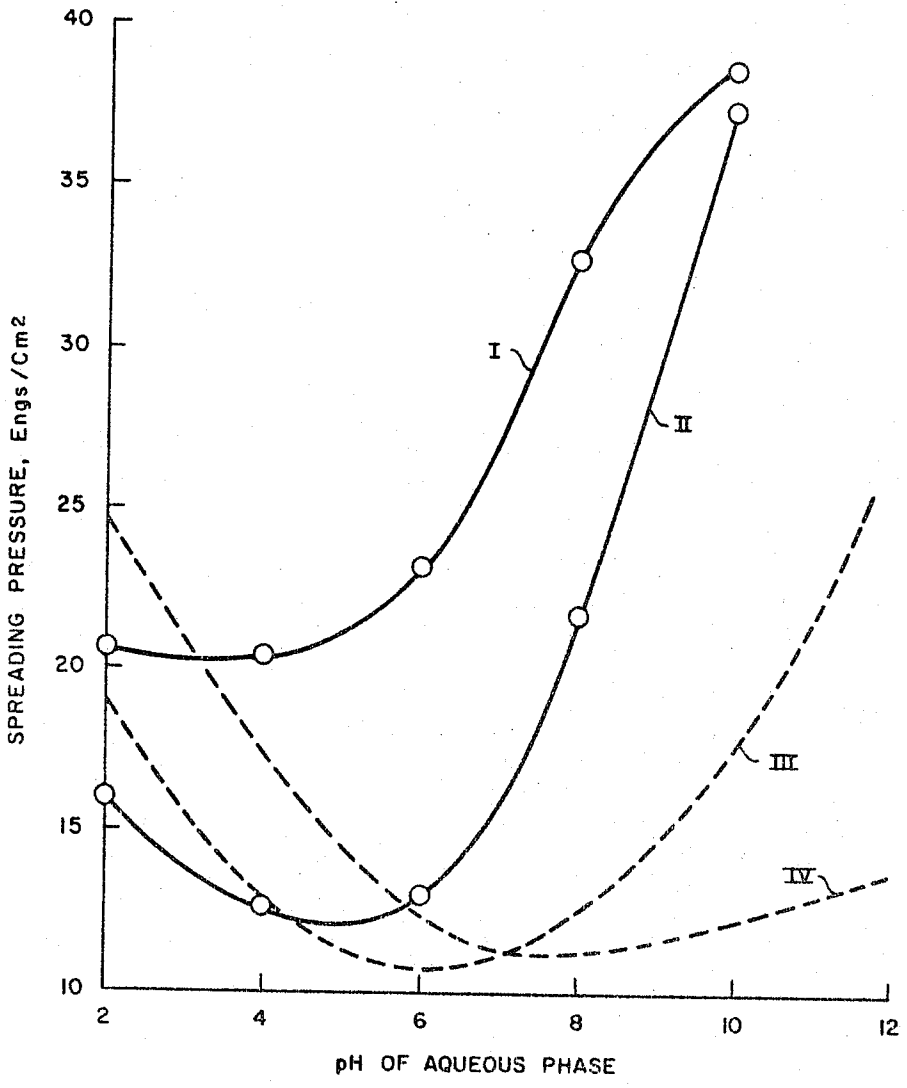
Aug. 23, 1966 W. C. SIMPSON 3,267,998

SEPARATION PROCESS

Filed June 1, 1964 3 Sheets-Sheet 1



INTERFACIAL ACTIVITY OF HEAVY OILS FROM TAR SANDS AND NORMAL OIL-BEARING STRATA AT AQUEOUS INTERFACES OF VARIOUS pH

FIG. 1

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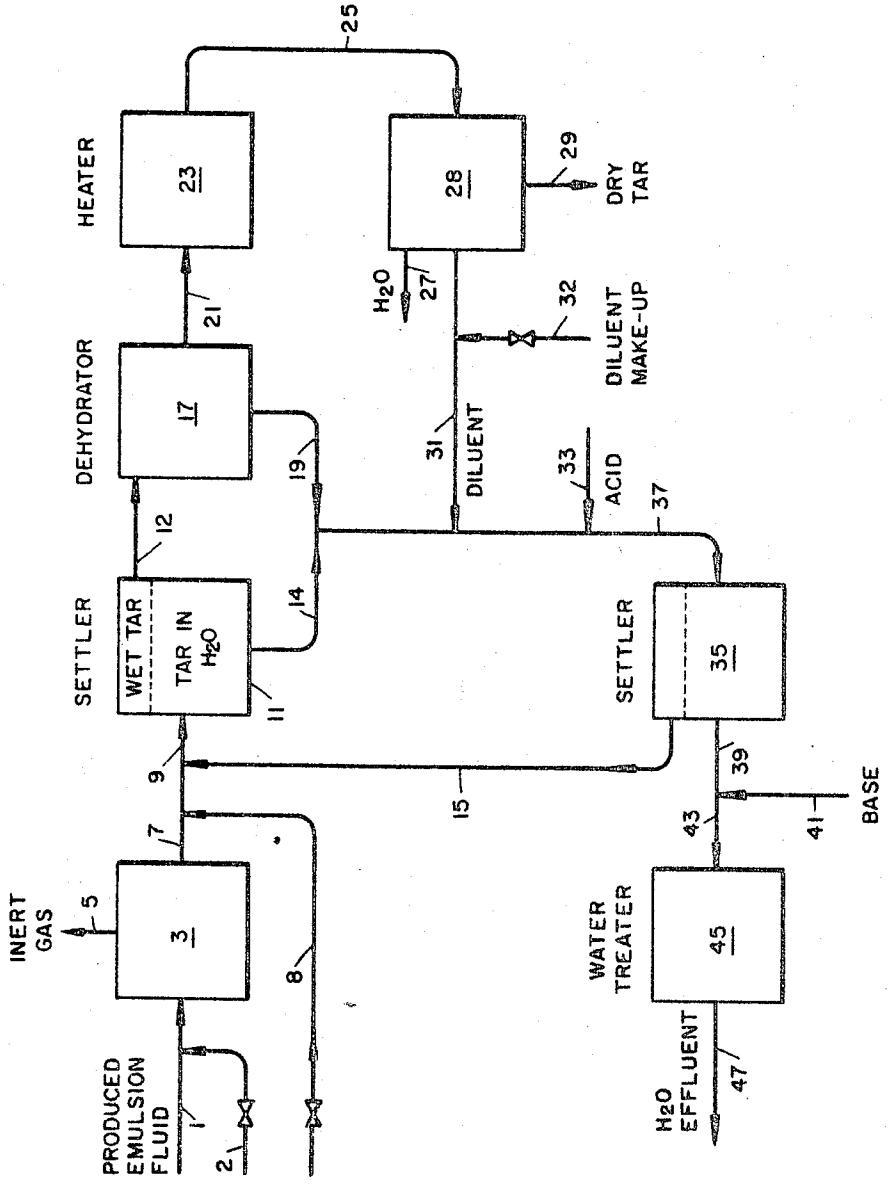


FIG. 2

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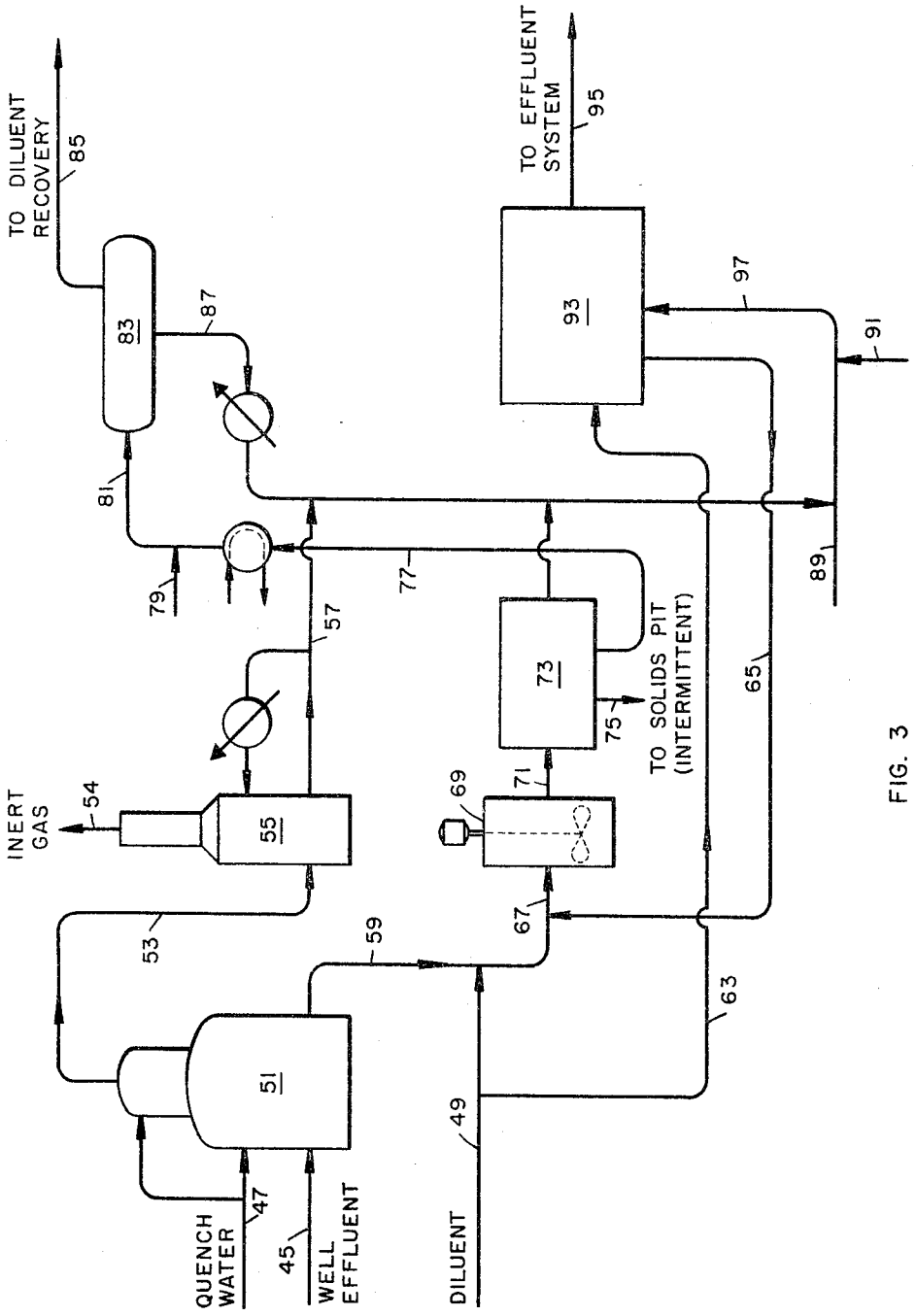


FIG. 3

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5 Claims. (Cl. 166—7)

This invention relates to a process for recovery of heavy hydrocarbon crude from heavy hydrocarbon crude and water mixtures. More particularly, this invention pertains to a process for separating heavy hydrocarbon crude from water mixtures thereof which are produced by extraction from bituminous tar sand by the injection of steam or dilute aqueous alkaline solutions into the subterranean tar sands. The invention also pertains to a process for recovering viscous hydrocarbon oil from underground crude oil reservoirs or normal oil bearing strata wherein the heavy oil is obtained mixed with water.

As is well known, there are various places throughout the world which have large deposits of tar sands. Usually the tar in these tar sands has a density approaching or even greater than water. The most extensive and perhaps best known deposits of this type occur in the Athabasca District of the Province of Alberta, Canada. These Athabasca tar sands extend for many thousands of square miles and occur in thicknesses varying up to about 200 feet. Although in some places these tar sand formations and deposits are practically on the surface, generally they are located under an overburden which may range in thickness from a few feet up to as much as 1000 or more feet in depth.

Various methods have been proposed previously for separating crude oil from these tar sands but none of these methods has met with any substantial success. Since the crude oil obtainable from this type of tar sand is a relatively viscous material having a high tar content, but a relatively low commercial value in comparison with other crude oils, a successful commercial process must involve relatively little expense in the separation of crude oil from the tar sands. Operating costs of previously conceived methods for separating the oil from bituminous sands have been sufficiently high so as to discourage commercial exploitation.

Recently, however, it has been discovered that an extremely effective manner of recovering the tar from the subterranean deposits thereof is to inject steam and/or dilute alkaline solutions directly into the formation adjacent to fractures between at least two spaced wells drilled into the formations and thereby subjecting the tar sands to leaching and emulsifying actions by said solutions and then conveying steam through the said tar sand formation to heat the oil and force the emulsion formed by the action of the aqueous alkaline solution or steam towards an output or production well. The emulsion may then be recovered from the output or production well by subsequent separation and recovery of the hydrocarbon therefrom.

Techniques of this type are the subject of U.S. patent applications of Doscher Serial No. 261,830, filed February 28, 1963; patent application of Doscher Serial No. 261, 846, filed February 28, 1963; and Canadian Patent No. 639,050, issued to Doscher et al. March 27, 1962, the disclosures of which are herein incorporated by reference.

While these methods have proven extremely effective in separating the tar from the sand deposits so that there remains an extremely low solids content in the oil, all of the processes, nevertheless, produce a type of fluid emulsion mixture which in the past has presented some difficulty in separation. In fact, it has in the past some times been considered desirable to substantially eliminate water from recovery processes. See U.S. 3,131,141, issued April 28, 1964, to West.

The produced fluid emulsion mixture (hereinafter referred to as the produced fluid) is composed principally of at least the following materials: (1) as the main and continuous phase, water; (2) tar; (3) gas (either air or an inert gas usually introduced into the system during the leaching operation); (4) undissolved inorganic solids (usually small platelets of kaolinite and illite); and (5) dissolved solids (in the water). Thus a poly-inter-face system is present which includes tar droplets dispersed in the water which are usually associated with (either attached onto or within) an air bubble, water droplets inside the tar, and even smaller tar droplets inside each water drop. The inorganic platelets referred to above are usually covered with tar, and inside the continuous water phase are the dissolved solids.

The problem of separation of such a complex system appears to consist principally of three major parts: (1) separating a water-in-tar emulsion from an oil-in-water emulsion, (2) separating the tar-in-water emulsion, and (3) separating the water-in-tar emulsion.

In accordance with the instant invention, it has been found that the heavy hydrocarbon crude may be economically and effectively recovered from the produced fluid (aspect 2 of the above problem) by an emulsion breaking technique based on minimizing the spreading pressure of the surface active components present in the hydrocarbon crude in water emulsion by adjusting the pH of the water phase of the mixture to a value within a specified critical range.

In another aspect, the invention pertains to a process for separating and recovering the heavy hydrocarbon crude from a heavy hydrocarbon crude water emulsion produced fluid which comprises degasifying said fluid to remove inert gases and producing a degasified fluid, diluting the degasified fluid by adding a heavy hydrocarbon crude/diluent phase produced from a secondary separation zone defined hereinafter thereto to form a diluted fluid, passing said diluted fluid to a primary separation zone wherein a wet heavy hydrocarbon crude/diluent layer and a heavy hydrocarbon crude-in-water emulsion layer are recovered as substantially separate phases, passing said heavy hydrocarbon crude/diluent layer to a dehydrating zone, recovering a water phase and a heavy hydrocarbon crude diluent phase from said dehydrating zone as separate phases, recovering as a product of said process a heavy hydrocarbon crude product by removing said diluent from said dry heavy hydrocarbon crude/diluent phase, adjusting the pH of said heavy hydrocarbon crude in water emulsion layer from said primary separation zone to a value between 3 and 7 to produce a pH adjusted phase having a minimum spreading pressure, passing said pH adjusted phase to a secondary separation zone, recovering from said secondary separation zone a heavy hydrocarbon crude/diluent phase and an aqueous phase as separate phases and passing said heavy hydrocarbon crude/diluent phase to said primary separation zone for dilution of said degasified fluid and rejecting said aqueous phase as the effluent from the process.

While the process of the invention is, of course, not in any way limited by any particular theory, it is believed that the adjustment of the pH to the critical range of from 3 to 7 results in the attainment of minimum spreading pressure from the surface active component which occurs naturally in heavy hydrocarbon crudes which tend to otherwise stabilize the emulsion.

Emulsions of heavy oils in water produced from normal oil bearing strata or recovered from tar sands are generally stabilized by naturally occurring surface active compounds which usually comprise petroleum acids such as naphthenic acids, and, in some cases, basic substances such as basic nitrogen compounds. These substances stabilize oil-in-water emulsions by being selectively adsorbed at the surface of the oil droplets where they are ionized to form

acidic or basic groups which give the oil drops either a negative or a positive charge.

These compounds may have different degrees of stabilizing effect since the basic or acidic groups may be affixed to naphthenic ring structures, benzoid, naphthenoid or higher catacondensed aromatic cyclic structures, etc. The stability of the emulsions results from the natural repulsion of the negatively, or as the case may be, positively charged oil drops. The quantity of charge per unit area on the surface of the oil drops is directly determined by the tendency of the surface active compounds to be adsorbed at and spread over the oil-water interface between the drop and the surrounding aqueous phase.

Other advantages of the invention will also become apparent in the description thereof hereinafter which is made with reference to the accompanying drawing which consists of FIGURES 1, 2, and 3. FIGURE 1 is a plot illustrating the interfacial activity of heavy oils from tar sands and normal oil-bearing strata at the respective aqueous interfaces obtained at various pH values. FIGURES 2 and 3 each represent schematic diagrams of typical oil-water separation schemes set up in accordance with embodiments of the invention.

By "spreading pressure" is meant the term used to quantitatively define the tendency of the surface active components present in petroleum crudes to be adsorbed and to spread at the oil-water interface of oil-in-water emulsions. This property may be expressed in ergs per square centimeter and can be measured by means of film balances of the type conventionally used in the study of the physical chemistry of surface films. These balances may be either the well known "PLAWM" (Pockels, Langmuir, Adam, Wilson, McBain) or by other less tedious film balance methods such as the type suggested by Wilhelmy and revised by Dervichian.

In accordance with the latter method as described in Annalen der Physik, 119, 177 (1863) and J. Physique (7), 6, 221 (1935), a variety of oil-water systems containing various types of heavy hydrocarbon crudes were measured under conditions of acidity of the aqueous phase which varied from pH's of 12 to 2.

Referring now to FIGURE 1, it illustrates a plot of curves representing different heavy oils extracted from tar sands or normal oil bearing strata which have been mixed with water and wherein the aqueous phase has been adjusted to different pH values. Curves I and II represent typical tars recovered from tar sands in the Athabasca area. Curve III represents a heavy waxy oil recovered from normal oil-bearing strata produced at New Ulm, Texas, and IV a Uinta, Utah oil.

The condition of lowest spreading pressure and lowest emulsion stability is not always in a high acidic region as indicated by the minimum in the New Ulm, Texas, oil water system at a pH of 6 (Curve III) and the Uinta, Utah case at pH 7 (Curve IV). The differences in results, of course, depend somewhat on the geographical location of the particular heavy oil or oil bearing strata.

As previously described at high pH's the acids are the surface active components which are preferentially adsorbed at the oil-water interface. However as the pH decreases, this tendency is minimized. If one goes lower than that point then the nitrogen bases begin to become preferentially adsorbed at the interface and the spreading pressure rises.

Unexpectedly, it was found in every case examined that there is a particular condition of acidity at which the tendency of the petroleum acids to be adsorbed and to spread at the oil-water interface (the spreading pressure) goes through a minimum value and that these values are within a range of pH's between 3 and 7. It was further found that the stability of the oil-in-water emulsion is also brought to a minimum value under these conditions, which if maintained for a reasonable time, allows the ready coalescence of the oil drops into a distinct and separable (from the water) oil layer.

Referring now to FIGURE 2, the feed comprising the produced emulsion fluid which results from in situ separation of tar from subterranean tar sands by the steam injection process referred to previously is introduced into a degassing foam tank **3** by means of line **1** and, depending on the temperature at which the produced fluid is obtained, either quenching or heating water may be introduced through line **2** so that the temperature of the fluid which is removed from foam tank **3** is lower than the boiling point of the aqueous phase at the particular pressure employed (preferably atmospheric).

From the foam tank is withdrawn an inert gas stream, line **5**, and a degasified fluid stream is passed from the foam tank by means of line **7** where it may optionally be diluted with a light hydrocarbon diluent by means of line **8** and a tar/diluent phase produced from the secondary separation zone **35** is introduced by means of line **15** into line **7** and the resulting mixture is transported by means of line **9** to the primary separation zone **11** from which a wet tar/diluent layer is recovered by means of line **12** and a tar emulsion layer is obtained and removed therefrom by means of line **14**. The wet tar diluent layer is transported to dehydrator **17** which may comprise any conventional dehydration technique, i.e., chemical, chemical-electrical, or electrical dehydrating means to produce a relatively dry tar layer which is transported by means of line **21** to heater **23** and then by means of line **25** to a distillation zone wherein the remaining traces of water are rejected into line **27**. The dry tar product is recovered by means of line **29** and the diluent is transported by means of line **31** to be mixed with the streams in lines **14** and **19** and passed to the separation zone **35**. The tar and water emulsion recovered from the primary separation zone by means of line **14** and the water layer from the dehydrator which is obtained through line **19** are added together with the diluent from line **31** (additional diluent make-up may be added by means of valved line **32**) is sent to the secondary separation zone after the pH has been altered to a value which is within the critical range of 3–7. While it is generally preferred to add an acid such as sulfuric acid to accomplish this, it is obvious that other acids or bases may be employed so long as the pH which is obtained is between the particular desired range to provide a minimum spreading pressure for that particular emulsion. The aqueous phase from the secondary recovery zone comprises the water effluent from the process and may be treated in any conventional manner prior to disposal in a waste stream.

A further example of an embodiment of the instant invention is set forth in FIGURE 3 which involves introducing a produced fluid (i.e., well effluent) at a temperature of 250° F. into a degassing foam tank **51** by means of line **45** wherein it is contacted with a sufficient amount of quenching water added through line **47** to reduce the temperature of the degassed fluid leaving the tank by means of line **59** to 210° F. The vapor, comprising mainly inert gases and water, leave overhead through line **53** to quench tower **55** from which the inert gases are permitted to escape through pipe **54** and the small amount of water recovered therein is sent by means of line **57** to be combined with the water stream **87** recovered from the electrostatic dehydrator **83**. The degassed fluid in line **59** is mixed with diluent introduced through line **49** (also some diluent is added by means of line **63** to the secondary separation zone to assist in the lowering of the specific gravity of the tar layer) and with the tar phase recovered from the secondary separation zone transported in line **65**. The mixture of various streams is agitated in mixer **69** and the mixed diluted fluid is passed through line **71** to a primary separation zone **73** wherein a wet tar/diluent layer is recovered and transported by means of line **77** to the electrostatic dehydrator **83**. The tar (still containing a small amount of water) and diluent is sent by means of line **85** to a diluent recovery wherein diluent is recovered for re-use in the process and a dry tar product is obtained. Another product of the primary separation zone comprises

a tar-in-water emulsion layer which is transported to the secondary separation zone **93**. Also withdrawn from the primary separation zone are small amounts of solids which may be intermittently removed by means of line **75**. The secondary separation zone **93** produces an effluent through line **95** which (after a conventional water treating technique) may be disposed directly into a waste stream. Also introduced into the secondary separation zone through line **91** is a sufficient amount of a substance capable of changing the aqueous phase of the tar in water emulsion to a pH value between 3 and 7 so that a minimum spreading pressure is obtained which will permit an easy separation of the emulsion. As previously mentioned, line **65** transports a tar diluent phase from the secondary separation zone to be mixed with the degassed produced fluid.

The particular diluent employed has a two-fold purpose: (1) to reduce the particular gravity of the produced fluid to the proper value so that separation in the primary separation zone may be more easily accomplished and (2) to reduce the viscosity for easier handling of the fluid. While in most cases it is desirable to use a kerosene hydrocarbon fraction of a boiling range of from about 300 to 500° F., it will also be apparent to those of ordinary skill in the art that any other diluents adequate to satisfy the above purposes may be used.

Moreover, it is contemplated not only to use diluents lighter than water, but also those having a density greater than water so long as the resultant hydrocarbon diluent phase has an effective density after dilution which is substantially different from that of water. While kerosene is adequate as one particularly desirable diluent, other particularly desirable diluents are cracked hydrocarbon fractions recovered from the separated tar at a later stage of the oil production.

The ratio of diluent to produced fluid may be set between wide ranges, however, it is preferred to employ from about 5 to about 35% by volume of diluent per volume of wet tar diluent mixture. In some cases, it may be desirable to add as high as 50% by volume of diluent per volume of wet tar/diluent mixture.

Example

A process arrangement similar to that shown in FIGURE 3 is used to extract tar from a produced fluid comprising an emulsion of tar, water, solids (and some gas from a gas lift operation), in the following manner:

About 430,000 barrels per day of a produced fluid from a well treated by the steam and alkaline injection technique referred to previously, and which emulsion comprises about 30.66% by weight bitumen, 69.24% by weight water, and .10% by weight solids at a temperature of 250° F. is passed to a degassing unit where it is contacted with about 18,000 barrels per day of quenching water maintained at an initial temperature sufficient to lower the temperature of the fluid to about 210° F. 443,000 barrels per day of the degassed fluid is passed through line **59** and diluted with 65,000 barrels per day of diluent introduced through line **49** and the diluted mixture is further blended with 19,778 barrels of the tar/diluent phase recovered from a secondary settler **93**. After this blend is mixed, it is passed to the primary settler from which are recovered 228,134 barrels per day of wet oil-diluent which is sent to an electrostatic dehydrator **83**. 295,614 barrels per day of a tar-in-water emulsion layer is obtained from the primary settler and passed to the secondary settler in which is also added other waste water from other related process steps not shown through line **89**. Solids are intermittently withdrawn from the primary settler through line **75** in an average rate of about 1.27 barrels per day.

The relatively dry tar-diluent phase (197,167 barrels per day) is recovered from the electrostatic dehydrator and is sent to a diluent recovery zone (not shown) from which 130,000 barrels per day of dry diluent free product tar is obtained.

Line **91** is used to supply sufficient sulfuric acid (6 milliequivalents per 1000 cc. of aqueous phase supplied from the primary separation zone) so that the resulting pH is approximately 3 to lower the spreading pressure of the aqueous phase to a value of 20 ergs/cm.^{2}. The reject water removed from the secondary settler **93** by means of line **95** contains 25 p.p.m. of oil and is, after being treated to meet pollution standards, passed into a waste stream. Also withdrawn from the secondary separation zone, as mentioned previously, is a tar diluent phase which is blended with diluted, degassed produced fluid.

I claim as my invention:

1. A process for separating and recovering the heavy hydrocarbon crude from a produced fluid comprising a heavy hydrocarbon crude-water emulsion which comprises degasifying said fluid to remove inert gases and producing a degasified fluid, diluting the degasified fluid by adding a heavy hydrocarbon crude/diluent phase produced from a secondary separation zone defined hereinafter thereto to form a diluted fluid, passing said diluted fluid to a primary separation zone wherein a wet heavy hydrocarbon crude/diluent layer and a heavy hydrocarbon crude-in-water emulsion layer are recovered as substantially separate phases, passing said heavy hydrocarbon crude/diluent layer to a dehydrating zone, recovering a water phase and a dry hydrocarbon crude/diluent phase from said dehydrating zone as separate phases, recovering a dry heavy hydrocarbon crude product by removing said diluent from said dry heavy hydrocarbon crude/diluent phase, adjusting the pH of said heavy hydrocarbon crude-in-water emulsion layer from said primary separation zone to a value between 3 and 7 to produce a pH adjusted phase having a minimum spreading pressure, passing said pH adjusted phase to a secondary separation zone, recovering from said secondary separation zone a heavy hydrocarbon crude/diluent phase and an aqueous phase as separate phases and passing said heavy hydrocarbon crude/diluent phase to said primary separation zone for dilution of said degasified fluid and rejecting said aqeous phase as the effluent from the process.

2. The process of claim **1** wherein said heavy hydrocarbon crude water emulsion produced fluid is obtained from injecting steam directly into a tar sand formation adjacent to fractures between at least two spaced wells drilled into said formations, subjecting the tar sands to leaching and emulsifying action, and conveying steam through said tar sand formation to heat the tar and force the emulsion toward an output well.

3. The process of claim **2** wherein the injected steam contains a dilute aqueous alkaline solution.

4. The process of claim **1** wherein said heavy hydrocarbon crude water emulsion produced fluid contains a heavy petroleum hydrocarbon obtained from normal oil-bearing strata.

5. The process of claim **1** wherein said diluent comprises a kerosene hydrocarbon fraction having a boiling range of from 300–500° F.

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