In a separate experiment, Example 4 was repeated to assess the solubility of soft white paraffin wax in the solvents listed in Example 1a. In each case the solubility appeared to be low at ambient temperature but at 60°C more than 60% by weight of wax cound be dissolved in each of the solvents.

Example 5

Weighed metal coupons were coated with the wax described in Example 4 by smearing the soft paraffin onto the coupon surface and tested for wax removal by *iso*-propyl benzoate using the method described in Example 2. The amount of wax was about 10% by weight of the solvent. At ambient temperature, a small amount of wax was removed giving a cloudy solution, but at 59°C all the wax was readily removed from the coupon surface.

Example 5a

In a separate experiment, Example 5 was repeated using soft white paraffin wax and the solvents listed in Example 1a. Each of the solvents removed all the wax at ambeint temperature giving cloudy solutions. Visual inspection of the extent of cloudiness suggested that the ranking of the solvents in this test was (from best to worst):

iso-stearyl benzoate ~ *iso*-stearyl benzoate > nonyl benzoate ~ 2-ethyl hexyl benzoate > ethyl benzoate ~ *iso*-propyl benzoate ~ 3:1 by weight mixture of *iso*-propyl benzoate and nonyl benzoate.

CLAIMS

1 A method of removing from, or preventing or inhibiting the deposition in, a well, pipe or vessel, of asphaltenes and/or petroleum waxes which comprises contacting the asphaltene and/or petroleum wax or the well pipe or vessel adjacent a location where deposition of asphaltene and/or petroleum wax is expected, with a solvent including at least one compound of the formula (I):

$$R^1 - (AO)_n - OOC - (CH_2)_m - Ph - (R^2)_p \qquad (I)$$

where

R^1 is a C_1 to C_{20} hydrocarbyl group;

AO is an alkyleneoxy group and may vary along the (poly)alkyleneoxy chain;

n 0 or from 1 to 100;

m is 0, 1 or 2; and

Ph is a phenyl group, which may be substituted with groups $(R^2)_p$; where each R^2 is independently a C_1 to C_4 alkyl or alkoxy group; and p is 0, 1 or 2;

and subsequently removing the solvent with softened, dissolved or dispersed asphaltenes and/or petroleum waxes from the well, pipe or vessel.

2 A method as claimed in claim 1 wherein m, n and p are all 0.

3 A method as claimed in either claim 1 or claim 2 wherein R^1 is a C_3 to C_5 branched alkyl group.

4 A method as claimed in any one of claims 1 to 3 wherein the solvent is or includes *iso*-propyl benzoate.

5 A method as claimed in either claim 1 or claim 2 wherein R^1 is a C8 to C20 branched and/or unsaturated alkyl or alkenyl group.

6 A method as claimed in any one of claims 1 to 5 wherein the asphaltene and/or petroleum wax is contacted with the solvent at a superambient temperature.

7 A method as claimed in any one of claims 1 to 6 wherein the solvent includes a dispersant for the asphaltene and/or petroleum wax.

8 A method as claimed in any one of claims 1 to 7 to treat an oil storage tank, vessel, or oil refinery pipework to remove deposits of asphaltenes and/or petroleum waxes, in which a solvent including a compound of the formula (I) as defined above, is introduced into the tank, vessel or pipework at or adjacent the location of a deposit of asphaltene and/or petroleum wax, and subsequently softened dispersed or dissolved asphaltene and/or petroleum wax is removed from the tank, vessel or pipework.

9 A method as claimed in any one of claims 1 to 7 to treat an oil well to treat an oil well to remove a deposit of asphaltenes and/or petroleum waxes, in which a solvent including a compound of the formula (I) as defined above, is introduced into the oil well in or adjacent to a deposit on a surface or in a rock formation and subsequently softened dispersed or dissolved asphaltene and/or petroleum wax is removed from the surface or formation.

10 A method as claimed in any one of claims 1 to 7 to treat an oil well to inhibit or prevent the deposition of asphaltenes and/or petroleum waxes, in which a stream of a solvent including a compound of the formula (I) as defined above, is introduced into the oil well in a location, particularly onto a surface or into a rock formation, where deposition is expected thereby carrying away asphaltenes and/or petroleum waxes before they are deposited on the surface or in the formation.