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DISSEMINATION OF WETTING AGENTS IN SUBTERRANEAN
HYDROCARBON-BEARING FORMATIONS

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Filed April 16, 1951

2 Sheets-Sheet 1

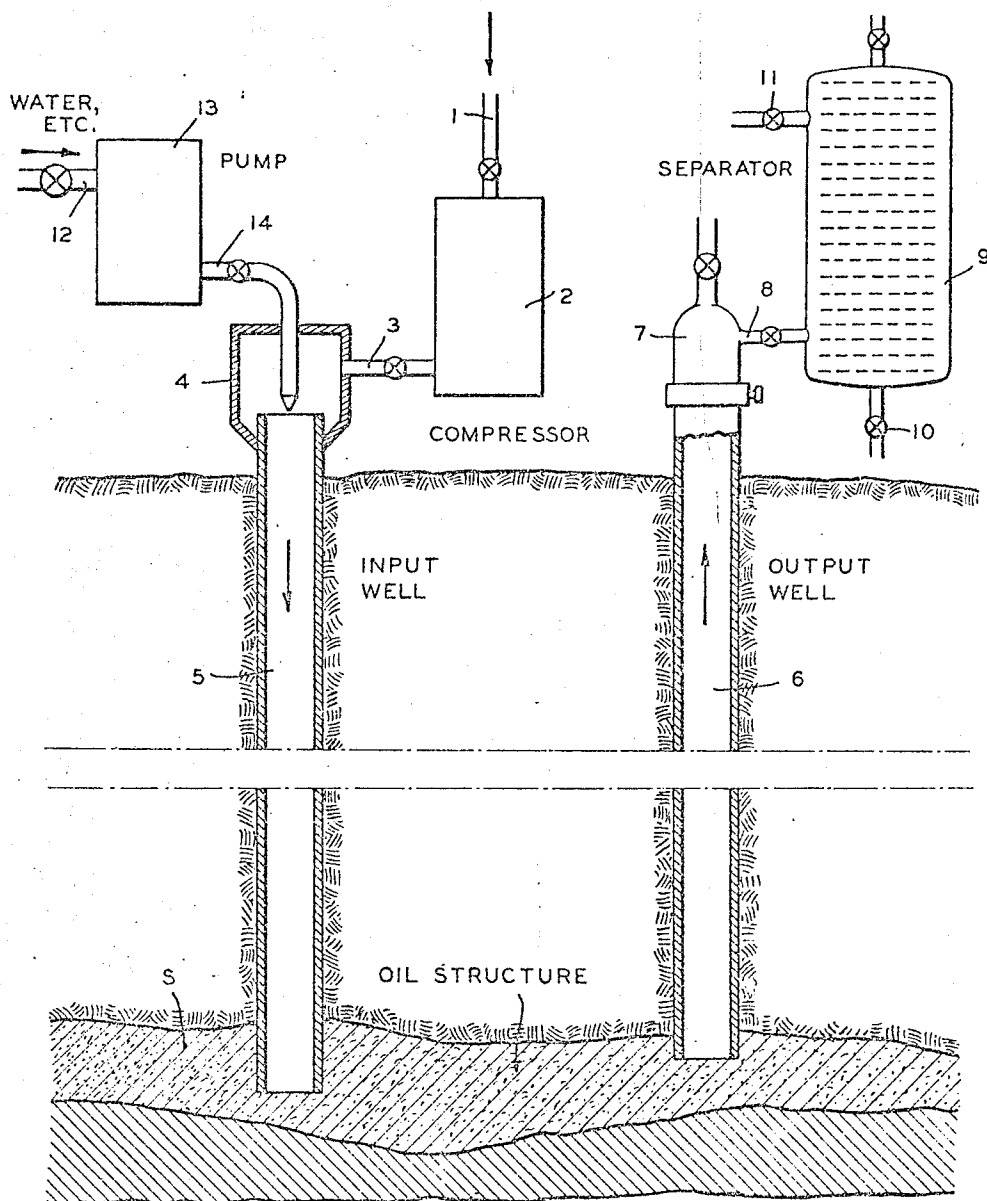


FIG. 1

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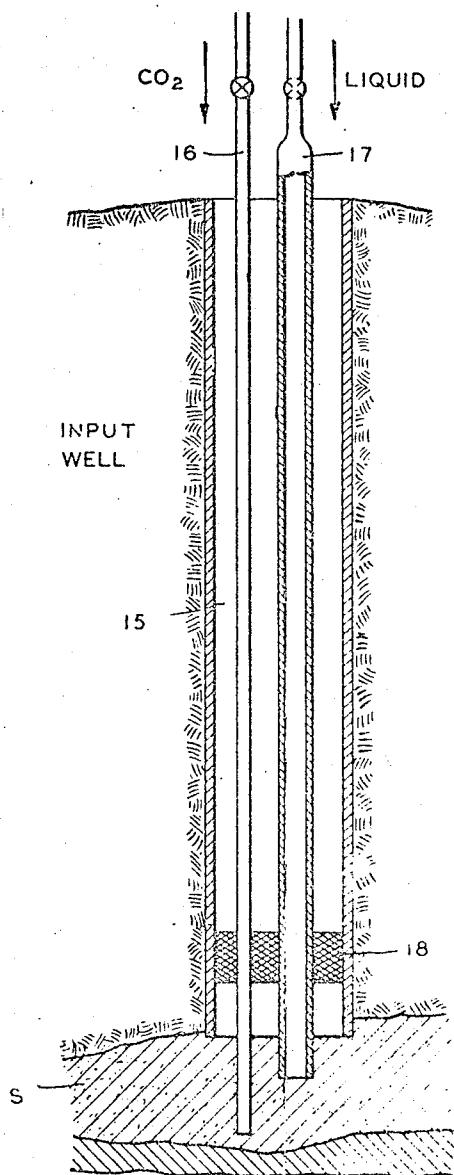
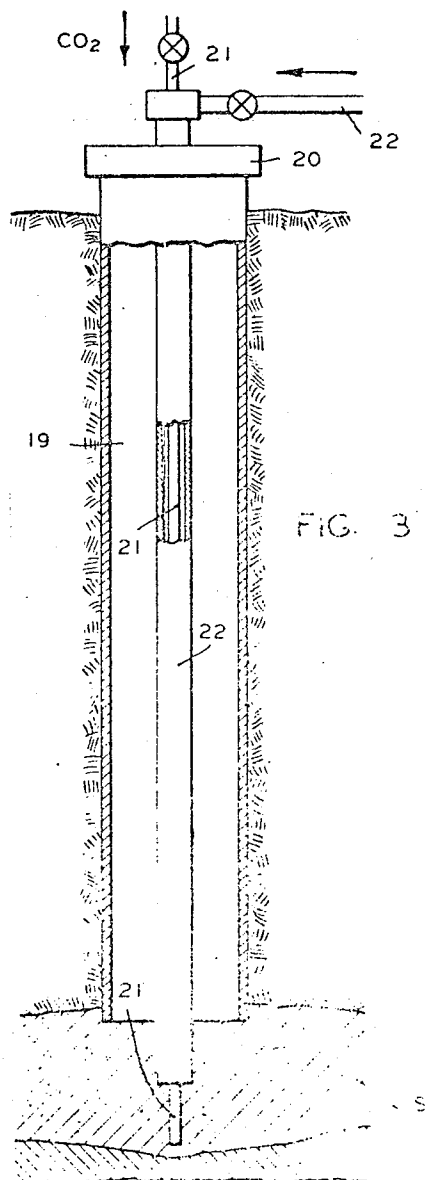


FIG. 2



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DISSEMINATION OF WETTING AGENTS IN SUBTERRANEAN HYDROCARBON-BEARING FORMATIONS

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Application April 16, 1951, Serial No. 221,226

33 Claims. (Cl. 166—9)

This invention relates to methods of disseminating wetting agents in subterranean hydrocarbon-bearing formations, particularly formations which cannot be economically worked by methods heretofore available in the art such as petroleum bearing horizons, for recovery of said hydrocarbons.

It has long been known that the recovery of oil or related hydrocarbons from subterranean strata or formations is quite inefficient from the standpoint of the oils or similar hydrocarbons which are left in the strata or formations. By the methods of what may be called primary recovery where the oil and gas are obtained under the pressures naturally existing in the strata, it has been variously estimated that only a fraction of the oil or other hydrocarbons is obtained possibly about 20 to 30% depending on the particular fields and conditions. As a result many methods have been suggested for recovering such residual oil or hydrocarbons from the subterranean horizons. Such methods include procedures for driving out residual oil or hydrocarbons and various fluids have been proposed and utilized in such drives. Gaseous drives employing air, nitrogen, natural gas or methane, etc., have been proposed and to some extent utilized.

Liquids, principally water, have been used in water flooding in efforts to drive out residual oil from the strata. Where surface active agents have been used, they have not penetrated substantially through the formation, but instead have been localized near the input well. At best therefore even with the gas drives and water flooding operations some 30% more or less of the original oil or other hydrocarbons in the subterranean strata or formations remains therein and no methods have been devised in the prior art which are feasible commercially for obtaining greater recoveries.

In application Serial No. 64,402 filed December 9, 1948, now abandoned, it is pointed out that "CO₂ reacts on petroleum crudes as a mild oxidizing agent and tends to form such compounds as aldehydes and the lower fatty acids and their soaps." . . . "These lower fatty acids and many of the compounds associated with them in petroleum are very hygroscopic and will rapidly dissolve in both the connate and the free water or salt solution native to most reservoir rocks. The characteristic of these acids and esters that is of greatest interest in this connection is that even in very small concentrations they greatly lower the surface tension of the oil. This causes them to have a profound effect on the flow of oil through the oil sand."

In application Serial No. 102,306, filed June 30, 1949, now abandoned, of which the present application is a continuation-in-part, the employment of carbon dioxide under critical conditions has been set forth for recovery of hydrocarbons from subterranean formations whereby it is possible to effect recoveries of so great a degree that residual hydrocarbons left in the formation may be 10% or less, in sharp contrast to the results of the prior art.

In application Serial No. 103,236, filed July 6, 1949,

now abandoned, of which the present application is a continuation-in-part, there is described and claimed the utilization of carbon dioxide under critical conditions in the presence of aqueous solutions of a carbon dioxide solubility modifying component to effect improved recoveries of hydrocarbons from subterranean formations.

Among the objects of the present invention are methods in which surface active agents are disseminated within subterranean, oil containing strata or formations through an extended area thereof.

Other objects include dissemination of wetting agents through the strata by means of carbonated water particularly where the combined action thereof is employed to accomplish the desired result.

Still further objects and advantages of the present invention will appear from the more detailed description set forth below, it being understood that such more detailed description is given by way of illustration and explanation only, and not by way of limitation, since various changes therein may be made by those skilled in the art, without departing from the scope and spirit of the present invention.

The following detailed description is taken in connection with the accompanying drawings, in which:

Figure 1 is a vertical section through a system utilizing the present invention;

Figure 2 depicts a vertical section through a modified input well for use in the system shown in Figure 1; and

Figure 3 shows a further modified form shown in vertical section where a single well is employed.

In accordance with the present invention, a surface active agent is disseminated into and through an extended portion of a subterranean hydrocarbon bearing formation for the recovery of oil and hydrocarbons from such subterranean strata and formations containing such oils or hydrocarbons. It has been found that the dissemination of a surface active agent into and through a substantial part of the formation materially reduces the residual oil content of the strata or formation below the residual oil content of such strata or formation where recovery is carried out in the absence of the surface active agent.

The most effective way of introducing the surface active agent into the strata, whether as a liquid or in solution, suspension or dispersion, is by means of carbonated water and where the surface active agent and carbonated water are introduced either simultaneously or separately but act conjointly. Thus the surface active agent may be introduced prior to the carbonated water and the latter used as the drive, or intermittent introduction of the materials may be employed, or they may be introduced in repetitive alternation. The surface active agent may be used in solution, suspension or dispersion, and the medium may contain aqueous liquids. A solution of the surface active agent in carbonated water, is an economically feasible method to employ that is particularly useful. Such solution may contain substances which modify the solubility of carbon dioxide in the vehicle.

While a variety of different types of surface active agents may be employed, and cationic agents may be used under some circumstances, desirably a non-ionic agent is employed because there is a substantial difference in utilization of such agents for present purposes. In general the anionic agents are adsorbed or absorbed to a substantially higher extent than are the non-ionic agents, so that the latter are more economically employed in the present invention than are the anionic agents.

As non-ionic surface active agents, water-soluble types are preferred to oil-soluble agents although a number of them are both water-soluble and oil-soluble. Hydrophyllic (or lyophilic) agents attracted to the water phase

are most desirably employed. Exemplary non-ionic agents are those obtained by reaction of a hydrophobic hydroxy compound such as a phenol or alcohol with several moles of an alkylene oxide principally ethylene oxide or propylene oxide. Water solubility increases with the number of moles of the alkylene oxide reacted. Such reaction products from oleyl alcohol, alkylated-B-naphthol, alkyl phenol such as dodecyl phenol, may be mentioned as exemplary. Similarly alkylene oxide (ethylene oxide) reaction products of higher fatty acids are well known as well as of fatty acid esters, including ethylene oxide reaction products of fatty acid esters of anhydrosorbitols. Lauric, palmitic, oleic, and stearic acids are commonly used for such esters which may generally be referred to as polyoxyalkylene derivatives of hexitol anhydride partial long chain fatty acid esters. The hexitol is usually sorbitol. Other non-ionic agents include phosphoric acid esters of polyethylene glycol; low-order condensation products of polyhydric alcohols with polybasic water-soluble acids such as glycol tartrate, glycerol citrate, esterified with stearic acid; higher fatty acid reaction products with alkylolamines, such as coconut fatty acids with diethanolamine; saponins; etc. "Tween 60" which is a polyoxyethylene sorbitan monostearate sold by Atlas Powder Co. will be used to illustrate the preferred group of non-ionic surface active agents below it being understood that other non-ionic agents may be substituted for the "Tween 60" in those examples. "Tween 60" is soluble in water, dilute acids, dilute alkalis, alcohol and toluol, but is insoluble in mineral oil.

The amount of surface active agent which is introduced into the strata or formation may vary within wide limits, and the wide ranges of solubility of such agents in water for example, enables a wide selection of proportions to be made. However as a matter of economy, there is no need to use other than relatively small amounts of surface active agent as for example from a few thousandths of a percent up to higher amounts. Upper ratios may be 1%, 2%, and higher but are unnecessary as a general rule since small fractions of a percent are all that generally need ever be used. .005% to .5% in water solution may be cited as a typical ratio, all percentages being by weight. Regardless of how it is introduced, the effect sought is that obtainable with an amount of from .005-.5%. The concentration of wetting agent may be stated in a different manner as not less than one part per million based on the carbonated water injected. Such ratios of surface active agent may for example be used in carbonated water solution, and may if desired contain substances which affect the solubility of carbon dioxide.

Thus, on an unconsolidated sand carrying a naphthenic base crude oil, a straight carbonated water drive at 900 p. s. i. left an average residual oil content of 21.6% of pore space in the sands, while a carbonated 0.1% water solution of "Ultrawet K" (an aromatic sodium sulfonate wetting agent made by Atlantic Refining Co.) at 900 p. s. i., resulted in an average residual oil content of 15.4% of pore space.

Using a non-ionic surface active agent, where a carbonated water drive at 900 p. s. i. on an unconsolidated sand carrying such naphthenic crude oil, gave an average of 17.1% residual oil a carbonated 0.1% water solution of a typical non-ionic agent "Tween 60" reduced the residual oil to 8.8% of pore space; while the respective figures for a mixed paraffinic type crude oil in unconsolidated sands, using a carbonated water drive at 900 p. s. i. and a carbonated 0.1% water solution of "Tween 60" respectively, were 16.6% and 9.1%.

In a series of tests on actual oil sand cores taken from the Mid-Continent area the average results indicated that in cores initially containing oil at an average of 31% of pore space, flooding with carbonated water alone reduced the oil to about 15% of pore space and flooding with carbonated water containing 0.1% to 0.01% of

"Tween 60" reduced the oil to a range of 7% to 13% of pore space.

In removing adsorbed or absorbed surface active agents from sands treated therewith, the following results are illustrative, these results having been run on consolidated sands saturated with surface active agents. Using a consolidated sand of about 10.4% porosity and fairly high permeability, tests were run on such sand saturated with non-ionic "Tween 60" and with anionic "Ultrawet K" respectively, using carbonated water and uncarbonated water, portion-wise in equal amounts. The data was as follows:

TABLE I

Recovered wetting agents

Type of Drive	Non-Ionic "Tween 60"	Anionic "Ultrawet K"
	Portions needed to recover 89.5% of wetting agent	Portions needed to recover 88% of wetting agent
Carbonated H ₂ O at 800 p. s. i.	4	11
Water at 800 p. s. i.	6	11

The data show carbonated water removed the non-ionic surface active agent more rapidly than did uncarbonated water, the volume ratios being 2:3. However, both required the same volume to remove the anionic.

Using a consolidated sand having a porosity of about 13.7% and a very low permeability, it was found this sand adsorbed more of the anionic "Ultrawet K," but upon washing, about the same percentage was recovered by the same volume of water used in Table I. The amount adsorbed by this sand was 0.357 part by weight and the amount removed by carbonated water at 800 p. s. i. was 0.312 part by weight using 1000 parts of wash. The amount removed by uncarbonated water wash was 0.315 after 1100 parts of wash. These results show equal effectiveness of carbonated water and of uncarbonated water in removal of the anionic wetting agent from the consolidated sands.

Further tests on a consolidated sand, showed that recovery of adsorbed non-ionic surface active agent was independent of the pressure employed. The data, using a sand of very low permeability and a maximum flow rate at 400 p. s. i. of 100 ml. per 15 minutes was

TABLE II

Portions	Parts by Weight "Tween 60" Recovered			
	Uncarbonated Water		Carbonated Water	
	400 p. s. i.	900 p. s. i.	400 p. s. i.	900 p. s. i.
1.....	0.088	0.088	0.100	0.100
2.....	0.025	0.025	0.020	0.020
3.....	0.006	0.006	0.000	0.000
4.....	0.000	0.000	0.000	0.000
5.....	0.000	0.000	0.000	0.000
Total.....	0.119	0.119	0.120	0.120

Total adsorption of "Tween 60" at 800 p. s. i. was 0.136.

The data in Table II shows that at 400 p. s. i. the same quantity of carbonated water was required as at 900 p. s. i. for the same recovery. The same results were obtained for uncarbonated water. However, at all pressures tested, more uncarbonated water than carbonated water was required to recover the adsorbed (or absorbed) non-ionic surface active agent.

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The following data illustrates secondary recovery from consolidated sands (dolomitic):

Run	Crude Oil	Type of Flood	Remain- ing oil, Percent of Porosity
1----	Mixed Paraffinic	Uncarbonated water, 850 p. s. i.	43.0
2-----	do	Carbonated water, 850 p. s. i.	31.5
3-----	do	Uncarbonated water, 0.1% "Tween 60," 850 p. s. i.	33.1
4-----	do	Carbonated water, 0.1% "Tween 60," 850 p. s. i.	23.6
5-----	Naphthenic	Uncarbonated water, 850 p. s. i.	42.7
6-----	do	Carbonated water, 850 p. s. i.	34.2
7-----	do	Uncarbonated water, 0.1% "Tween 60," 850 p. s. i.	34.7
8-----	do	Carbonated water, 0.1% "Tween 60," 850 p. s. i.	28.4

These results indicate that the use of non-ionic surface active agents and carbonated water for secondary oil recovery is superior to the use of anionics. Further, if the non-ionic surface agent is used and then followed by a carbonated water drive, that portion of the non-ionic agent which is adsorbed at the input well can be recovered by the carbonated water and thus made useful in the subsequent secondary recovery of the oil between the input and output wells. Since the secondary recovery is greatly enhanced by the non-ionic surface active agent, and only a small portion of the agent need be left adsorbed by the sand, and further that portion adsorbed may be recovered for use with a relatively small quantity of carbonated water, non-ionic wetting agents in conjunction with carbonated water are particularly desirable in recovery of hydrocarbons from strata.

Since aqueous solutions are readily carbonated particularly under the high pressures utilized, when carbon dioxide and an aqueous solution are introduced simultaneously or intermittently into an input well or into an underground stratum, carbonation of the solution takes place rapidly in situ and such expedient may be used in lieu of directly introducing carbonated solutions, such as brines.

In the solutions containing the surface active agent, various salts or other compounds both inorganic and organic may be used for particular effects. Various inorganic salts or compounds may be used such as the various alkali metal salts, i. e., sodium, potassium, lithium, ammonium, alkaline earth metal salts such as calcium, magnesium, strontium, barium, and other heavy metal salts including those of iron, chromium, aluminum, nickel, cobalt, manganese, zinc, copper, mercury, etc. particularly such salts which are soluble under the conditions employed. As acid anions for such salts, there may be mentioned chlorides, bromides, iodides, phosphates, arsenates, cyanides, thiocyanates, cyanates, or combinations of any of these salts. Even the free acids of such hereinbefore mentioned salts may be used. Brines, either natural or artificial, may be effectively employed, a good example being sea water. Since the solubility of carbon dioxide varies with the particular salt or salts present in the solution at any given temperature and pressure, these factors of salt or mixture of salts, temperature and pressure may be employed to control the extent of carbonation of the brine or other solution. As exemplary of salts that may be employed there may be mentioned specifically the halides of alkali metals and alkaline earth metals such as sodium chloride, potassium chloride, ammonium nitrate, calcium nitrate, magnesium nitrate, the sulphates of the alkali metals such as sodium sulphate, sodium bisulphate, ammonium sulphate, magnesium sulphate; bicarbonates of sodium, potassium, ammonium, magnesium calcium, etc., and of course as illustrated in some of the brines below, any combinations or mixtures of these salts and acids may be employed.

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The term aqueous solution of a carbon-dioxide solubility modifying component may be used generically for these solutions, while the term brine will be used herein to cover such solutions when they contain at least sodium chloride as such components, regardless of what else may be present. The concentration of salt or other such component may vary widely. Limits corresponding with those equal to the solubility of sodium chloride in water at the particular temperature and pressure employed will usually be sufficient. For example, for sodium chloride the amount present may be from 0.2 to 5.0 and higher, moles of sodium chloride per liter of solution. Other salts may be used in the same proportions although much higher concentrations of salts more soluble than sodium chloride may be employed.

While inorganic compounds have been particularly referred to above, organic compounds, particularly those which are miscible with water to at least a limited extent may be used to modify the solubility of carbon dioxide in aqueous solution containing the wetting agent, with or without any of the inorganic compounds set forth above. For example there may be employed aliphatic and aralkyl alcohols both mono- and polyhydric such as methyl alcohol, ethyl alcohol, propyl alcohol, isopropyl alcohol, amyl alcohol, glycerine, mannitol; dextrose, lactose, levulose, sucrose and other sugars; glycols, such as ethylene glycol, propylene glycol, etc. and their ethers such as diethylene glycol, "Carbitol" etc.; aminoalcohols aldehydes, ketones and acids, both aliphatic and aromatic including chloral, acetone, acetic acid, citric acid, butyric acid, propionic acid, formaldehyde, benzaldehyde, benzoic acid; esters such as amyl formate, amyl acetate, isobutyl acetate, methyl acetate, etc.; halogenated compounds both aliphatic and aromatic including dichlorohydrine, benzyl chloride, bromobenzene, ethylene dibromide, chlorobenzene, carbon tetrachloride, propylene bromide, amyl bromide, chloroform, etc.; nitro compounds such as nitrobenzene; phenols such as phenol, pyrogallol, quinol, resorcinol; carbon disulfide, etc. In general inorganic compounds are preferred particularly brines.

Carbonated aqueous solutions containing wetting agents, may be used in conjunction with carbon dioxide so that the considerations which apply to using carbon dioxide gas or a solution in water may be employed in connection with the present invention and such material is set forth below as taken from the application No. 102,306 referred to above, in respect to the use of carbon dioxide.

The pressures utilized in the flood or drive are not critical. It has been found that carbonated water under high pressures may be used, that is pressures of about 600 p. s. i. or above the range from about 600 to 700 p. s. i., up to any higher value such as 1000 p. s. i. and higher depending to some extent on the nature of the oil or other hydrocarbons being recovered, and the character of the formations being treated. Lower or any desired pressure may be used if desired as long as it serves under particular circumstances to carry the surface active agent into the formation.

By this invention, the residual oil or other hydrocarbons in the formation may be reduced to as little as 10% and less, in sharp contrast to the residual oils of as much as 40% left in such subterranean strata by the use of prior art methods.

When carbonated water and wetting agent are used and in addition carbon dioxide per se is used, high pressure of the latter may give unique results in carrying out the present invention. However as will be illustrated below, other methods and procedures may be utilized with the carbonated water treatment in accordance with the present invention, and other materials may be used prior or subsequent to or concurrently or conjointly with, the carbonated water and wetting agent in accordance with the present invention.

A factor to be noted is reduction of surface tension, which probably begins to exert its effect prior to the acceleration of the solubility of the oil on CO_2 . It aids solubility by tending to release the oil from the smaller pores of the oil sand. There are indications that CO_2 below 100 p. s. i. in an oil-water mixture has negative effect on the release of oil from oil-sands but at pressures above 100 p. s. i., it has a slowly increasing advantageous effect. The pH of CO_2 in water solution, which is fairly constant above 100 p. s. i., increases rapidly below 100 p. s. i. and is neutral at 0 p. s. i. a. The possibility of CO_2 acting to reduce surface tension is indicated by the fact that carbonic acid (H_2CO_3) is known to react as a hydroxy derivative of formic acid. Traces of formic acid and other fatty acids and their soaps have the power of materially lowering the surface tension of oils. The CO_2 :oil ratio in the unfavorable pressure range below 100 p. s. i. is believed to be best indicated by the solubility of CO_2 in oil and brine at pressures below 100 p. s. i. Such solubility is not above 5 volumes which is about 1.2 in percent by weight. Thus the CO_2 :oil ratio may be in the neighborhood of 1:84. However CO_2 in concentrations above 1% or in CO_2 :oil ratio less than 1:80 has a beneficial effect on the separation of oil from sand; this beneficial effect may be due to a decrease in surface tension of the oil. Wetting agents may exhibit a marked effect on surface tension. In the reduction of surface tension, time probably plays an unimportant role—the surface tension is conceivably reduced rapidly on contact with a definite minimum concentration of CO_2 .

The present invention may be applied to various types of fields including those where oil containing strata are present but natural production or pressure flow is not exhibited or where once exhibited has ceased, or where the pressures are not sufficient to yield sufficient quantities for economical recovery under the natural pressures prevailing in the strata; the invention may be applied to depleted, exhausted or abandoned fields; it may desirably be applied to fields which have previously been subjected to a fluid drive such as air, or natural gas, or which have been subjected to water flooding; that is, it may be applied in general to any subterranean oil containing strata or formations which do not lend themselves to economical recovery by the methods of secondary recovery ordinarily heretofore practiced. And the method of the present invention may be applied to various types of geological structures of the character set forth including consolidated and unconsolidated sands, limestone formations, etc. The methods may be employed in the recovery of oils of any character including paraffinic base, naphthenic base, and asphaltic base, mixed paraffinic, mixed naphthenic, etc., oils. Although with paraffinic base oils, a higher overall recovery of the hydrocarbons from the strata may be obtained than with asphaltic oil recoveries, the naphthenic base oils giving recoveries more closely analogous to the yields obtained with paraffinic oils. Thus, there is a greater recovery of oils with lighter density than those of heavier density, but in all instances the overall recoveries by the methods of the present invention far exceed those possible with prior art methods.

The methods of the present invention may be practiced in any desired manner and in any combination with other steps so long as the treatment includes dissemination of the surface active agent into and through at least a substantial portion of the formation.

The carbonated water may be used at pressures indicated above such carbonated water being employed as a carbonated water drive which is very effective in connection with surface active agents in the recovery of oils from subterranean strata at the pressures indicated. For such purposes carbonated water may first be prepared and then introduced at the desired pressures into the subterranean stratum. Since carbonation of water by carbon dioxide takes place extremely rapidly, at the high

pressures a stream of water and of carbon dioxide at the higher pressures indicated may be passed intermittently or concurrently into the input well whereupon carbonation takes place rapidly and the carbonated water will be introduced into the stratum undergoing treatment.

The fact that carbonated water may be effectively employed to produce high recoveries of hydrocarbons such as oil from strata containing the same enables the present process to be applied effectively to many fields which have been flooded in prior art secondary recovery methods. For such purposes the carbon dioxide under the pressures indicated may be introduced directly into the water flooded field, producing carbonation of the water in situ and driving the carbonated water into the formations to produce effective recoveries of hydrocarbons therefrom.

Carbonated water containing surface active agent may be used as the only drive, or it may be used in conjunction with other fluid drives as for example and particularly with carbon dioxide drives at the pressures of the order indicated. The carbonated water may be forced into the stratum first followed by introduction of the carbon dioxide per se under the pressures indicated or the dry carbon dioxide may first be introduced into the subterranean strata followed by the carbonated water. Where carbonated water at the pressures indicated is utilized for introduction into the subterranean strata, after the carbonated water has been introduced, an air or methane or other fluid drive may be employed. Where a combination of treatment with dry carbon dioxide followed by a liquid drive is employed, the oil bearing horizons may first be conditioned with carbon dioxide at pressures above 600 p. s. i. followed by a carbonated water drive.

In lieu of surface active agent containing carbonated water, carbonated brine or other carbonated aqueous solutions of carbon dioxide solubility modifying component including wetting agents may be employed in the same way as given above for carbonated water. It should be noted that the matter given above with respect to the use of carbonated brine or other carbonated aqueous solutions of carbon dioxide solubility modifying components apply in this case. It is important to note that the use of carbonated brines give the highest percentage recovery of hydrocarbons from subterranean formations.

The time element, namely the length of time that the treatment is carried out in accordance with the present invention, involves a number of considerations. The treatment should be carried out for a sufficient length of time to produce a hydrocarbon or oil recovery from the effluent that is economically justifiable. The actual time involved will necessarily depend on a number of factors including the nature of the strata or formation, the character of the oil therein contained, the pressures employed, the form in which the drive or flood is employed, etc. It is therefore difficult to specify individual time treatments except in a comparative way. It is however important to note that the bulk of the oil or hydrocarbon in the strata may be removed in periods of time that are much shorter than with any of the prior art methods, since most of the hydrocarbons or oil recovered are obtainable in the first fraction of time of treatment. Thus under a given set of conditions where oil was removed from sands of relatively high porosity it was found that nearly the same amount of the oil was removed from the sands in one-fourth of the time as was obtained in the full period of treatment, that even in one-sixth of the time a large fraction of the removable oil was obtained, and in periods as short as one-twelfth of the full period of treatment, significant amounts of the recoverable oil were also obtained.

The utilization of carbonated water as taught herein together with surface active agents for the dissemination of the latter in subterranean strata may be employed as set forth above without any initial treatment or pretreatment of the formation or strata. However if desired, the formation may be subjected to various types of treat-

ments before utilizing the carbonated water methods of the present invention. For example the formation may be treated to make it more permeable to oil and less permeable to water, acidizing treatments may be utilized, etc. Insofar as acidizing is utilized, it is not essential where carbon dioxide is employed in accordance with the present invention, since CO_2 acts as an acid to produce acidizing of the formation.

The system employed for utilizing the treatments set forth herein may in general make use of the equipment which has heretofore been employed in the use of various types of fluid drives, modified however where necessary to provide the operations required in accordance with the present invention. To exemplify systems that may be employed in carrying out the present invention and referring to the drawing, Figure 1 is a diagrammatic representation of a system employed in secondary recovery utilizing an input well into which the treating agents are introduced and passed into the strata to be recovered through the output well, carbonated water being used. As there shown, carbonated water carrying surface active agent entering from any desired source through inlet pipe 1 passes through compressor 2 if desired, where its pressure may be raised to the order of pressures set forth above for use, passing from compressor 2 through pipe 3 by way of head 4 into the input well 5 which conducts the carbonated water, etc. under the desired pressure into subterranean oil strata or formations 5. The carbonated water etc. passes through such oil structure 5 driving out and/or carrying with it oil and other hydrocarbons removed from such oil structure which effluent enters outlet well 6 and is removed therefrom through head 7 by valved pipe 8 into separator 9 where separation is made between the liquids and gases, liquids being withdrawn through valve outlet 10 and gases being removed through valved outlet 11; the liquid products may then be worked up as desired. Gaseous hydrocarbons in the effluent gases removed through the pipe 11 may be recovered from such gases by appropriate treatment and any desired portion of recovered gases recycled. Unless removed therefrom, such recycled gases when employed may carry gaseous hydrocarbons such as methane obtained from the oil structure and may be utilized to enhance the action of the carbonated water without additions from external sources.

The surface active agents and other agents may either be introduced with the carbonated water through the inlet 1, or such agents may enter through valved inlet pipe 12 into pump 13 and injected through valved inlet pipe 14 at the desired pressures into the head 4 where such injected agents mix with the carbonated water entering the head 4 through the pipe 3. Where any liquid is employed together with the carbonated water it may be introduced in this way through the pipe 12, pump 13, and pipe 14. Thus carbonated water and brine may be introduced in this way. Or any adjuvant gases such as methane may be introduced in this way. Water or brine when introduced simultaneously with the carbon dioxide will undergo carbonation quite rapidly in view of the high pressures prevailing in the concurrent movement of water and carbon dioxide down through the input well 5 so that the water or brine as it arrives in the oil structure 5 or in part during its passage through the oil structure 5 is subjected to carbonation. Instead of concurrent feeding of surface active agent together with the carbonated water, intermittent operation may be carried out.

In Figure 2, a diagrammatic vertical section is shown of an alternative input well that may be employed in secondary oil recovery for example, in lieu of the input well of Figure 1. In this case the input well 15 is provided with separate induction pipes 16 for a fluid such as carbonated water under pressure as desired and 17 for adjuvant liquids carrying wetting agents such as water or brine or for the use of carbonated water or brine carrying wetting agents as well as for gases. Where no casing-head is employed in the well, a packer 18 may be utilized

near the bottom of the well. An input well of the type shown in Figure 2 may be employed in lieu of that shown in Figure 1 for the input well there illustrated, the system in utilization otherwise being like that described above in connection with Figure 1. In this case, it will be noted that it is possible to use a fluid drive under pressure high enough to force any liquid previously introduced through the pipe 17, into the oil structure formation 5; or a liquid drive introduced through pipe 16 may be utilized subsequent to a treatment with carbonated water etc. under desired pressures. Any variation in procedures may readily be employed in this system similar to that in connection with Figure 1. In the use of systems of the character shown in Figures 1 and 2 for secondary recovery, the number of output wells per input well will be determined in accordance with the usual practice in the art and may of course vary depending on the particular conditions.

The methods of the present invention may be employed to carry out treatments in a single well which serves both for input and output purposes, as illustrated in Figure 3. In this case, the well 19 provided with casing-head 20 is supplied with valved inlet pipe 21 which may be employed for the fluid such as carbonated water with or without surface active agent under pressure as desired and valved inlet pipe 22 for any surface active agent and other adjuvant, these pipes being shown as concentric and extending down to the oil formation 5. The fluid under pressure and any other adjuvants or liquids to be employed concurrently or intermittently or otherwise with the fluid are introduced in the same manner as described above for the systems of Figures 1 and 2. The injected fluids will permeate into the oil formation 5. After treatment for the desired length of time, the introduction of carbonated water and other materials is discontinued, and effluents then taken off from the well 19 utilizing the same pipes 21 or 22 for withdrawal or separate removal pipes may be employed. Similar arrangements may be employed in systems where the carbonated water is introduced at the top of the well, and recovered oil withdrawn from the bottom, such practice being indicated in certain oil horizons.

In any of these methods and systems, provision may be made to recover the wetting agent from effluent material, and such wetting agent returned to the system. In effect such recovery and reuse constitutes recycle of the wetting agent in solution, suspension, dispersion, etc. Thus a solution of wetting agent may be circulated through the strata, oil or other hydrocarbons and any other materials separated, the wetting agent fortified with added wetting agent when necessary or with addition of adjuvants as set forth herein, when the latter are used, and the recovered wetting agent recycled.

Having thus set forth our invention, we claim:

1. A method of treating a subterranean hydrocarbon bearing formation which comprises disseminating a non-ionic surface active agent within said formation through an extended area thereof by CO_2 carbonated water at a pressure of CO_2 of at least 400 p. s. i.
2. A method as set forth in claim 1 in which the surface active agent is in solution in the carbonated water.
3. A method as set forth in claim 1 in which the amount of surface active agent is not less than 1 part per million based on the carbonated water injected.
4. A method as set forth in claim 1 in which the hydrocarbon is a crude petroleum oil.
5. A method of treating a subterranean hydrocarbon bearing formation which comprises driving a non-ionic surface active agent through said formation by CO_2 carbonated water at a pressure of CO_2 of at least 400 p. s. i.
6. A method as set forth in claim 5 in which the surface active agent is in solution in the carbonated water.
7. A method as set forth in claim 6 in which the hydrocarbon is a naphthenic base crude oil.

8. A method as set forth in claim 6 in which the hydrocarbon is a paraffinic base crude oil.

9. A method of recovering hydrocarbons from a hydrocarbon bearing formation penetrated by an input well and an output well communicating through said formation with the input well, which comprises introducing a non-ionic surface active agent and CO₂ carbonated water at a pressure of CO₂ of at least 400 p. s. i. through the input well into said formation and subsequently recovering hydrocarbons and the surface active agent at the output well.

10. A method as set forth in claim 9 in which the hydrocarbon is a crude petroleum oil.

11. A method as set forth in claim 9 in which the surface active agent is in solution in the carbonated water.

12. A method of treating a subterranean hydrocarbon bearing formation which comprises driving a non-ionic surface active agent through said formation in the presence of CO₂ carbonated water at a pressure of CO₂ of at least 400 p. s. i. to produce an effluent product, recovering hydrocarbons and surface active agent from said effluent product, and recycling said recovered surface active agent to said formation.

13. A method as set forth in claim 12 in which the hydrocarbon is a naphthenic base crude oil.

14. A method as set forth in claim 12 in which the hydrocarbon is a paraffinic base crude oil.

15. A method of treating a subterranean hydrocarbon bearing formation which comprises disseminating a non-ionic surface active agent within said formation through an extended area thereof by CO₂ carbonated water at pressure of the carbon dioxide of at least 600 p. s. i.

16. The method of claim 15 in which the amount of carbon dioxide introduced is more than 20 cu. ft. of CO₂ per cu. ft. of liquid in the reservoir.

17. The method of claim 15 in which the amount of carbon dioxide introduced is more than 52 cu. ft. of CO₂ per cu. ft. of liquid in the reservoir.

18. In a method of increasing the recovery of hydrocarbons from a subterranean hydrocarbon bearing formation, the step of introducing into said formation a surface active agent in the presence of CO₂ carbonated water at pressure of carbon dioxide of at least 400 p. s. i.

19. The method of claim 18 in which the pressure of the carbon dioxide is at least 600 p. s. i.

20. The method of claim 19 in which the agent is in solution in the carbonated water.

21. A method of increasing the recovery of hydrocarbons from a subterranean hydrocarbon bearing formation penetrated by an input well and an output well communicating through said formation with the input well, which comprises introducing into said formation through the input well a surface active agent in the presence of carbonated water at pressure of carbon dioxide of at least

600 p. s. i., removing an effluent containing hydrocarbons from the outlet well, and recovering hydrocarbons from said effluent.

22. The method of claim 21 in which the agent is in solution in the carbonated water.

23. The method of claim 22 in which the hydrocarbon is crude petroleum oil.

24. The method of claim 23 in which the oil is naphthenic base crude oil.

25. The method of claim 23 in which the oil is paraffinic base crude oil.

26. The method of claim 18 in which the surface active agent is a polyethylene glycol ether of an alkylated phenol.

27. The method of claim 18 in which the surface active agent is a polyoxyalkylene ether of a hexitan partial ester of a long chain fatty acid.

28. The method of claim 18 in which the surface active agent is a polyethylene glycol ether of an N-alkylolated higher fatty acid amide.

29. The method of claim 18 in which the surface active agent is a polyethylene glycol ether of a long chain alcohol.

30. The method of claim 18 in which the surface active agent is non-ionic.

31. In a method of increasing the recovery of hydrocarbons from a subterranean hydrocarbon-bearing unconsolidated formation the step of introducing into said formation a surface active agent in solution in carbonated water, the amount of agent present in the solution being from about .005% to .5% of the solution, the carbon dioxide having a pressure of at least 600 p. s. i., to reduce materially the ratio of residual oil to pore space in the formation.

32. The method of claim 31 in which the agent is anionic.

33. The method of claim 31 in which the agent is non-ionic.

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