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SECONDARY RECOVERY OF HYDROCARBONS WITH SULFUR TRIOXIDE

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This invention relates to an improved method for recovering hydrocarbon material from an underground, permeable, oil-bearing formation, which may be in the form of an oil sand, oil shale or tar sand. The invention pertains more particularly to a method for the secondary recovery of oil, particularly a viscous oil, or other hydrocarbon material that is difficult to displace under reservoir conditions and contains at least a minor amount of aromatic components in its makeup.

This invention constitutes an improved method for supplying heat and/or other energy in the form of a driving medium to an underground oil-bearing formation for the purpose of increasing the oil recovery therefrom. The method is applicable to permeable formations containing oil of high viscosity which may be non-productible, i.e., non-flowable under original conditions and to those containing low to medium viscous oils of which varying amounts may have been recovered by conventional primary means.

The primary production of petroleum hydrocarbons from oil-bearing formations is usually effected by drilling through or into the oil-bearing sand and providing access to the formation around the borehole so as to permit oil to flow into the borehole from which it may be recovered by conventional methods and apparatus. If the formation contains an oil of low or medium viscosity at reservoir conditions, the well may be produced either by flowing or pumping in a manner well known to the art. If on the other hand the formation contains a highly viscous oil at reservoir conditions, it may be necessary to heat the formation in the vicinity of the borehole to reduce the viscosity of the oil so that the oil may flow into the borehole. In time, even the wells containing free-flowing oil become depleted although a substantial amount of oil still remains in the producing formation underground. The residual oil left in the formation underground is very difficult to produce and considerable research has been carried out on secondary methods of recovering this residual oil. Various methods have been devised such as heating, underground combustion, flooding with water or a miscible fluid, etc. These methods involve the injection of water, gas, air, fuel, solvents, etc. or a combination of these into the formation through one or more input wells while the hydrocarbons or components thereof are withdrawn through one or more output or producing wells.

The flooding of underground formations for primary or secondary of hydrocarbon materials such as oil presents many problems. In the water flooding of an oil-bearing underground formation, it is necessary to employ flood-water free of clays, colloidal material, undissolved salt, etc., which would tend to plug the face of the oil formation and perhaps within the oil formation itself when the water is injected thereinto. In addition, many producing formations being flooded contain a certain amount of swelling clays in the form of bentonite or montmorillonite clay, which upon swelling, reduce the permeability of the formation. The use of solvents as a flood or the use of chemicals added to water for flooding a formation is often prohibitive in cost. Additionally, many of the oils left in the formation are very viscous and it is essential that they be heated in order to cause them to flow to a producing well. While underground combustion is successful in many fields, it has the drawback that it destroys or uses as fuel some of the hydrocarbons in the formation.

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It is therefore a primary object of the present invention to provide a method for treating an underground hydrocarbon-bearing formation in a relatively inexpensive manner so as to increase the yield of oil from the formation.

A further object of the present invention is to provide a method for secondary recovery of oil in a formation by injecting into the formation a heat-creating chemical, i.e., one that reacts exothermically in the formation with the hydrocarbons and/or the formation waters contained therein.

Another object of the present invention is to provide a method of recovering a substantial amount of oil from a formation by flooding or merely contacting under pressure the oil-bearing formation with a chemical material which facilitates extraction of the oil from the oil-bearing formation.

Still another object of the present invention is to provide a method for secondary recovery of oil which makes use of aromatic components contained within the oil in order to form petroleum sulfonates within the formation which act to break the oil free of the formation and/or to emulsify the oil with water to create a flooding composition which is especially effective in driving oil from a formation.

These and other objects of this invention will be understood from the following description.

The method according to the present invention contemplate producing liquid or liquefiable hydrocarbons from a permeable hydrocarbon-bearing subsurface formation which is penetrated by at least one well, by introducing into the well a quantity of sulfur trioxide in an amount sufficient to react with a portion of the hydrocarbon material of the formation so as to form petroleum sulfonates in the formation while at the same time liberating heat so as to heat the surrounding formation and reduce the viscosity of the oil in the vicinity. The petroleum sulfonates in contact with the petroleum of the formation reduce the surface tension of the petroleum so that it may be moved more readily through the formation or separated therefrom more readily. A further heating of the in situ hydrocarbons takes place when sulfur trioxide contacts and reacts with formation waters whereby this heat of reaction also aids in raising the temperature of the adjacent formation to further reduce the viscosity of the hydrocarbons in the vicinity. In the event that any limestone is present in the formation, sulfuric acid formed from the sulfur trioxide would react with the limestone and become neutralized at the same time liberating carbon dioxide and additional amounts of heat which both aid in driving the oil from the formation. Preferably, however, the method of the present invention is carried out in formations in which most of the matrix is composed of minerals other than limestone or other acid-soluble material so as to make use of most of the sulfur trioxide by reacting it with the oil of the formation rather than the mineral components. In addition, the sulfur trioxide is preferably injected in the form of a liquid slug containing enough sulfur trioxide to ensure the continued sulfonation of the oil during the displacement of the slug throughout substantially the entire flow path from the point of injection to the point of production. The hydrocarbons of reduced viscosity together with the petroleum sulfonates are displaced by further fluid injection through the formation.

The present method of selectively heating a reservoir formation can be utilized in numerous ways. For example, in the event that the oil-bearing formation contains natural fractures or has been previously hydraulically fractured between wells or out from a single well, sulfur trioxide may be injected into the fractured zone to heat the walls of the fractures and the permeable portions of the formation. Additionally, with or without fractures between closely spaced wells in relatively permeable reser-

voir formation, the use of sulfur trioxide in accordance with the present invention may be employed to reduce the viscosity in the vicinity of the wells, or the flow paths between wells, to facilitate production of the oil. The method of the present invention may be employed in a single well to treat the formation surrounding the well and facilitate back flow of oil into the well.

The use of sulfur trioxide or a liquid reactant containing sulfur trioxide for secondary recovery purposes in an oil-bearing formation is advantageous in view of the relatively high heat of hydration that is released upon contact with formation water, as well as the high heat of neutralization that is released upon contact with a basic substance or solution within the formation. Most important is the fact that aromatic hydrocarbons contained in the formation are converted to sulfonic acids that are effective, per se, or in the form of their alkali metal salts, as oil-emulsifying surfactants. The sulfur trioxide to be used in accordance with the present invention may comprise liquid-sulfur trioxide, but is preferably in the form of oleum, i.e., concentrated sulfuric acid having an excess of SO_3 present.

In one form of the method of the present invention the sulfur trioxide is injected into a single well to reduce the viscosity of the hydrocarbons in the formation surrounding the well after which the hydrocarbons of reduced viscosity are allowed to flow back into the well from which they are produced by conventional means. In other forms the use of oleum or sulfur trioxide as a flooding material may be combined with other flooding materials in the secondary production of an oil formation. Thus, water may be forced down the injection well in back of the liquid sulfur trioxide to displace the petroleum sulfonates and hydrocarbons of reduced viscosity through the formation to treat a greater section of the formation or to force the hydrocarbons to a producing well. Neutralization of the acids or sulfur trioxide around a single well may take place by pumping caustic or any other suitable material down the well and into the formation before opening the well and reducing the pressure therein so as to allow the hydrocarbons of reduced viscosity in the formation to flow back into the well. In the event that a two well system is used, any acid being forced into the second or producing well may be neutralized therein.

Using a liquid reactant to produce heat within an underground reservoir formation has inherent advantages over a similar use of a gaseous reactant. The liquids require no compressor equipment and thus require significantly less bulky and expensive equipment at the well site. The reactive components can be present in a liquid phase in concentration wells above those in which they can be present in a gas phase. Since the liquid reactants may be highly concentrated they may be used in the form of a slug amounting to a minor proportion, such as 20% of the pore volume, of the zone to be swept that is displaced through that zone by a low cost material such as water. In such a procedure the reactants heat the oil to be displaced only in the places and at the times the displacement is occurring.

We claim as our invention:

1. A method of producing liquid or liquefiable hydrocarbons from a hydrocarbon-containing subsurface formation, said formation being penetrated by at least one well, said method comprising

introducing into a well a quantity of sulfur trioxide in an amount sufficient to react with a portion of the hydrocarbon of said formation,

contacting and reacting said hydrocarbon with a portion of said sulfur trioxide to form petroleum sulfonates in said formation,

maintaining said petroleum sulfonates in contact with said petroleum of said formation for a time sufficient to reduce the surface tension of the petroleum and heat the formation,

heating in situ hydrocarbon of said formation further by contacting and reacting another portion of said sulfur trioxide with formation water whereby the heat of reaction raises the temperature of the adjacent formation to reduce the viscosity of the hydrocarbon, displacing the previously formed petroleum sulfonates, the hydrocarbon of reduced viscosity and additional quantities of sulfur trioxide into the hydrocarbon-bearing formation,

said petroleum sulfonates and said hydrocarbon being forced toward a second well in communication between the formation and the surface,

said hydrocarbon-producing formation including carbonate material which neutralizes said sulfur trioxide which is converted to sulfuric acid by formation waters, said acid being substantially neutralized by said carbonate material as the acid is displaced from said first to said second well, and

producing hydrocarbon of reduced viscosity to the surface.

2. The method of claim 1 including the step of neutralizing in said second well any residual acid being forced thereinto.

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