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(54) **Steam foam drive process**

(57) A steam foam drive process for displacing oil within a subterranean

reservoir is improved by injecting into the reservoir a steam-foam-forming mixture of steam, and an olefin sulfonate-containing surfactant component.

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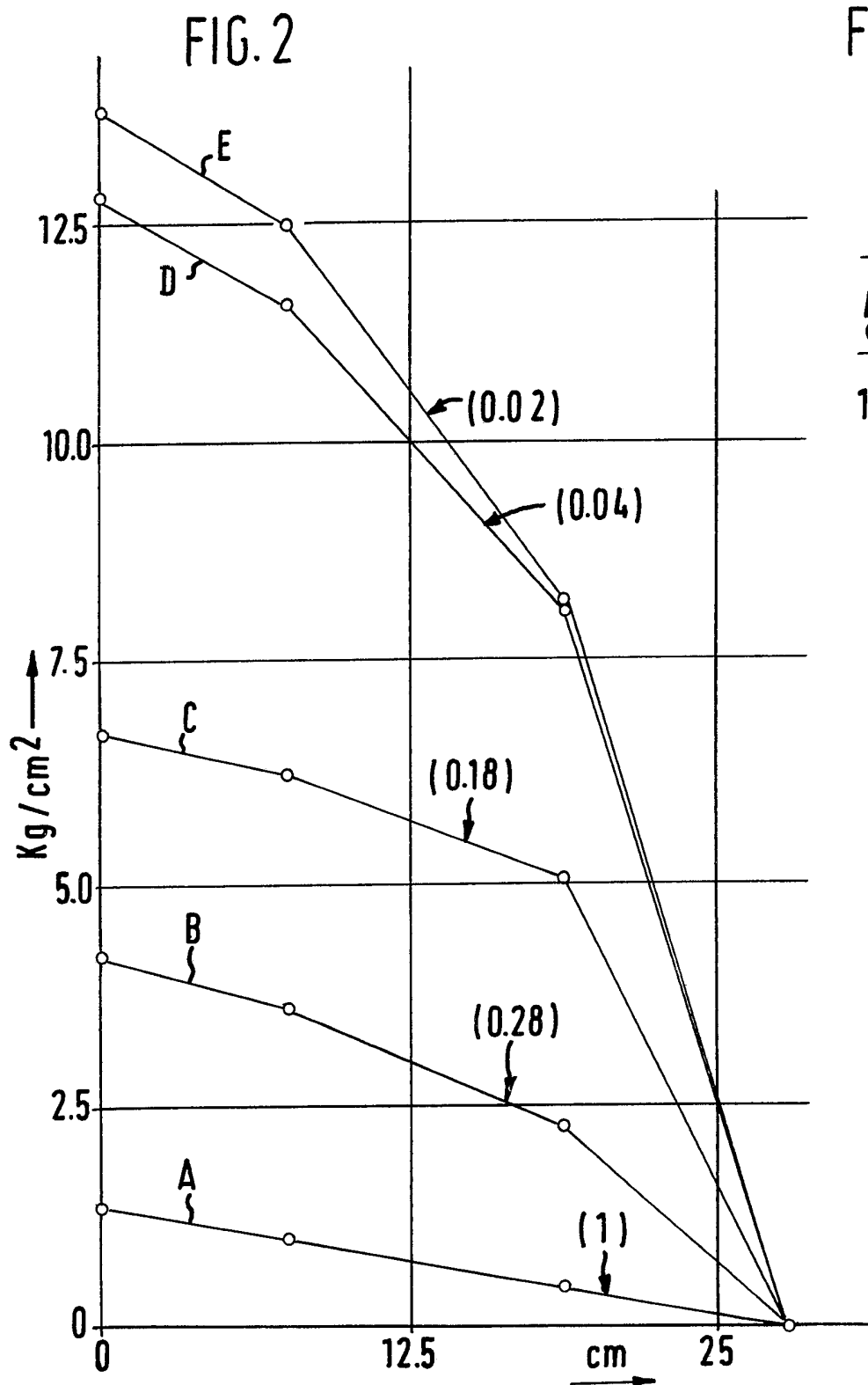
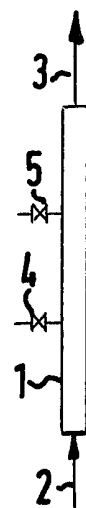


FIG. 1



SPECIFICATION

Steam foam drive process

The invention relates to a steam foam drive process for producing oil from, or displacing oil within, a subterranean reservoir. The invention is particularly suited for use in reservoirs in which stratification due to differences in the absolute permeabilities of individual layers of rocks does not confine a significant portion of injected steam within the layers of highest absolute permeability.

In certain respects, this invention is an improvement in the steam-channel-expanding steam foam drive process described in U.S.A. patent specification 4,086,964 (inventors: R. E. Dilgren, G. J. Hirasaki, H. J. Hill, D. G. Whitten; filed 27th May, 1977; published 2nd May, 1978).

The invention is particularly useful in an oil producing process of the type described in the above patent specification. In this process steam is injected into, and fluid is produced from, horizontally spaced locations within a portion of an oil reservoir in which the disposition of a steam flow path is determined by gravity and/or oil distribution, rather than being substantially confined within layers of relatively high absolute permeability. After a steam channel has been formed and extended until a steam breakthrough into a production location is at least substantially imminent, the composition of the fluid being injected is changed from steam to a steam-foam-forming mixture. The composition of the mixture is correlated with the properties of the rocks and the fluids in the reservoir so that the pressure required to inject the mixture and to move it through the steam channel exceeds that required for steam alone but is less than the reservoir fracturing pressure. The composition and rate of injecting the mixture is subsequently adjusted to the extent required to maintain a flow of steam foam within the channel at a relatively high pressure gradient at which the oil-displacing and channel-expanding effects are significantly greater than those provided by the steam alone. Oil is recovered from the fluid produced from the reservoir.

As used herein the following terms have the following meanings: "steam foam" refers to a foam and/or gas-liquid dispersion which (a) is capable of both reducing the effective mobility, or ease with which a fluid containing such a foam or dispersion will flow within a permeable porous medium and (b) has steam in the gas-phase thereof. "Mobility" or "permeability" refers to an effective mobility or ease of flow of a fluid within a permeable porous medium. A "permeability reduction" or "mobility reduction" refers to reducing the ease of such a fluid flow due to an increase in the effective viscosity of the fluid and/or a decrease in the effective permeability of the porous medium. A reduction in such a mobility or permeability can be detected and/or determined by measuring differences in internal pressures within a column of permeable porous material during a steady state flow of fluid through a

column of such material. "Steam quality" as used regarding any steam-containing fluid refers to the weight percent of the water in that fluid which is in the vapor phase of the fluid at the boiling temperature of that water at the pressure of the fluid. For example: in a monocomponent steam-containing fluid which consists entirely of water and has a steam quality of 50%, one-half of the weight of the water is in the vapor phase; and, in a multicomponent steam-containing fluid which contains nitrogen in the vapor phase and dissolved or dispersed surfactant and electrolyte in the liquid phase and has a steam quality of 50%, one-half the weight of the weight of the water in the multicomponent steam-containing fluid is in the vapor phase. Thus, the steam quality of a steam-containing fluid can be calculated as, for example, 100 times the mass (or mass flow rate) of the water vapor in that fluid divided by the sum of the mass (or mass flow rate) of both the water vapor and the liquid water in that fluid.

"Steam-foam-forming mixture" (or composition) refers to a mixture of steam and aqueous liquid solution (or dispersion) of surfactant, with some, all, or none, of the steam being present in the gas phase of a steam foam. The gas phase may include noncondensable gas(es) such as nitrogen.

Object of the invention is an improved process for displacing oil within an oil-containing subterranean reservoir by flowing a steam-containing fluid in conjunction with a surfactant component through a relatively steam permeable zone within said reservoir.

According to the invention the surfactant component comprises in substantial part olefin sulfonate.

The olefin sulfonate-containing steam-foam-forming mixture may include an aqueous solution of electrolyte and may further also include a substantially noncondensable gas; with each of the surfactant, electrolyte and gas components being present in proportions effective for steam-foam-formation in the presence of the reservoir oil. The invention also relates to the olefin sulfonate-containing steam-foam-forming mixtures which are described herein.

The invention is useful where it is desirable to remove oil from, or displace oil within, a subterranean reservoir. For example, the invention can be used to move oil or an emulsion of oil and water away from a well borehole in a well-cleaning type of operation, and/or to displace oil into a producing location in an oil-recovery operation.

In particular, the present invention relates to a process for recovering oil from a subterranean reservoir, comprising:

injecting steam and producing fluid at horizontally spaced locations within a portion of an oil reservoir in which the disposition of a steam flow path is determined by the effect of gravity and/or oil distribution, rather than being substantially confined within at least the one most permeable layer of reservoir rocks; maintaining rates of steam injecting and fluid

production such that a steam channel has been extended from the injection location;

changing the composition of the fluid being injected from steam to a steam-foam-forming mixture including steam and an aqueous, electrolyte-containing solution or dispersion of an olefin sulfonate-containing surfactant, whilst continuing to produce fluid from the reservoir;

correlating the composition of the steam-foam-forming mixture with the properties of the rocks and fluids in the reservoir so that the pressure required to inject the mixture and foam it forms or comprises into and through the steam channel exceeds that required for steam alone but is less than the reservoir fracturing pressure; and

adjusting the composition of the fluid being injected into the steam channel to the extent required to maintain a flow of both steam and foam within the channel in response to a relatively high pressure gradient at which the oil-displacing and channel-expanding effects are significantly greater than those provided by steam alone, without plugging the channel.

The invention will now be described in more detail by way of example with reference to the drawings, wherein:

Figure 1 is a schematic illustration of an apparatus suitable for testing the steam mobility-reducing capability of a given steam-foam-forming mixture; and

Figure 2 is a plot of the variations in internal fluid pressure with distance along a sand pack as steam or steam-foam-forming mixture is flowed through the pack.

The invention provides unobvious and beneficial advantages in oil displacement procedures by the use of the olefin sulfonate surfactant in the steam-foam-forming compositions. For example, where a steam-foam-forming mixture contains such a surfactant and an electrolyte in proportions near optimum for foam formation, the present surfactant components provide exceptionally strong steam foams having mobilities many times less than those of steam foams using other surfactants. In addition, significant reductions are reached in the mobilities of the steam foams at concentrations which are much less than those required for equal mobility reductions by the surfactants which were previously considered to be the best available for such a purpose. The use of the present olefin sulfonate surfactant components involves no problems with respect to thermal and hydrolytic stability. No chemical or physical deterioration has been detectable in either the present olefin sulfonate surfactants or the previously used alkylaryl sulfonate surfactants that were recovered along with the fluids produced during productions of oil from subterranean reservoirs. In each of those types of sulfonate surfactants the sulfur atoms of the sulfonate groups are bonded directly to carbon atoms. The surfactants which were recovered and tested during the production of oil has travelled through the reservoirs at steam temperatures for significant times and distances.

The present olefin sulfonate-containing steam foams have been found to represent a substantial improvement in oil-displacing efficiency over foams based on the alkylaryl sulfonates e.g., dodecylbenzene sulfonates. The alkylaryl sulfonates were heretofore particularly suggested as superior surfactants for steam-foam service; for instance, in the process of the U.S.A. patent specification 4,086,964 and also in the related process described in Progress Review No. 22 (DOE/BETC-80/2), "Contracts for Field Projects and Supporting Research on Enhanced Oil Recovery and Improved Drilling Technology", published for the first quarter of 1980 by the Bartlesville Energy Technology Center of the U.S. Department of Energy, p. 107—108, Kern Front Field Stream Drive with Ancillary Material.

The present invention further relates to compositions containing olefin sulfonate, and steam, electrolyte, and optionally noncondensable gas, that are suitable for use in oil-displacing and/or producing processes. Of particular interest in this respect are steam-foam-forming compositions consisting essentially of (a) water, which is present in the composition, at a temperature substantially equalling its boiling temperature, at the pressure of the composition, in both a liquid phase and a vapor phase; (b) a surfactant component present in the liquid phase of the composition in an amount between 0.01 and 5 percent by weight, calculated on the weight of the liquid phase, said surfactant component comprising in substantial part olefin sulfonate; (c) an electrolyte present in the liquid phase of the composition in an amount between 0.1 percent by weight (calculated on the weight of the liquid phase) and an amount tending to partition the surfactant into a separate liquid phase; and (d) a noncondensable gas present in the vapor phase in an amount between about 0.0003 and 0.3 percent by mol, calculated on total mols in the vapor phase.

Illustrative of the olefin sulfonate surfactants suitably employed in steam-foam drive processes of enhanced performance, according to the invention, are the olefin sulfonates obtained by hydrolysis and neutralization of the product of reacting sulfur trioxide with olefins having a carbon number in the range from 10 to 24 inclusive. Particularly suitable for purposes of the invention is an olefin sulfonate derived from substantially linear alpha-olefins in the C₁₄ to C₂₀ range, and, most particularly, those derived from linear alpha-olefins in the C₁₆ to C₁₈ range.

Different reservoir oils have different debilitating effects on the strength of a steam foam. Tests should therefore be carried out to determine the olefin sulfonates or olefin sulfonate-containing steam-foam-forming compositions that perform optimally in a given reservoir. This is preferably done by testing the influence of specific olefin sulfonates on the mobility of a steam-containing fluid having the steam quality selected for use in the reservoir in the presence of the reservoir oil.

Such tests are preferably conducted by flowing steam-containing fluids vertically upward through an oil-containing sand pack. The permeability of the sand pack and foam-debilitating properties of the oil in the sand pack should be at least substantially equivalent to those of the reservoir to be treated. Comparisons are made of the mobility of the steam-containing fluid with and without the surfactant component. The mobility is indicated by the substantially steady-state pressure drop between a pair of points located between the inlet and outlet portions of the sand pack in positions which are substantially free of end effects on the pressures.

Some laboratory tests to determine steam mobility will now be described with reference to Figures 1 and 2.

Figure 1 shows schematically a sand pack test apparatus which can be made of currently available apparatus components. The apparatus consists of a cylindrical tube 1 that is 30 millimetres in diameter and 275 millimetres long. Such a tube is preferably arranged for an upward flow of fluid from an inlet 2 at the bottom of an outlet 3 at the top. The tube is preferably provided with at least two pressure taps 4 and 5. The locations of the taps are chosen so as to divide the length of the tube 1 approximately into thirds. The tube 1 contains a permeable and porous column of suitable material, such as a sand pack, which is capable of providing an adequately realistic laboratory model of a subterranean reservoir.

At the inlet end 2, the sand pack or equivalent column of permeable material is arranged to receive separate streams of steam, noncondensable gas such as nitrogen, and one or more aqueous liquid solutions or dispersions containing a surfactant to be tested and/or a dissolved or dispersed electrolyte. Some or all of those components are injected at constant mass flow rates proportioned so that steam of a selected quality, or a selected steam-containing fluid or composition, or a steam-foam-forming mixture of a selected steam quality can be injected and will be substantially homogeneous substantially as soon as it enters the face of the sand pack.

In the tests, steam-foam-forming mixtures are compared with and without surfactant components added thereto, by measuring pressure gradients formed within a sand pack during flows through the pack at the same substantially constant mass flow rate. The flow rate used in such tests is preferably within the range of from about 2 to 4 millilitre/minute of water, where about half of the water is dry steam and remainder is an aqueous liquid containing the surfactant and electrolyte. The gas-phase of such a steam may contain a small proportion of noncondensable gas. However, laboratory and field tests have shown that the proportion of noncondensable gas which provides a significant effect in a field operation tends to be too small to be significant in laboratory tests of steam-containing fluids which are free of surfactant

component. In general, the rate at which the steam-containing fluid is flowed through the pores of the sand pack is preferably substantially equivalent to the flow rate to be utilized in flowing such a fluid through the near-well portion of a reservoir.

Numerous tests have been made of different steam-foam-forming mixtures using sand packs composed of a reservoir sand such as an Ottawa sand containing Kern River crude oil and having a high permeability, such as 4 darcys. The pressures were measured with pressure detectors (such as piezoelectric devices) installed at the inlet 2 and at the taps 4 and 5 of the tube 1. The results of such tests have proven to be very consistent with the results obtained in field tests.

In the laboratory tests, the steam-foam-forming components were injected at constant mass rates until substantially steady-state pressures were obtained at the inlet and at the taps. The steady-state pressures at the taps were used with equations for isothermal single phase flow of an ideal gas to calculate the effective mobility (or effective permeability) to the steam by itself and mixed with the foam-forming surfactant component. The ratio of the latter to the permeability to steam in the absence of the surfactant component can be termed "the permeability reduction factor". The smaller this factor, the stronger the steam foam and the lower the mobility of the steam-foam-forming mixture.

The laboratory tests are preferably conducted in the presence of the reservoir oil or an oil substantially equivalent to it with respect to viscosity and steam-foam-debilitating properties. In a preferred procedure the packs are prepared by flooding them with a given oil at an elevated temperature, to provide oil saturation in the order of 70 to 80% of the pack pore volume. Hot water floods, usually amounting to 9 to 10 pack pore volumes, are conducted to reduce the oil saturations to hot water residuals of about 60 to 70%. The hot water floods are followed by wet steam drive using about 8 to 9 pack pore volumes of water converted to steam of a selected quality, such as 50%. This reduces the oil saturation to a range such as 30 to 50% (at which some oil can be produced by a wet steam drive but is an amount which is small in proportion to the amount of drive fluid).

Figure 2 illustrates the results of comparative tests with steam and various steam-foam-forming mixtures in sand packs prepared as described above. The figure shows the variation of the pressure in kg/cm² (Y-axis) with distance in centimetres (X-axis) from the pack inlet 2. The pressures were measured at the inlet 2, at the taps 4 and 5, and at the outlet 3 of the pipe 1 of Figure 1. Curve A relates to the displacement wherein a mixture of 50% quality steam was used as a displacing composition. The pressure performance of such a steam has been found to be substantially identical with that of a steam which has the same quality but has a gas-phase that contains 0.006 mole fraction of nitrogen gas.

Curve B relates to using a steam-containing fluid having a steam quality of 50% and a water-phase which contains 1% by weight sodium chloride and 0.5% by weight of surfactant. In the Curve B test, the surfactant was a branched side-chain dodecylbenzene sodium sulfonate available from Witco Chemical Company under the trademark Witco EXP 4498-43B surfactant.

Curve C relates to using the mixture used for Curve B except that the surfactant was a branched side-chain dodecylbenzene sodium sulfonate available from Alcolac Incorporated under the trademark Siponate DS-10 surfactant.

In the tests represented by Curves D and E the formulation was the same as those used in the tests represented by Curves B and C except that the sulfonate components were olefin sulfonates, in accordance with the present invention. Curve D relates to the use of the Alcolac Saponate alpha-olefin sulfonate product A-168 (trademark), obtained via the sulfonation, hydrolysis, and neutralization of an olefin mixture characterized in terms of carbon number as about 55% C₁₆ and 45% C₁₈, and further characterized in terms of molecular structure as about 70% linear terminal, about 20% branched terminal, and about 10% linear internal. Curve E relates to the use of an alpha-olefin sulfonate prepared by Stepan Chemical Company via the sulfonation, hydrolysis, and neutralization of an olefin mixture characterized as about 55% C₁₆ and about 42% C₁₈, and further characterized as about 94% linear terminal, about 3% branched terminal, and about 2% linear internal.

The greatly improved steam permeability reduction performance of the presently described olefin sulfonate-containing surfactant component is clear from the Curves D and E as compared to the Curve B and C in Figure 2.

The greatly improved performance is also illustrated by the permeability reduction factors, which are the numbers between brackets that refer to the Curves A—E in Figure 2. The smaller this factor, the stronger and more effective is the steam foam. The permeability reduction factor for the olefin sulfonate surfactant used in the test represented by Curve D is less than one fourth of that for the previously preferred alkaryl sulfonate surfactant, and thus, the olefin sulfonate used in the Curve D test is more than four times more effective as a surfactant component of a steam-foam-forming composition. A comparison of the Curves A and D shows that when steam is foamed with that olefin sulfonate surfactant the steam mobility is reduced to about one-twenty-fifth of the mobility in the absence of any surfactant. And, such a comparison of Curves A and E shows an even greater reduction, to one-fiftieth of the mobility in the absence of surfactant.

Field Test I (prior art)

In this field test, steam was injected and fluid produced at horizontally spaced locations within a relatively non-stratified viscous oil reservoir. Rates

of injection and production were maintained until steam breakthrough in the production well was imminent. A steam channel was thereby formed extending from the injection well towards the production well. Thereafter, the composition of the fluid that was being injected was changed from steam to a mixture of about 70% quality steam, dodecylbenzene sulfonate (Siponate DS-10) surfactant and sodium chloride electrolyte. This part of the field test corresponds with the "Field Test II" described in the USA patent specification 4,086,964, which was carried out in a single 5-spot pattern of wells.

This single 5-spot pattern was subsequently expanded to four contiguous 5-spot patterns, and the above measures were repeated therein.

The surfactant used in the expanded pattern was the previously used dodecylbenzene sulfonate (Siponate DS-10) surfactant. The steam-foam-forming mixture which was injected has a steam quality of about 50%. That mixture contained within its liquid-phase about 0.5% weight surfactant and 4.0% weight sodium chloride. The gas-phase of the mixture contained about 0.006 mole fraction of nitrogen.

The steam-foam-forming mixture was initially injected into only three of the injection wells. In those wells, the bottom hole injection gauge pressures increased rapidly from about 1.4—2.1 kg/cm² to about 8.4—8.75 kg/cm². The formulation was then changed to include 1.0% sodium chloride in the liquid-phase—which caused little change in bottom hole injection pressure. When nitrogen was introduced into the fourth injection well at the rate of 100 liters per minute, the bottom hole injection gauge pressure climbed rapidly to about an average pressure of 7.7 kg/cm². The sodium chloride concentration of the steam-foam-forming mixture entering the fourth injector was then increased to 4.0%, (making the concentration of all components the same as that employed in the other three injection wells) and the bottom hole injection gauge pressures within the pattern maintained an average value of about 8.4 to 9.1 kg/cm².

Field Test II (present invention)

The steam-foam-forming mixture being injected in Field Test I into the four test wells was subsequently modified by switching from the sodium dodecylbenzene sulfonate DS-10 surfactant to the olefin sulfonate surfactant A-168 in accordance with the present invention. The use of the olefin sulfonate surfactant component (without otherwise altering the composition of the steam-foam-forming mixture being injected) increased the average value of the bottom hole injection gauge pressures to about 11.2—11.9 kg/cm². The change-over also caused an increase in the average daily rate of oil production. The DS-10 surfactant (prior art) caused an increase of from about 135 BDO (barrels per day of oil) to 240 BDO and the A-168 surfactant (present invention) caused a further

increase of from about 240 BDO to a value of about 363 BDO, which is still increasing.

During the startups of the injections of the DS-10 and A-168 surfactants, prior to the inclusion of the nitrogen and sodium chloride components of the steam-foam-forming mixtures, the following observations were made regarding the bottom hole injection pressures. With the DS-10 surfactant (prior art), during the first three days the gauge pressure increased from about 1.75 to about 3.15 kg/cm².

The A-168 surfactant (present invention) was initially injected (without nitrogen or sodium chloride) into a well in which the injection gauge pressure had been increased to about 9.8 kg/cm² by a prior injection of the DS-10 surfactant (prior art) with nitrogen and sodium chloride. During the first three days of injecting the mixture of only steam and the A-168 surfactant, the bottom hole injection pressure decreased to about 8.26 kg/cm². Part of the decrease was due, of course, to the lower foam strength of the gas and electrolyte-free mixture. Part of the decrease was also due to a four-hour well shutdown. But within two more days the pressure had stabilized at about 8.75 kg/cm², which was almost triple the value obtained by the similarly gas-and-electrolyte-free steam-foam-forming fluid containing the DS-10 surfactant. And, although the injection pressure fluctuated due to additional shutdowns, the near 8.75 kg/cm² value was maintained until it was increased to the 11.2—11.9 kg/cm² range by the inclusion of the gas and electrolyte components of a preferred steam-foam-forming mixture of the present invention.

Compositions and procedures suitable for use in the present invention

For purposes of the present invention, the surfactant components of the steam-foam-forming mixture is necessarily comprised in substantial part of olefin sulfonate, a known material which has heretofore found commercial utility, for example, in detergent formulations for industrial, household and personal care application.

A class of olefin sulfonates very suitable for use in the present invention is that derived from a particular class of olefins, which may be defined for present purposes in terms of the configuration and number of carbon atoms in their molecular structure. (In the chemical arts, olefin sulfonates are commonly described in terms of the olefins from which they can be prepared.) These olefins have a carbon number in the range from 10 to 24, such as in the range from 14 to 22, or in the to 22, or in the range from 15 to 20. Extremely good results will be obtained when at least 50% of the olefin sulfonate content of the surfactant component of the steam-foam-forming mixture be derived from olefins in the C₁₆ to C₁₈ range.

In terms of molecular structure, these olefins are aliphatic (or acyclic) and suitably either linear or branched or alicyclic. Less than 50% of the olefin molecules may have branched carbon chains. At least about 75% (such as 85% or 90%)

of the olefin molecules in the C₁₀ to C₂₄ range may be of a linear (normal) configuration. Either alpha or internal olefins are considered suitable for use in the invention. Good results will be obtained when using olefins which are in major part alpha-olefins or olefins in which less than 25% of the molecules are internal olefins. For purposes of derivation of olefin sulfonates for use in the invention, olefins may be applied in which at least 90% of the molecules are alpha-olefins.

In exemplification of specific ones of these olefins which are suitable for use in synthesizing sulfonates having utility as surfactant components in the process of the present invention, mention may be made of olefins prepared according to a variety of known methods and available from a number of commercial sources. Particularly suitable olefins of high linear alpha-olefin content, manufactured by the cracking of paraffin wax, are available as the Chevron Alpha Olefin product series (trademark) sold by Chevron Chemical. Commercial production of olefins in the C₁₀ to C₂₄ range is more commonly accomplished by oligomerization of ethylene utilizing Ziegler catalysts. Alpha-olefin rich products obtained in this manner are marketed in the United States of America by Gulf Oil Chemicals Company under the trademark Gulfene and by Ethyl Corporation under the trademark Ethyl Alpha-Olefins. In comparison to other commercial alpha-olefins the Ethyl product is relatively high in its content of branched vinylidene olefins (about 20%) and internal olefins (about 10%). Good results for the practice of the invention have been obtained utilizing sulfonates of the Ethyl olefin products, particularly sulfonates of C₁₆ and C₁₈ alpha-olefin mixtures as described above, regarding Curve D of Figure 2. Particularly attractive are sulfonates derived from the Gulf-produced alpha-olefin products or the Neodene alpha-olefins (trademark) sold by Shell Chemical Company, in part for their linear structure and high alpha-olefin content, i.e., greater than 90% in each case. The Neodene alpha-olefins are prepared by ethylene oligomerization. Products having a high content of internal olefins in the C₁₀ to C₂₄ range are also commercially manufactured, for instance, by the chlorination-dehydrochlorination of paraffins or by paraffin dehydrogenation, and can also be prepared by isomerization of alpha-olefins. Internal-olefin-rich products are manufactured and sold, for example, by Shell Chemical Company and by Liquichemica Company.

For preparation of olefin sulfonates, the olefins as described above are subjected to reaction with sulfur trioxide. The term "sulfur trioxide" as used in the present specification and claims is intended to include any compounds or complexes which contain or yield SO₃ for a sulfonation reaction as well as SO₃ per se. This reaction may be conducted according to methods well known in the chemical arts, typically by contact of a flow of dilute SO₃ vapor with a thin film of liquid olefin at a temperature in the range of about 5 to 50°C.

The reaction between the SO₃ and the olefin yields an intermediate, believed to be in the nature of a sultone, which is subsequently hydrolyzed by reaction with water and neutralized by reaction with a base, preferably an alkali or alkaline earth metal hydroxide, oxide, or carbonate. In illustration of the composition of the typical olefin sulfonate product, if the olefin is of high alpha olefin content and the base utilized is sodium hydroxide, the sulfonation, hydrolysis, and neutralization reactions yield a complex mixture of sulfonated compounds principally comprising alkene sulfonic acid sodium salts, hydroxy-alkane sulfonic acid sodium salts and alkene disulfonic acid disodium salts. Although the composition of the sulfonate product varies somewhat depending on a number of factors, particularly the nature of the olefin and the sulfonation reaction conditions, these three principal components are usually present in the product in quantities of about 50 to 70% by weight (%w), 20 to 40%w, and 5 to 15%w, respectively. This sulfonate product would also contain other sulfonated compounds, usually in lesser amount, particularly the higher order alkene sulfonate and hydroxy-alkane sulfonate sodium salts.

The specific composition of olefin sulfonates prepared as described above (and also, for instance, the methods used for sulfonation, hydrolysis, and neutralization of the specified olefins) have not been found to be a critical factor to the performance of the surfactant in the steam foam drive process of this invention. In this regard, it is observed that factors which have conventionally governed the choice of sulfonation conditions, e.g., product color, clarity, odor, etc., do not carry the same weight in the preparation of olefin sulfonates for purposes of use in the invention that they have been accorded in detergent manufacture. Consequently, reaction conditions outside of those heretofore considered desirable for olefin sulfonation are still suitably applied in the preparation of surfactant components suitable for use in the steam-foam-forming mixture.

For purposes related to maintaining product stability, conventional manufacture typically yields a dilute solution of the olefin sulfonates, for instance, a 30%w solution in water. Such dilute solutions may be directly applied to the preparation of steam-foam-forming mixtures for purposes of this invention.

Suitable olefin sulfonates, generally prepared by methods such as described above, are themselves commercially available products. Representative of such olefin sulfonate materials are those within the scope of current specifications for products sold under the trade names Allfoam (Chemithon Corp.); BioTerge AS40 (Stepan Chemical Co.); Conco AOS-40 and Conco AOS-90F (Continental Chemical Co.); Polystep A-18 (Stepan Chemical Co.); Sterling AOS (Canada Packers, Ltd.); Sulfotex AOS (Textilona Division of Henkel, Inc.); Sulframin AOS 14-16 and Sulframin AOS 90 Flakes (Witco Chemical Corp.); Ultrawet

AOK (Arco Chemical Co.); Elfan OS 46 (Akzo Chemie); Hostapur OS (Hoechst AG); and Lipolan 327N, Lipolan 1400, Lipolan AO, Lipolan G, and Soft Detergent 95 (Lion Corp.).

The strength of the foam formed by the steam-foam-forming composition including olefin sulfonate tends to increase with increases in the proportion of the surfactant and/or electrolyte components of the composition. Also, there tends to be an optimum ratio of surfactant and electrolyte components at which the surface-activity of the composition is maximized.

The steam-foam-forming composition of the present invention can form a steam-foam capable of providing a permeability reduction factor lower than about 0.18, and even, lower than about 0.10, thus reducing the effective mobility of the steam to less than about 1/6th and more, to less than about 1/10th of the mobility it would have within a permeable porous medium in the absence of the surfactant.

Where the surfactant component of the present steam-foam-forming mixtures or compositions contains one or more surfactants other than the present specified olefin sulfonate surfactant, the proportion of the olefin sulfonate should be large enough so that the composition is capable of providing a steam-foam strength (e.g., as indicated by a permeability reduction factor) exceeding that provided by a similar composition in which the surfactant component consists of only said other surfactant.

The steam used in the present process and/or compositions can be generated and supplied in the form of substantially any dry, wet, superheated, or low grade steam in which the steam condensate and/or liquid components are compatible with, and do not inhibit, the foam-forming properties of the foam-forming components of a steam-foam-forming mixture of the present invention. The steam quality of the steam as generated and/or amount of aqueous liquid with which it is mixed be such that the steam quality of the resulting mixture may be from 10 to 90%, such as from 30 to 80%. The desired steam-foam is advantageously prepared by mixing the steam with aqueous solution(s) of the surfactant component and optionally, an electrolyte. The water content of these aqueous solutions must, of course, be taken into account in determining the steam quality of the mixture being formed.

In general, the noncondensable gas used in a steam-foam-forming mixture of the present invention can comprise substantially any gas which (a) undergoes little or no condensation at the temperatures and pressures at which the steam-foam-forming mixture is injected into and displaced through the reservoir to be treated and (b) is substantially inert to and compatible with the foam-forming surfactant and other components of that mixture. Such a gas is preferably nitrogen but can comprise other substantially inert gases, such as air, ethane, methane, flue gas, fuel gas, or the like. Suitable

concentrations of noncondensable gas in the steam-foam mixture fall in the range of from 0.0003 to 0.3 mole percent such as 0.001 and 0.2 mole percent, or between 0.003 and 0.1 mole percent of the gas-phase of the mixture.

In general, the electrolyte used should have a composition similar to and should be used in a proportion similar to those described as suitable alkali metal salt electrolytes in the above-mentioned USA patent specification 4,086,964. An aqueous solution may be applied that contains an amount of electrolyte substantially equivalent in salting-out effect to a sodium chloride concentration of from 0.1 to 5% (but less than enough to cause significant salting out) of the liquid-phase of the steam. Some or all of the electrolyte can comprise an inorganic salt, such as an alkali metal salt, an alkali metal halide, and sodium chloride. Other inorganic salts, for example, halides, sulfonates, carbonates, nitrates and phosphates, in the form of salts of alkaline earth metals, can be used.

Generally stated, an electrolyte concentration may be applied which has approximately the same effect on mobility reduction of the foam as does a sodium chloride concentration of between 0.1 and 5 percent by weight (but less than a salting out-inducing proportion) of the liquid phase of the steam-foam-forming mixture. The electrolyte concentration may be between 0.1 and 5 percent (such as between 1 and 4 percent) calculated on the same basis. The weight ratio of electrolyte to surfactant may be in the range of from 0.5 to 6 (such as from 1 to 4).

In compounding a steam-foam-forming mixture or composition in accordance with the present invention, the steam can be generated by means of substantially any of the commercially available devices and techniques for steam generation. A stream of the steam being injected into a reservoir is preferably generated and mixed, in substantially any surface or downhole location, with selected proportions of substantially noncondensable gas, aqueous electrolyte solution, and foam-forming surfactant. For example, in such a mixture, the quality of the steam which is generated and the concentration of the electrolyte and surfactant-containing aqueous liquid with which it is mixed are preferably arranged so that (1) the proportion of aqueous liquid mixed with the dry steam which is injected into the reservoir is sufficient to provide a steam-containing fluid having a steam quality of

from 10—90% (such as from 30—80%); (2) the weight proportion of surfactant dissolved or dispersed in the aqueous liquid is from 0.01 to 5.0 (such as from 1.0 to 4.0); and (3) the amount of noncondensable gas is from 0.0003 to 0.3 mole fraction of the gas-phase of the mixture.

60 Claims

1. In a process for displacing oil within an oil-containing subterranean reservoir by flowing a steam-containing fluid in conjunction with a surfactant component through a relatively steam-permeable zone within said reservoir, the improvement which comprises:

employing a surfactant component which comprises in substantial part olefin sulfonate.

2. The process of claim 1, wherein an electrolyte is employed in the flow within the reservoir in conjunction with the steam-containing fluid.

3. The process of claim 1 or 2, wherein a substantially noncondensable gas is employed in the flow within the reservoir in conjunction with the steam-containing fluid.

4. The process of claim 1, wherein the surfactant component comprises in substantial part olefin sulfonate obtained by hydrolysis and neutralization of the product of reacting sulfur trioxide with C_{10} to C_{24} olefins.

5. The process of claim 4, wherein the olefin sulfonate is derived from C_{14} to C_{22} olefins, at least about 50 percent of which have linear carbon chains.

6. The process of claim 4, wherein the olefin sulfonate is derived from C_{15} to C_{20} olefins.

7. The process of claim 4, wherein the aqueous liquid phase of the steam-foam-forming composition contains between about 0.01 and 5 percent by weight of olefin sulfonate.

8. The process of claim 4, wherein the olefin sulfonate is derived in major part from C_{16} to C_{18} olefins.

9. The process of claim 4, wherein at least about 50 percent of the olefins are alpha-olefins.

10. The process of claim 4, wherein at least about 75 percent of the olefins have linear carbon chains and at least about 75 percent of the olefins are alpha-olefins.

11. The process of claim 4, wherein at least about 90 percent of the olefins have linear carbon chains and at least about 90 percent of the olefins are alpha-olefins.