

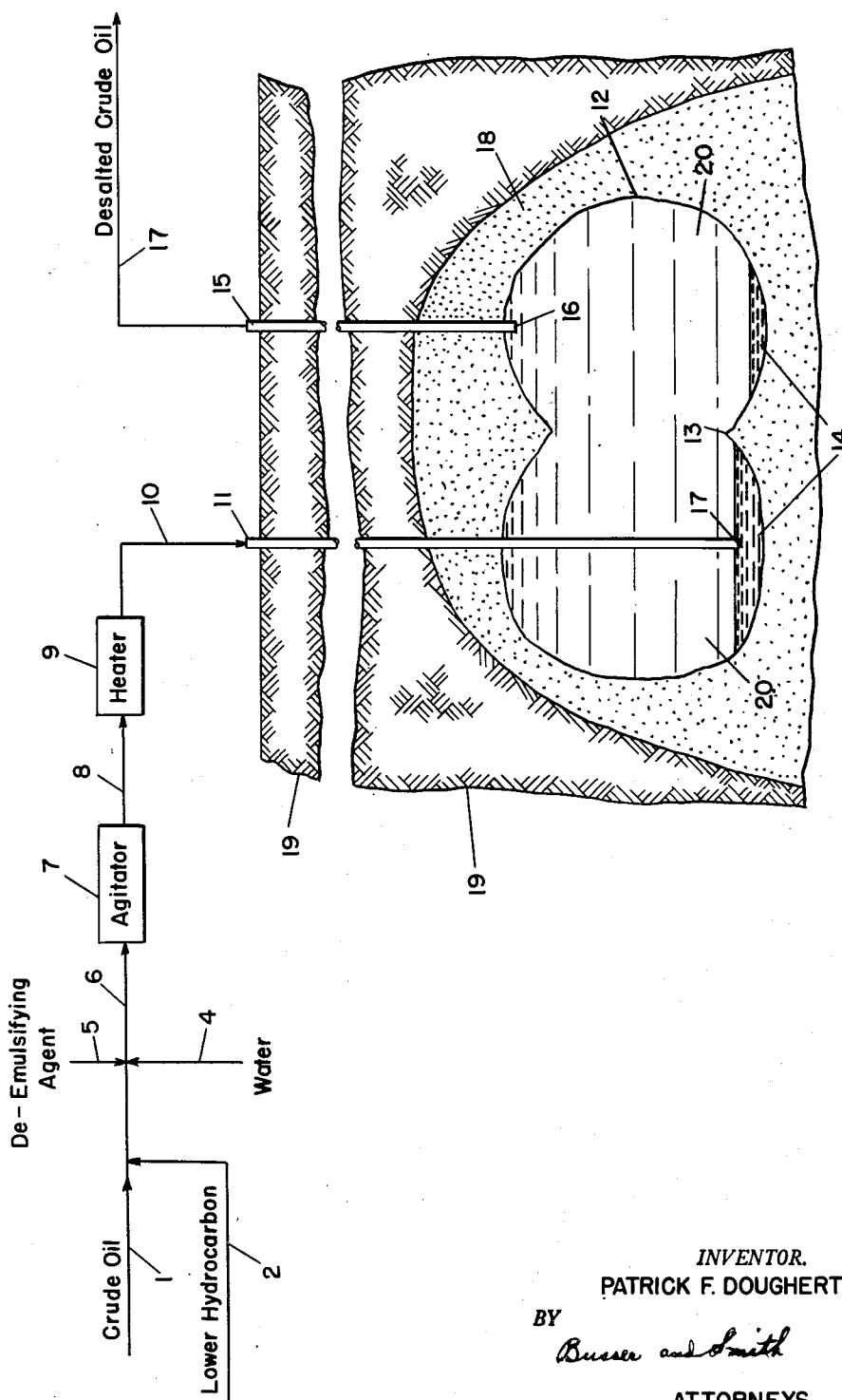
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PROCESS FOR REMOVING CONTAMINANTS FROM CRUDE OILS

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PROCESS FOR REMOVING CONTAMINANTS
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This invention relates to an improved process for removing impurities from petroleum crude oils, and more particularly relates to an improved process for removing inorganic materials such as salts, water, and mixtures thereof, from crude oil.

Crude oils frequently contain water, other inorganic materials such as inorganic salts, or mixtures of such inorganic materials, as impurities. For example, the chlorides of sodium, magnesium or calcium, or mixtures thereof are frequently present in crude oils. The impurities may occur naturally or by reason of operations such as acid treatment of oil wells. The salts may be present in the form of a brine emulsified in oil, or in the form of suspended crystalline particles. These impurities cause serious difficulties in refining processes, especially those performed at elevated temperatures. For example, salts form deposits upon hot surfaces and thus destroy the efficiency of and plug equipment such as stills, heat exchangers and the like, and cause serious corrosion problems. The presence of contaminants in relatively viscous oils presents an especially difficult problem, since known methods for their removal usually require either a prohibitively long residence in a settler, or a prohibitively high temperature during settling.

A further difficulty involves the transportation of crude oils by pipe line from oil field to refinery. Such transportation is relatively difficult to perform with high viscosity crude oils because of excessive pumping requirements. To overcome this difficulty, lower hydrocarbons, such as normally gaseous hydrocarbons, may be dissolved in the crude oil in order to decrease the viscosity thereof. This method of operating is not feasible with crudes containing salt as an impurity where desalting is performed after transporting the crude oil to the refinery. The difficulty is that in order to achieve satisfactory desalting, it is necessary to heat the crude at some stage in the desalting process. The presence of the lower hydrocarbons requires that a vessel capable of withstanding high pressures be employed, which, in view of the large quantities of crude which must be processed, renders the process inoperable from a practical standpoint. Furthermore, desalting prior to transporting crude oil is difficult after adding lower hydrocarbons because the same dif-

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ficulty as above described is encountered, whereas if desalting is attempted prior to adding the lower hydrocarbons, the viscosity of the oil inhibits the desalting process to such an extent that a prohibitively long residence time in a settler may be required, as above described. Substantially the same difficulties are encountered when water is present as a contaminant.

An object of the process of the present invention is to provide a process for removing contaminants from petroleum crude oils. Another object is to provide a process for desalting crude oil after reducing the viscosity thereof, so that rapid desalting of a crude oil suitable for pipeline transportation is achieved. A further object is to provide a process for separating water from crude oil. Other objects will be apparent from the following description of the invention.

It has now been found that by forming an emulsion of petroleum crude oil, water, and an added de-emulsifying agent, introducing the emulsion into an underground salt cavity where it is maintained in a relatively quiescent state at de-emulsifying temperature, crude oil having a decreased quantity of contaminants may be recovered from the salt cavity, and the above and other difficulties are overcome. It has been further found that the present process is made especially applicable to relatively viscous crudes by introducing lower hydrocarbons as a component of the emulsion.

A preferred embodiment of the process of the present invention is the desalting of relatively viscous crude oil, and hence the following description is directed principally to this embodiment.

In the preferred embodiment, a relatively viscous salt containing crude oil is admixed with water, a de-emulsifying agent, and a lower hydrocarbon or a mixture of lower hydrocarbons, to form an emulsion. The resulting emulsion is introduced into an underground salt cavity where it is maintained at a temperature sufficient to obtain rapid separation of oil and water. By adding a lower hydrocarbon or mixture of lower hydrocarbons to the crude oil, the viscosity thereof is decreased so that rapid de-emulsification is obtained and pipe-line transportation is facilitated. Artificial salt cavities, used as the settling vessel in the present process,

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withstand any pressure encountered on storing an admixture of crude oil and lower hydrocarbons at desalting temperatures, and the residence time of the crude oil in the salt cavity is not a significant factor in the process because of the large capacities of such cavities.

In the salt cavity a water layer containing salt or other inorganic impurity separates from the oil and settles to the bottom. Desalted oil containing added normally gaseous hydrocarbons dissolved therein is removed from the upper portion of the salt cavity. By reason of the reduced viscosity of the recovered desalted crude oil, it is especially suitable for pipe-line transportation. Other means of transportation may be employed, such as tankers, and the reduced viscosity enhances the ease of loading and unloading. At periodic intervals the water layer is removed from the cavern by any convenient means, such as by pumping or by forcing it out with gas pressure. The salt cavity presents a smooth surface insoluble in the hydrocarbon layer, and hence additional contamination by reason of using a salt cavity is not observed.

Lower hydrocarbons to add to the crude oil are preferably normally gaseous hydrocarbons, such as ethane, propane and the butanes, or mixtures thereof. Normally liquid hydrocarbons such as pentanes, hexanes, heptanes, octanes, mixtures thereof, and normally liquid hydrocarbon fractions such as gasoline and kerosene may also advantageously be employed with crudes of high viscosity. By "lower hydrocarbon" is meant a hydrocarbon boiling in the kerosene range or lower, i. e., boiling below about 500° F.

Underground salt cavities are unique in their adaptability to the present process. Other underground cavities are not suitable. For example, depleted oil wells are not suitable because porous formations therein prevent stratification of the water and oil layers, and additional salt impurities may be introduced into the hydrocarbons. Furthermore, recovery of oil from depleted wells is difficult. Artificial salt cavities suitable for use in the present process may be made in salt beds or salt domes. Suitable salt beds are commonly found close to oil fields and usually are from 500 to 4,000 feet below the surface, and usually are from about 50 to 1,000 feet deep. Salt domes similarly located may also be used.

The preparation of underground salt cavities may be accomplished by the methods heretofore known. The usual method is to drill to a point close to the bottom of a salt stratum or to a point within a salt dome and dissolve salt therefrom by contacting with water circulated into and out of the borehole. It is preferred to drill two wells spaced so that on dissolving salt therefrom, the two cavities join to form a single large cavity. The single cavity will be separated at the bottom by a ridge which operates as a baffle. The emulsion is introduced through one borehole to a point near the bottom of the cavity, and the desalted oil is removed through the other borehole from a point near the top of the cavity. The ridge separating the cavities at the bottom serves as a baffle to maintain the water layer in a quiescent state.

The accompanying figure illustrates a preferred embodiment of the present process. Salt-containing crude oil is introduced to the process from a source (not shown), such as a producing well or storage tank, through line 1 and admixed with a lower hydrocarbon introduced through

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line 2, water introduced through line 4, and a de-emulsifying agent introduced through line 5. The order of admixing the various components is not important, but with highly viscous crude oils it is advantageous to first admix the lower hydrocarbon with the crude oil to lower the viscosity thereof so that the introduction of the remaining components is not difficult. The resulting admixture is passed through line 6 to agitator 7, wherein the admixture is thoroughly agitated. From agitator 7, the admixture passes through line 8 to heater 9 where it is heated to de-emulsifying temperature. The heated admixture is passed through line 10, borehole 11, and into salt cavity 12 through outlet 17 located near the bottom of salt cavity 12. Salt cavity 12 is shown as having been prepared in salt dome 18 by drilling two boreholes, 11 and 15, and circulating water through each to dissolve salt until the two cavities join, as above described. Formations surrounding the salt dome are indicated by 19. In the salt cavity, the admixture is maintained in a quiescent state so that water layer 14 separates from oil 20 and settles to the bottom of cavity 12. Ridge 13, formed in the preparation of cavity 12, as above described, operates as a baffle to assist in maintaining the emulsion in a quiescent state. Oil is removed through second borehole 15 through outlet 16 located in the upper portion of cavity 12. Recovered desalted crude oil admixed with added lower hydrocarbons is removed from the process through line 17. The so-recovered desalted crude oil is especially suitable for pipe-line transportation and subsequent refining. Pumps, valves, meters, and the like, the location and operation of which will be apparent to those skilled in the art, have been omitted.

The salt cavities contemplated for use in the present process, as above described, withstand any pressure encountered in heating to desalting temperatures crude oil containing substantial proportions of normally gaseous hydrocarbons. Any desired residence time may be obtained by regulating the throughput of the oil, or by adjusting the quantity of oil in the cavity by regulating the height of the water-oil interface. A further advantage of using salt cavities is that the temperature therein will usually be from about 90 to 250° F., which temperature may be substantially the same as that required to achieve rapid settling of the water layer. By use of relatively long residence time in the cavity, the temperature therein may be sufficient to achieve de-emulsification without heating the inflowing emulsion. By the expression "desalting temperature," as used herein, is meant the temperature at which rapid separation of water from oil is achieved, which in general will be from about 100° F. to about 300° F. A further substantial advantage of the present process is that the settled water layer will dissolve salt from the cavity bottom. This increases the density of the water layer resulting in an increase in the difference in density between the water and oil layers. Hence, the interface between the two layers is sharply defined and is not broken in the event of surges of incoming emulsion which is advantageously introduced below the liquid interface into the water layer.

The present process is not limited to the use of any particular de-emulsifying agent, and any de-emulsifying known in the art may be employed. De-emulsifying agents such as benzene sulfostearic acid, or its monoammonium or di-

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ammonium salt, and the ammonium salts of petroleum sulfonic acids give good results. The de-emulsifying agent may be introduced without dilution, or as a solution or dispersion, for example, in water, gasoline, or kerosene. The quantity of de-emulsifying agent to employ is a de-emulsifying quantity which will vary according to the emulsion being treated and the temperature of treatment, a smaller quantity being required at relatively high temperatures. Usually the weight ratio of agent to emulsion will be between 1 to 1,000 and 1 to 30,000.

Any crude oil may be desalted in accordance with the present process. The present process is especially advantageous for use with crude oils of relatively high viscosity. The salt content of such crudes is usually within about 20 to 100 pounds of salt per 1000 barrels of oil, and the present process gives good results therewith, the salt content being reduced to about 2 to 5 pounds per 1000 barrels in the usual operation. If desired, the salt content can be further substantially reduced by adjustment of operating variables.

As above stated, water is admixed with crude oil. The quantity of water to employ will vary according to the quantity of salt present in the crude oil and with the amount of desalting desired, but usually will be within the range of from about 2 to 20% by volume, but more or less may be used as required. The amount of lower hydrocarbons to introduce depends principally upon the initial viscosity of the oil. For high viscosity oils, from about 5 to about 20% by volume of lower hydrocarbons, as above defined, should be employed. With lower viscosity oils a smaller quantity may be employed. As above described, the process of the present invention is especially suitable for the desalting of relatively viscous crude oils, which includes crude oils having a viscosity of above about 100 seconds Saybolt at 100° F. However, an important embodiment of the process is the desalting of a relatively low viscosity oil, say a viscosity of below about 100 seconds Saybolt at 100° F., in which case the process is operated as above described except that the addition of lower hydrocarbons may be omitted. The same advantages, except decreased viscosity, are obtained as above described.

A further important embodiment of the present process is the desalting of relatively high viscosity crude oil at high temperatures, say above 350° F., with or without the addition of lower hydrocarbons, which is possible through the use of a salt cavity and has the advantages as above described. In using relatively high temperatures, it is of advantage to employ heat exchange between the inflowing emulsion and outflowing desalted crude oil, which may be performed within a borehole, in heat transfer equipment above the ground surface, or both.

Another embodiment of the present process is to recover added lower hydrocarbons from desalted oil and recycle the recovered hydrocarbons. This embodiment is especially advantageous where a decrease in viscosity for desalting is advantageous, but is not thereafter important. Recovery of added hydrocarbons may be accomplished by any convenient method, such as by flashing in a fractionating tower.

Other embodiments and advantages of the process of the present invention will be apparent to those skilled in the art. For example, in the event that salt formations suitable for prepar-

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ing salt cavities are located near a refinery, lower hydrocarbons may be admixed with crude oil at the place of production, the admixture transported to the refinery, and there desalted in accordance with the process of the present invention.

In order to illustrate the process of the present invention, a crude oil having an API gravity of about 31, a viscosity of 35 seconds Saybolt at 100° F., and a salt content of 100 pounds per 1000 barrels is admixed with about 5% water, about 7% of a liquid mixture of normally gaseous hydrocarbon consisting principally of butanes, and a small quantity, about 1 part per 1000 parts of emulsion, of a de-emulsifying agent, and the admixture is vigorously agitated. The agitated mixture is then heated to about 250° F. and continuously introduced at a rate of about 17,000 barrels per day into a salt cavity at a depth of about 2000 feet having a capacity of about 100,000 barrels, the introduction being made at a point near the bottom of the cavity. Substantially salt free oil, i. e. oil containing less than 3 pounds of salt per 1000 barrels of oil, is continuously removed from the upper portion of the salt cavity. The desalted mixture, because of its low viscosity, is especially suitable for pipe-line transportation.

In a substantially identical manner, water may be removed from crude oil, except that the addition of water is not required.

The invention claimed is:

1. Process for removing contaminants from petroleum crude oil which comprises forming an emulsion of crude oil, water, and an added de-emulsifying agent, introducing said emulsion into an underground salt cavity, maintaining said emulsion at a de-emulsifying temperature therein in contact with the salt surface of said cavity whereby oil and water separate to form a lower water layer, dissolving salt from the surface of the cavity bottom with said lower water layer whereby the difference in densities of the water layer and the oil layer is increased, and recovering from said salt cavity crude oil having a decreased quantity of contaminants.

2. Process of desalting petroleum crude oil which comprises admixing salt-containing crude oil, water, and a de-emulsifying agent, introducing said admixture into an underground salt cavity, maintaining said admixture at de-emulsifying temperature therein in contact with the salt surface of said cavity whereby oil and water separate to form a lower water layer, dissolving salt from the surface of the cavity bottom with said lower water layer whereby the difference in densities of the water layer and the oil layer is increased, and withdrawing from said salt cavity crude petroleum oil having a reduced salt content.

3. Process of desalting petroleum crude oil which comprises admixing salt-containing crude oil with water, a lower hydrocarbon and a de-emulsifying agent, heating said admixture to de-emulsifying temperature, introducing said heated admixture into an underground salt cavity, maintaining said admixture at a de-emulsifying temperature therein in contact with the salt surface of said cavity whereby oil and water separate to form a lower water layer, dissolving salt from the surface of the cavity bottom with said lower water layer whereby the difference in densities of the water layer and the oil layer is increased, and withdrawing from said salt cavity petroleum crude oil having a reduced salt content.

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4. Process of desalting petroleum crude oil which comprises admixing with salt-containing crude oil from 2% to 20% by volume water, from 5% to 20% by volume normally gaseous hydrocarbons, and a de-emulsifying quantity of a de-emulsifying agent, heating said admixture to de-emulsifying temperature, introducing said heated admixture into an underground salt cavity wherein said heated admixture is maintained in a relatively quiescent state whereby a lower water layer and an oil layer separate, dissolving salt from the surface of the cavity bottom with said lower water layer, whereby the difference in densities of the water layer and the oil layer is in-

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creased, and withdrawing desalted petroleum crude oil from said oil layer.

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