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EXTRACTION METHOD

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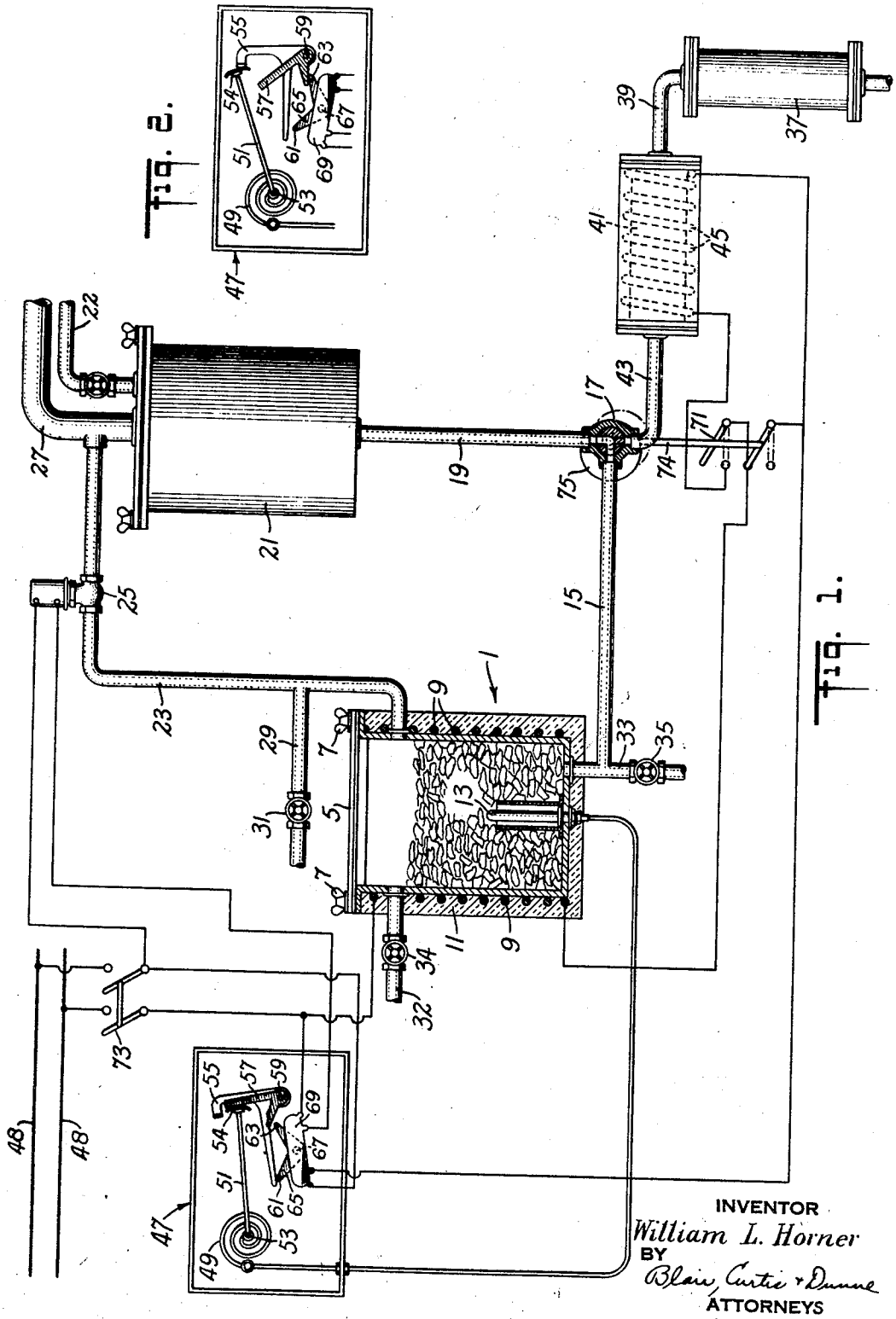

Fig. 1.

Fig. 2.

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EXTRACTION METHOD

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This invention pertains to extraction of soluble material from porous structures by means of solvents.

One of the objects of the invention is to provide an improved process for extracting soluble material from a porous structure by means of a solvent.

Other objects will be in part obvious and in part pointed out hereinafter.

In the accompanying drawing,

Figure 1 shows diagrammatically apparatus for carrying out a process embodying the invention.

Figure 2 shows diagrammatically switch mechanism shown in Figure 1 in a different position.

Corresponding reference characters refer to corresponding parts throughout the several views of the drawing.

The removal of hydrocarbons from oil-bearing organic materials or from oil-bearing minerals, such as sand, sandstone, shale, limestone and other porous minerals, is a commercially valuable operation, sometimes for the purpose of recovering oil for commercial use, and other times for analytical purposes to determine the nature of subsoil of an area being drilled for oil recovery. One customary method of removing such hydrocarbons is to heat the oil-bearing mineral formation to drive off the hydrocarbons by distillation. But this method has the disadvantage of breaking down some of the hydrocarbons because of the high temperature necessary to drive off higher fractions and of breaking down the structure of the stone being treated. Another procedure, that of washing the mineral with hot water, has the disadvantage of being slow and inefficient. Further, the use of hot water requires a preliminary grinding operation to pulverize the material prior to the water treatment. The practice of extraction of the oils by washing with solvents has also been inefficient and relatively unsatisfactory because it required either a long continuous washing process or long soaking of the minerals in the solvents to allow the solvent to penetrate the pores. And even after the penetration, lack of circulation through the pores made the process relatively ineffective and inefficient.

In the present process, which is an illustration of an embodiment of the invention, the solvent extraction method is modified by obtaining a forced penetration of the solvent into the pores and, in addition, causing the solvent to circulate through the pores to speed up the dissolving of the hydrocarbons or oils in the solvent.

To this end the oil-bearing permeable porous non-comminuted mineral mechanically treated to give it the desired size for convenient handling, is placed in a treating chamber. The pores of the material are first dried and freed of most of the air and insoluble gases by heating and passing through it a stream of dry heated gas, such as air. In this step the temperature is carried sufficiently high to vaporize lower hydrocarbon fractions present in the pores of the material and also to vaporize water present. These vapors generated within the pores purge the pores of air which would otherwise "bind" the circulation to be described. The vapors reaching the outside surface of the pieces of porous material are carried out of the chamber by the dry stream of air being circulated through it.

If desired, the hydrocarbon fractions thus removed may be recovered by usual methods such as by passing the vented gases through suitable condensers or absorbers.

The temperature to which the material is heated is determined by characteristics of the particular material being treated. Such characteristics may be the breakdown temperature of the hydrocarbon fractions present, the structure of the material, etc. Also the boiling point of the particular solvent necessary to dissolve the hydrocarbons is a factor. In any event, the temperature is preferably above the boiling point of water and the solvent used.

While the material is still raised to this temperature and the pores are still filled with water vapor or lower hydrocarbon vapors, or both, the heat is turned off and a suitable solvent is run into the chamber to cover the material. The solvent is preferably at a temperature slightly below the condensing point of the vapors in the pores of the material and so somewhat below the temperature of the material being treated. Immersion of the material in the relatively cooler solvent reduces the temperature of the vapors in the pores causing condensation. This condensation reduces the vapor pressure within the pores and creates a difference in pressure between the inside and outside of the pores. Inasmuch as the pores are surrounded by liquid solvent rather than air or gases, the solvent under the higher pressure forces its way into the pores to wash the hydrocarbons therein into solution.

The solvent now in the pores with its dissolved material is purged or forced from the pores in the next step which consists in supplying heat to the treating chamber by suitable means and the whole is eventually raised to the previously mentioned predetermined temperature, for ex-

ample between 212°–230° F., or higher for sandstone. During this heating stage an outlet at the top of the chamber is closed and the gradually rising temperature causing the vapor pressure of the solvent to increase proportionally forces the solvent out of the chamber through an outlet provided at the bottom of the chamber. The solvent preferably flows to a reservoir above the chamber whence it may flow back by gravity to the chamber. As the heating continues all the liquid solvent is driven out of the chamber and finally the temperature throughout the porous material is raised to the boiling point of the solvent in the pores. As the temperature of the porous material rises to the boiling point of the solvent in the pores it vaporizes and the increased vapor pressure forces liquid solvent and dissolved material out of the pores.

After the porous material has been heated to the predetermined temperature and the pores cleared of liquid, the solvent is again forced into the pores by shutting off the heat supply and releasing the pressure in the chamber to allow the relatively cooler solvent again to flow into the chamber to cover the material, again cooling it and causing condensation of the vapors present in the pores to create again the pressure difference which forces the solvent into the pores. This procedure may be repeated until the desired extraction is obtained.

In this manner a forced circulation of the solvent into and out of the pores is obtained and this circulation increases the rate of dissolving of the soluble material in the solvent since one of the functions of the rate of dissolving of a solid or liquid in a solvent is the movement of one relative to the other, which movement prevents the solvent from becoming locally saturated.

After the last heating operation the porous material is dried of the solvent by continuing the heating and passing dry heated air through the material. As an alternative to this step, to aid the drying the chamber may be connected with a vacuum.

The apparatus diagrammatically shown in Figure 1 for carrying out such a process as described above embodying the invention comprises a treating chamber, generally indicated at 1, adapted to receive the porous material having the substance to be extracted. The chamber has a removable top 5 adapted to be securely clamped by suitable means 7.

Around the chamber is placed a heating coil 9 suitably lagged by heat insulating material 11 on the outside. A temperature bulb 13 is suitably located within the chamber and is responsive to the temperature of the center of the mass of material being treated.

Connected with the bottom of chamber 1 through pipe 15, three-way valve 17 and pipe 19 is a reservoir 21 for the solvent. The bottom of the reservoir is preferably above the top of chamber 1 so that the solvent may run to the chamber by gravity. The reservoir may be connected with a suitable still, not shown, for separating the extracted hydrocarbons (if oil-bearing porous material is to be treated) from the solvent which is then returned to the reservoir 21. The bottom of chamber 1 is also provided with a drain pipe 33 (provided with a normally closed valve 35) for draining off liquid used in flushing out the chamber.

Connecting the top of chamber 1 with the top of reservoir 21 is a pipe 23 having a suitable solenoid-operated valve 25 adapted either to close or open the pipe, the valve normally being open when the solvent is flowing from the reservoir to the chamber and closed when the solvent is flowing from the chamber to the reservoir. Connected to pipe 23 is a pipe 29 connected with a source of low pressure such as a vacuum pump. A valve 31 normally closes this line. A pipe 32 having a valve 34 (normally closed) provides a vent during the period of heated air treatment.

Reservoir 21 is provided with a vent 27 exposed to atmosphere or to a known pressure so that the solvent is free to flow to and from the reservoir. A pipe 22 is provided in the top of the reservoir for filling it with solvent.

The supply of heated dry air to start the process and to finish it is provided by passing air from a suitable source through a dehydrator or dryer 37 which is of the usual type and which may be filled with a suitable drying material such as calcium chloride, etc. The top of dryer 37 is connected by pipe 39 to one end of a suitable heater 41, and the other end of the heater is connected to the three-way valve 17 by pipe 43. The heater 41 may be of a standard type for heating air. The heat may be supplied by a suitable resistance coil 45.

With this construction the manually operated three-way valve either connects chamber 1 with the dry heated air supply or the reservoir. The supply of current to the heating coils 9 and 45 and to the solenoid valve 25 is controlled by a standard controller, generally indicated at 47, operated by the thermometer bulb. Such a controller may comprise a helical pressure tube 49 of a known type which rotates a deflecting arm 51 about an axis 53 in response to the expansion of a liquid or gas in the bulb 13. Two bell-crank arms 55 and 57 are biased in a counterclockwise direction about an axis 59 and are periodically oscillated in a clockwise direction by suitable motor means, not shown, away from the deflecting element 51, leaving it free to pivot about its axis 53. The bell-crank arms respectively operate pins 61 and 63 mounted on a rocker arm 65 pivotally mounted about an axis 67 on which is mounted a mercury switch 69. If an adjustable stop 54 provided on the deflecting member 51 is in the range of bell-crank arm 57 and not in the range of bell-crank 55, the former will not be permitted to oscillate to its extreme counterclockwise position, but the latter will, as shown in Figure 1 and will throw the switch to its counterclockwise position by means of pin 61 on rocker arm 65. The deflecting member 51 assumes this position as the temperature drops to the low or minimum temperature indicated on the drawing as 160° F. Now, as the temperature rises, causing the member 51 to swing the stop 54 into the range of bell-crank 55, nothing happens until it swings out of the range of bell-crank 57, at which time bell-crank 57 oscillates the rocker arm in a clockwise direction to tip the switch to its clockwise position.

By adjusting the length of stop 54 the control apparatus is adjustable to vary the difference between the "on" and "off" or minimum and maximum temperatures. One adjustment that has proved satisfactory when treating shale with acetone is to have the switch throw "on" (Figure 1) as the temperature drops below 160° F. and to have the switch throw "off" (Figure 2) as the temperature reaches 230° F.

When the mercury switch is in the position shown in Figure 1, it connects power lines 48 with heaters 45 and 9 which are normally connected in series. When the switch is in its off

or maximum temperature position, it connects the power line with the solenoid valve 25 thereby opening the valve.

A switch 73 is provided between the power lines and the mercury switch to cut out the supply of electricity to the apparatus when it is not being used or when chamber 1 is being charged or discharged.

Inasmuch as heater 45 is not used during the time chamber 1 is connected with the reservoir, a switch 71 is provided to cut out heater 45 when the three-way valve is turned to connect the chamber and reservoir. The switch 71 is operated through a rod 74 by a cam 75 mounted to rotate with the movement of the three-way valve. When the rod is up and the chamber and reservoir connected, the switch is up and the heating coil 45 is cut out. When the valve is rotated counterclockwise to connect the chamber with the air stream, cam 75 pushes rod 74 down to cut in coil 45. Under certain conditions of operation it may be necessary to cut in additional resistance when the heater 45 is cut out in order to prevent the current in the heater 9 from going too high. However, such operation is well known and will not be discussed in detail herein.

In operation the chamber is first filled through the top with the shale, sandstone, limestone, or other oil-bearing porous mineral or material, after which the cover is clamped on and valve 34 is opened and valves 31 and 35 are closed. The three-way valve 17 is rotated to connect the air supply with chamber 1. Switch 73 is now closed. The temperature being low the member 51 has dropped below its 160° F. position and has permitted lever 55 to operate the switch to its counterclockwise position to connect the heater with the power supply.

The material in chamber 3 is now heated by the air and by coils 9, and during this initial heating process a large part of the moisture and air is removed from the pores as above described.

As the temperature rises to the point where the control instrument throws the switch, about 230° F. for example, when shale or limestone are being treated, bell-crank 57 is released and the switch is oscillated to its clockwise position, cutting out the heating coils and opening the solenoid valve 25.

Valve 34 is now closed and the three-way valve is now manually turned to its full line position to connect reservoir 21 with chamber 1 and cutting out the heating coil 45. The solvent (for example, carbon tetrachloride, acetone, ethylene dichloride, ether, naphtha, gasoline, or any mixture of these as determined by the material being extracted), previously put in the reservoir, runs by gravity into the chamber 1, the valve 25 being open to permit gases to escape from the top of chamber 1. The temperature of the solvent being below that of the material being treated cools the water vapor and hydrocarbon vapors present in the pores and causes condensation which, as above described, instigates a flow of the solvent into the pores. Eventually the cooler solvent reduces the temperature of the material being treated to that necessary to throw the switch "on" (160° F. as described in the present embodiment) which simultaneously closes the solenoid valve 25 and turns on the heating coil 9. The temperature of the solvent now begins to rise and as it rises the vapor pressure in the chamber increases, forcing the solvent back into the reservoir. The continued heating eventually raises the porous material to a temperature sufficient to vaporize some of the solvent in the pores which drives out the remaining liquid solvent. The solvent thus driven out carries with it dissolved hydrocarbons. As the temperature reaches the upper ("off") limit of the switch (a temperature picked so as not to damage the porous material or cause breakdown of the hydrocarbons), the valve crank 57 is again freed to oscillate the switch in a clockwise direction to cut out the heater and open valve 25. This relieves the pressure in chamber 1 and allows the relatively cooler solvent to run by gravity into the chamber to repeat the previously described condensing and circulating operation.

This cycle of vaporizing the solvent within the pores and then condensing it while the pores are submerged in the solvent to induce circulation of the solvent in the pores is carried on until the extraction has proceeded to the point desired. After the last heating operation the three-way valve is turned to connect the chamber and air stream which vaporize the solvent. Or an alternative operation for this last step is to turn the three-way valve to cut off both the air supply and the solvent supply and to open the valve 31 to place chamber 1 under a vacuum.

I claim:

1. Process for extracting soluble material from pores of a permeable porous non-comminuted structure by inducing circulation of a solvent in the pores comprising the steps of heating the structure to vaporize volatile substances in the pores, subsequently cooling the structure to cause the vapors to condense in the pores while the structure is immersed in a liquid solvent, and repeating the cycle until the extraction is carried to the extent desired.

2. Process for extracting soluble material from the pores of a permeable porous structure by inducing circulation of a solvent in the pores comprising heating the porous material in a stream of dry air to vaporize vaporizable constituents in the pores, cooling the structure while in contact with a liquid solvent to condense vapor in the pores and force the liquid solvent therein, heating the structure to vaporize part of the solvent in the pores to force the remaining liquid solvent out and repeating the last two steps in sequence until the desired extraction is obtained.

3. Process for extracting soluble material from the pores of a permeable porous structure by inducing circulation of a solvent in the pores comprising heating the porous material in a stream of dry air to vaporize vaporizable constituents in the pores, cooling the structure while in contact with a liquid solvent to condense the vapor in the pores and force liquid solvent therein, heating the structure to vaporize part of the solvent in the pores to force the remaining liquid solvent out and repeating the last two steps in sequence until the desired extraction is obtained, and subsequently separating the extracted material from the solvent.

4. The process for extracting soluble material from the pores of a permeable porous non-comminuted structure by inducing circulation of a solvent in the pores including the steps of heating the porous material in the presence of a stream of a hot dry gas to vaporize vaporizable constitutents initially present in the pores to force air from the pores, cooling the structure while immersed in a liquid solvent to condense the vapors in the pores thereby causing the solvent to enter the pores, and then alternately heating the structure and solvent to vaporize

solvent within the pores, and condensing the vapor left in the pores while the structure is immersed in the solvent.

5. Method of operating extraction apparatus for extracting soluble material from the pores of a permeable porous non-comminuted structure including a container having a bottom fluid connection comprising the steps of, heating a liquid solvent and the porous structure in the container while said container is closed except for said bottom connection to a temperature sufficient to raise the vapor pressure of the solvent to force the solvent out of the container through said connection, of continuing the heating to vaporize the solvent in the pores, of refilling said container with relatively cool solvent without admitting non-condensable gases to cool the structure and cause condensation of the solvent vapor within said pores while the structure is immersed in the solvent whereby the relatively cool solvent is drawn through and into said pores, and repeating the steps in the above sequence until a desired degree of extraction is obtained.

6. Method of operating extraction apparatus for extracting soluble material from the pores of a permeable porous non-comminuted structure including a container having a bottom fluid connection comprising the steps of, heating a liquid solvent and the porous structure in the container while said container is closed except for said bottom connection to a temperature sufficient to raise the vapor pressure of the solvent to force the solvent out of the container through said connection, of continuing the heating to vaporize the solvent in the pores, of refilling said container with relatively cool solvent without admitting non-condensable gases to cool the structure and cause condensation of the solvent vapor within said pores while the structure is immersed in the solvent whereby the relatively cool solvent is drawn through and into said pores, repeating the steps in the above sequence until a desired degree of extraction is obtained, and changing the steps at predetermined temperature conditions.

7. Method of extracting soluble material from the pores of a permeable porous structure by means of induced circulation of a solvent in the pores comprising the steps of heating the porous structure while in a closed space to vaporize vaporizable constituents in the porous structure, running by gravity a relatively cool liquid solvent into said closed space to immerse said heated porous structure in said solvent to cause condensation of the vapors in said pores, thereby lowering the pressure in said pores and creating a differential pressure which causes the solvent to flow into said pores, heating the liquid solvent and porous structure in said space to drive the liquid solvent from said porous structure and to vaporize solvent liquid in said pores, and repeating this cycle until the desired degree of extraction is reached.

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