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SECONDARY RECOVERY METHOD

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This invention relates to the recovery of hydrocarbons from depleted oil fields, and pertains more particularly to improved methods of flooding such sands to effect an effective and efficient secondary or tertiary recovery of oil therefrom.

It is well known that the so-called primary recovery techniques, which include natural flow, gas-lifting and pumping techniques, recover only a minor portion of the oil present in a given oil-bearing earth formation. Even the use of improved primary recovery practices, e.g., use of gas re-pressuring treatments, and the like, still leaves major quantities of oil, some of which may be adhering to the particles of sand or the particles of the oliferous structure, trapped in pores by capillary and hydrodynamic forces, etc.

For this reason there is a great deal of interest in the so-called secondary recovery techniques, the use of which permits the recovery from the partially depleted formation of addiitonal quantities of oil present therein. These secondary recovery techniques, in general, all utilize the principle of augmenting the remaining reservoir pressure after it has been depleted during oil recovery by the aforementioned primary recovery methods. This reservoir energy augmentation is effected by providing, e.g., by drilling, one or more injection wells extending downwardly into a permeable oil formation within suitable proximity to a producing well or wells which have been drilled into this same permeable oil bearing formation, a liquid or a gas, or mixtures thereof, being injected through the above-mentioned injection well to drive the oil to and thus increase the oil production from the producing well or wells.

Water is one of the practical fluids which has been generally used for the augmentation of depleted reservoir energy. In this general method, which is normally described as "water-flooding," water is pumped through an injection well and into the permeable partially-depleted oil-bearing formation, this water driving the oil from the zone near the injection well or wells towards the producing wells.

Since at least a portion of the oil remaining in a permeable oil-bearing formation after it has been partially depleted by use of the so-called primary recovery techniques, is relatively tightly bound or adhering to the particles of the oil-bearing structure, it is frequently desirable, if not essential, to use surface tension reducing and/or capillary active agents; these have been proposed and sometimes used as addition agents to the flooding water in an attempt to increase the efficiency of the water-flood.

Although frequently technical benefits are obtained from the use of these surfactants in flood-waters, there is at least one major objection, and that is the excessive cost. Thus, although the concentration of these surface tension reducing (i.e., wetting and/or emulsifying) agents in the water is quite low, e.g., in the order of between about 0.1% and about 3% to about 4% (or even somewhat higher), the total amount of the additive or additives employed in a given water-flood operation is quite high because of the very large total amount of water which has to be and is introduced into a given partially-depleted oil-bearing formation treated by the water-flood technique. This raises the cost of secondary recovery to a figure which is sometimes exorbitant and frequently

even uneconomical because of the relatively high price of the surfactant, particularly when the total cost thereof per water-flood operation is compared with the amount of oil recovered by the use of this technique.

It is therefore an object of this invention to avoid the above and other defects of the prior art, and to provide an efficient and economical water-flood method or technique.

It is a further object to provide a water-flood operation in which the surfactant or wetting agent is formed in situ under such conditions that more efficient utilization thereof is effected and the total amount of ingredients employed is such that their cost is markedly lower (compared to the costs of the surfactant heretofore employed in water-flood operations) without decreasing, and, in fact, while increasing the efficiency of the water-flood operations and also increasing the total yield of oil recovered thereby.

A still further object of the present invention is to provide a process of the character described in which, not only is the emulsifying addition agent formed economically in situ, but also its concentration varies so that the amounts thereof present in the various parts of the water-flood are arranged so as to avoid excess dilution of the emulsifying agent.

Yet another object is to provide a water-flood technique which accomplishes the above and other objects, and which also eliminates, or at least markedly decreases the break-through of columns of water used in the water-flood, which break-throughs normally cause channeling or fingering of the water through the oil-bearing zones, with the concomitant by-passing of oil which results in loss of ultimate yield thereof.

The above and other objects are attained, according to one aspect or phase of the process of the present invention, by first injecting into the oil-bearing formation (through one or more injection wells which have been drilled into said formation) first a body of an organic-acid-containing oil-miscible liquid, and thereafter injecting through said injection well or wells and into the aforesaid formation, behind said acid-containing liquid, a body of an alkali-containing aqueous solution. More specifically stated, the invention comprises introducing into an oil-bearing formation, and into contact with the oil to be recovered, a body of a soap-forming acid in the form of a solution thereof in an oil-miscible liquid, and thereafter injecting into the same formation, behind this acid-containing liquid, a body of an aqueous alkaline solution which neutralizes the aforesaid acid, thereby forming an emulsifier or interfacial tension-reducing material. The latter, in turn, promotes emulsification and/or extremely low interfacial tension between the oil and the aqueous solution, thereby bringing about near miscibility or an oil-in-water emulsion. Further injection of the aqueous alkaline solution, or, in the alternative, of water effects the displacement of the emulsion, which is recovered from the oil-bearing formation through one or more recovery wells, the oil being then separated in the usual manner from said emulsion.

In accordance with the present invention, it is possible to use any acid which when reacted with (i.e., neutralized by) the basic-acting compound described more fully hereinbelow, will produce a soap-type surface-acting agent capable of effecting the emulsification of an oil, such as the residual oil to be recovered in the aqueous solution used as the carrier for the basic-acting agent as well as the flooding and driving means. A preferred class of acids suitable for use in the process of this invention comprises the organic carboxylic acids, more preferably the monocarboxylic acids having from about six or eight carbon atoms per molecule to as high as about forty carbon

atoms per molecule. A sub-class of acids following within this class are the saturated and unsaturated aliphatic monocarboxylic acids exemplified by stearic, myristic, palmitic, lauric, oleic, undecylenic, and like acids. Another class of organic acids (which is particularly applicable in the process of the present invention because of the availability and reasonably low cost of the acids falling within said class) comprises the well-known naphthenic acids derived from petroleum oils. A large number of these acids, particularly those having from seven to fourteen carbon atoms per molecule are generally obtained by caustic extraction of naphtha, kerosene, and gas oil, while higher molecular weight naphthenic acids, e.g., those possessing from fourteen to thirty or more carbon atoms per molecule are present in and recoverable from many crude oils, and particularly from a variety of Gulf Coast and California crudes. These latter, which have been found to be especially suitable for use in the secondary recovery of residual oils according to the present process, are high molecular weight naphthenic acids having an average molecular weight as low as about 300 (or somewhat lower) and as high as about 400 to 420 (or even higher). When derived from crude oils or the like, they may be in a pure state, or may contain comparatively small, e.g., up to about 10%, of unsaponifiable matter, which is chiefly of a hydrocarbon nature. One such petroleum naphthenic acid composition which is commercially available and found quite satisfactory for the purposes mentioned above, has the following general properties:

Average molecular weight (deoiled)	415
Average molecular formula	$C_{28}H_{49}O_2$
Acid No., mg. KOH/gram	122
Unsaponifiables, weight percent	10
Density $_4^{20}$	0.992
Viscosity, S.U.S./210° F.	624
Bromine No.	12.1
Refractive index N_D^{20}	1.516
Pour point, ° F.	75
Distillation range:	
Initial	408° F. at 2 mm. Hg.
50%	509° F. at 2 mm. Hg.
E.P.	596° F. at 2 mm. Hg.
Recovery	95%.

In the illustrative examples presented further below this naphthenic acid composition will be termed as Naphthenic Acids "A."

Any oil-miscible liquid may be used as the carrier for the aforementioned acids. In fact, it is possible to use as such the petroleum crude oil which has been or is being recovered from the same or another formation. However, it is usually advisable or at least preferable to employ a somewhat lighter hydrocarbon oil, the viscosity of which is not substantially greater than that of an aqueous liquid. Thus, as such, it is possible to employ hydrocarbon fractions or distillates in the gas-oil, jet fuel, kerosene, naphtha, gasoline ranges, or even still lighter hydrocarbon fractions, e.g. liquefied normally gaseous hydrocarbons, such as liquefied C_4 hydrocarbons. The reason for the use of the lighter hydrocarbon oils, such as kerosene, or the like, as the carrier for the aforesaid acids is that these hydrocarbons can be more readily forced or driven by an aqueous liquid through the pores of the formation, e.g. sand, and can thus be more easily brought into contact with the residual oils present in the formation, which residual oils it is desired to recover.

As mentioned above, the introduction of the acid-containing hydrocarbon-miscible slug or body of liquid into the formation is to be followed, according to one aspect of the process of the present invention by the injection into the same formation of an aqueous basic-acting solution. The preferred solutions for this use are the aqueous solutions containing caustic alkali, such as the sodium or potassium hydroxides or ammonium hydroxide, or aqueous solutions containing alkali salts, e.g. carbonates, capable of reacting with the organic acids, e.g., the aforementioned naphthenic acids to form emulsifying soaps. Also, one may use water-soluble relatively strong organic bases, such as ethylamine, isopropylamine, morpholine, triethanolamine, and like compounds capable of reacting with the aforementioned acids to form amine soaps.

With regard to the function of producing in situ a soap or compound capable of lowering the interfacial tension between the residual oil and the water injected into the oil-containing formation, the quantity of the hydrocarbon solute as well as of the acid employed in conjunction therewith need not be limited. However, the total quantity of acid introduced into the formation and therefore mixed with residual oil should be controlled or limited with regard as to its function as a source of the surfactant or emulsifying agent formed therefrom in situ in the formation. Generally speaking, this acid should be present in such a quantity that the surface-acting soap formed by its neutralization (by the aqueous solution introduced into the formation) is present in a quantity sufficient to effect the emulsification of the residual oil and to stabilize the oil-in-water emulsion thus produced against breaking during passage through the formation.

It has been found experimentally that efficient recovery of residual oil in accordance with the present invention may be effected by introducing into the oil-containing formation an acid-containing hydrocarbon miscible liquid in an amount equal to between about 10% and about 20% of the pore volume of the formation from which the residual oil is to be extracted. Greater amounts, although obviously permissive, are in most instances to be avoided as generally wasteful. As to the concentration of the acid in these oil-miscible liquid compositions, it may likewise vary within wide limits, primarily depending on the amount of oil-miscible liquid which is to be injected into the formation ahead of the aqueous alkali solution. Generally, it has been found that an acid concentration of about 5% in the aforesaid liquid is quite sufficient, although 7% or even 10%, and higher concentrations may be and sometimes should be used. Likewise, it was found that concentrations of about 2½% or even less will be satisfactory at least in some instances.

In connection with the in situ formation of the surfactant or wetting or emulsifying agent (in accordance with the process or processes of this invention) it has been discovered that a particularly economical and efficient utilization of the organic acid (e.g., naphthenic acids) is obtained if its concentration in the hydrocarbon-miscible slug is graded or scaled in such a manner that the acid concentration is greatest in the forepart of said slug and least in the tail portion thereof. This concentration of the acid may be stepped down either in stages or gradually, the former being preferred because of obvious relative ease of blending such solutions. Thus, a portion of the total slug or body of hydrocarbon-miscible liquid may be mixed with such an amount of organic acid that the concentration of the latter in the liquid is, say, 15%; this is pumped or otherwise injected through the injection well into the formation. This slug is then followed by a second having, for example, 10% acid, and a third of 5% acid concentration, and, even a still another of a still lesser acid concentration, e.g., as low as 1%. The slugs and the acid concentrations therein should be correlated so that the desired total amount of acid is introduced into the oil-bearing formation, and also so that the average concentration of the acid in the whole liquid slug introduced is at the value selected, e.g., 5%.

Without any intention of being limited by any theory of the case, it is at present understood that this procedure of maintaining a gradient in the acid concentration (i.e., the gradual stage reduction in acid concentration in the introduced liquid) results in more efficient residual oil recovery because the first portion of the oil-miscible slug introduced, having the highest acid concentration, be-

comes mixed with the residual oil more readily, while the later or subsequently introduced slugs become mixed with formation oil which by then have already acquired a certain concentration of surfactant-forming organic acid. Thus, the whole body of formation (residual) oil have a greater tendency of receiving the necessary or desirable quantity or concentration of the acid.

It is to be reiterated that, according to this phase of the invention, the hydrocarbon-miscible liquid slug introduced into the formation should have the highest acid concentration in that portion which is first introduced into the formation and, therefore, comes first in contact with the formation oil to be recovered, that said acid concentration in the liquid introduced therewith should be either gradually or in stages decreased in the subsequent portions of said liquid, and that the various acid concentrations and the slugs of liquid having each acid concentration should be so adjusted and correlated that the total amount of both acid and of the acid-containing oil-miscible liquid are within the amounts or ranges of amounts set out more fully hereinabove.

The lowest concentration of the acid (i.e., the acid concentration of the last slug), for technical reasons, should be sufficient to emulsify with the aqueous phase, and, in general, not be below about 0.1% of the diluent oil (carrier) in which it is dissolved and introduced into the formation. The number of steps or stages may vary and is not important as long as the desired average acid concentration in the total diluent oil slug is maintained.

The aqueous phase which is introduced according to this invention into the formation after the acid-containing oil-miscible slug has been injected (and preferably became intermixed with the residual oil in said formation), preferably contains a rather low concentration of the basic-acting neutralizing agent capable of neutralizing the aforementioned organic acids to form the surfactant. When caustic soda, i.e., sodium hydroxide is used, its concentration in the aqueous phase is preferably in the order of about 0.1%, although lower concentrations, such as 0.05% or even still lower (e.g., 0.01–0.02%) may in some instances be employed; likewise, this concentration may be as high as about 1%, or even several percent.

The total quantity of the aqueous alkali solution which is to be injected into the oil-containing formation may vary within relatively wide limits, depending, in part, on the volume of the acid-containing oil-miscible liquid injected, the specific method used, volume of residual oil, etc. Generally speaking, this quantity of the aqueous alkali solution will vary from about 2 pore volumes (of the formation treated) to as many as 10 or even 15 pore volumes. However, in most instances, satisfactory, if not excellent recovery of the residual oil will be obtained if and when the acid injection is followed up by the introduction into the formation of six or five or even four pore volumes of this alkali-containing water phase. Instead of introducing this relatively large volume of an aqueous alkali solution, it is possible to inject a lesser amount of this solution, e.g., as low as 2 or 3 pore volumes, and follow this with several pore volumes of plain water, which latter in this case merely acts as flooding water to push the formed emulsion (containing the extracted residual oil) to the production well or wells. In such instances, it may be advisable to use a somewhat high alkali concentration in the aqueous solution thereof used in the process.

Generally, and especially when the formation containing the residual oil to be recovered is sufficiently porous, the removal and recovery of the residual oil therefrom may be effectively realized by consecutive injection thereinto of first the acid-containing oil-miscible liquid slug and then of the aqueous alkaline solution (optionally followed by water-flood). The acid-containing slug displaces oil and the acid becomes dispersed in the residual oil, and, after neutralization by the basic-acting compound, forms the surfactant which aids in emulsifying the residual oil in the water, this emulsion being thus forced from the vicinity of the injection well or wells to the production well or wells. It is to be noted that one of the advantages of the process is the fact that a comparatively lesser amount of the costlier ingredients, i.e., acid, is used.

In the case of less porous formations which are permeated only with difficulty, it may be preferable to use a surging or pulsating back and forth motion both for the acid-containing liquid, and especially for the aqueous alkali solution. This type of surging motion (which aids penetration and emulsification) may be induced by a wide variety of known means, not necessary for specific enumeration here.

One of the defects of water drives or water floods, whether the latter contain soaps or soap-forming, i.e., surfactant-producing, compounds, resides in the fact that frequently such use of aqueous solutions permits "fingering," that is by-passing of some of the oil in the formation, particularly that which is present in some of the denser or relatively less porous portions of the formation. It has now been discovered that this by-passing or fingering may be prevented or at least materially inhibited by adjusting the viscosity of the aqueous alkali solution so that the ratio of the oil phase (i.e., of the acid-containing slug) to the water phase is less than about 15 to 1, and preferably is less than about 2 to 1. This can be attained by using viscosity-enhancing additives in the aqueous phase. One class of these viscosity-enhancing agents, suitable for use in the aqueous solutions employed in the process of the present invention comprises the alkali metal or ammonium salts of carboxyalkyl cellulosic acids, such as sodium carboxymethylcellulose, potassium carboxymethylcellulose, lithium carboxymethylcellulose, sodium carboxyethylcellulose, potassium carboxyethylcellulose, etc., and mixtures thereof. Various hydrophilic colloids and proteins, such as gelatinous cellulose derivatives, may likewise be used as viscosity-enhancing agents. Thus, hydroxyethylcellulose sold by Hercules Powder Company under the name "Natrosol," as well as resins of the type of high molecular weight carboxyvinyl polymers sold by B. F. Goodrich under the name "Carbopol," fall within the class of compounds defined above.

The quantity of this viscosity-enhancing agent in the aqueous phase may vary within wide limits, the sole limitation being solubility of the agent in the water and the viscosity of the aqueous solution obtained; this latter, as pointed out above, should have such a viscosity that the ratio of the viscosity of the oil phase in the formation to the viscosity of this aqueous solution is less than about 15:1 and preferably less than about 2:1. Very satisfactory results (in the case of an operation involving use of kerosene as a carrier of the acid) have been obtained when the concentration of the sodium carboxymethylcellulose was 0.1%. This resulted in an aqueous solution or aqueous phase having a viscosity of 5 centipoises; the residual oil in this case had a viscosity of 15 centipoises, while the viscosity of the kerosene was 1.5 centipoises.

The following specific examples are presented hereinbelow by way of illustration, and not as limitations on the scope of this invention. These examples also show the benefits and advantages attained when secondary recovery of residual oil from oil-bearing formations is in the manner described herein.

In all of these cases the sand containing the residual oil to be recovered was an Ottawa sand having a 150/200 mesh. The sand had an average permeability of about 4.5 darcies and a porosity of about 35%. Also in these examples the residual oil to be recovered from the above sand formation in accordance with the process described and claimed herein was a Ventura crude oil having a specific viscosity of 15 centipoises. Prior to treatment according to the present process the sand formation con-

taining said oil was water flooded until the ratio of the oil to the water in the effluent decreased to less than about 1/200. This water-flooding left in the sand an amount of residual oil equal to about 27% of a pore volume.

Example I

In this example a slug of kerosene equal in volume to 20% of a pore volume and containing 5% of the aforementioned Naphthenic Acids "A" was introduced into the above-described sand containing the defined amount of Ventura crude oil. Thereupon an aqueous solution of sodium hydroxide, concentration of which latter was equal to 0.1%, was conveyed through the sand behind the acid-containing kerosene. At the end of passage of 5 pore volumes of this dilute aqueous sodium hydroxide solution, 79.5% of the residual oil was recovered (in addition to the recovery of the whole amount of the acid-containing slugs), while the recovery of this residual oil was equal to 80.7% at the end of 7 pore volumes of the aqueous sodium hydroxide solution.

It is to be noted that the residual oil in this sand remained after a water-flooding operation. In fact, flooding of such sand containing said residual oil with an aqueous alkaline solution, e.g., sodium hydroxide solution, or with an aqueous solution containing a soap, e.g., sodium soap, of the aforementioned naphthenic acids, resulted in the further recovery from said sand of only an insignificant amount of the residual oil. Likewise, when said sand was treated with a slug of kerosene amounting to 20% of a pore volume, and when this kerosene treatment was followed by flooding with distilled water (using the same technique as described further above under Example I), the introduction of 5 pore volumes of this water caused the recovery of only 34% of the residual oil remaining in the sand pack.

Example II

In this example the same sand containing the same amount of the Ventura crude oil was treated with the same quantity of kerosene, namely, 20% pore volume, except that the Naphthenic Acids "A," although present in the same total amount, namely, 5% based on the kerosene, in this case was graded in concentration in said kerosene slug. Thus, in this case the first or leading portion of this kerosene slug amounting to slightly over ¼ of the total kerosene slug, contained the Naphthenic Acids "A" in a concentration of 15%, the second or central portion of said slug (equal to slightly over 50% of the total slug) contained the acid in a concentration of 3% while the remaining or trailing portion contained the acid only in a concentration of 1%. Thus although the total quantity of naphthenic acids thus introduced was the same in both Example I and Example II, in the latter the concentration of the acid was graded.

As in Example I this introduction of the acid-containing kerosene was followed by passage through the thus treated oil-containing sand of an aqueous sodium hydroxide solution, the concentration of the sodium hydroxide of which was equal to 0.1%. At the end of the passage of 5 pore volumes of these dilute alkali solutions, 90% of the residual oil was recovered.

Example III

In this example all of the operations were identical with those described above in connection with Example II, except that the aqueous sodium hydroxide solution in addition to 0.1% NaOH, also contained 0.1% of sodium carboxymethylcellulose. The passage of this aqueous solution through the oil-containing sand which has been first treated wtih acid-containing kerosene in which the acid concentration was graded as described in Example II, resulted in the recovery of 99.4% of the residual oil at the end of the passage of only 4 pore volumes of said viscosity-enhanced aqueous sodium hydroxide solution. The viscosity of the acid-containing kerosene was 1.5 centipoises while that of the aqueous sodium hydroxide solution containing the carboxymethylcellulose was 5 centipoises, producing a ratio of the viscosity of the oil-miscible carrier liquid to the viscosity of the aqueous phase of 0.3 to 1.

Example IV

In this example a slug of the Ventura crude, which equaled 10% of a pore volume and contained 5% of the Naphthenic Acids "A," was introduced into the sand containing the same (above-mentioned) amount of the residual Ventura crude. Following the slug injection, the system was water-flooded until an amount of oil equaling the amount injected as the acid-containing slug was displaced. The system was then flooded with aqueous 0.1% sodium hydroxide by the procedure used in the preceding examples. At the end of the passage of 5 pore volumes of the aqueous sodium hydroxide, 94% of the residual oil was recovered.

Example V

In this example a pack of the same sand was used, except that it was not first water-flooded. This left the pack filled with 87% of a pore volume of the crude oil. A slug of kerosene, which equaled to 20% of a pore volume and contained 5% of the Naphthenic Acids "A," was introduced. An aqueous 0.1% sodium hydroxide was passed through the sand pack by the procedure of Example I. At the end of the passage of 3 pore volumes of the aqueous alkali, 90% of the oil was recovered.

I claim as my invention:

1. A secondary recovery process in which at least one injection well and at least one production well penetrates an oil bearing formation from which oil is to be recovered consisting of the steps of:

(*a*) introducing through said injection well and into contact with the oil in said formation a slug of a light hydrocarbon crude oil distillate having a boiling point below the boiling point of gas-oil in an amount equal to between 10 and 20% of the pore volume of said formation, said slug containing between 2.5% and 10% by weight of a high boiling naphthenic acid having a molecular weight from 300 to 420;

(*b*) thereafter introducing through said injection well an aqueous sodium hydroxide solution in an amount of several pore volumes of said formation whereby some of the dispersed high boiling naphthenic acid is converted to a surface active compound which is capable of emulsifying and maintaining in an emulsion state a portion of said formation oil and thereby facilitating the displacement of said formation oil toward said production well by said aqueous solution introduced through said injecton well; and

(*c*) recovering formation oil from said production well.

2. A secondary recovery process according to claim 1 in which the high boiling naphthenic acid consists of a mixture of such acids having molecular weights from 300 to 400.

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