

Oct. 13, 1959

E. V. MURPHREE

2,908,617

SYSTEM FOR RECOVERING OIL FROM SOLID OIL-BEARING MATERIALS

Filed Feb. 13, 1956

2 Sheets-Sheet 1

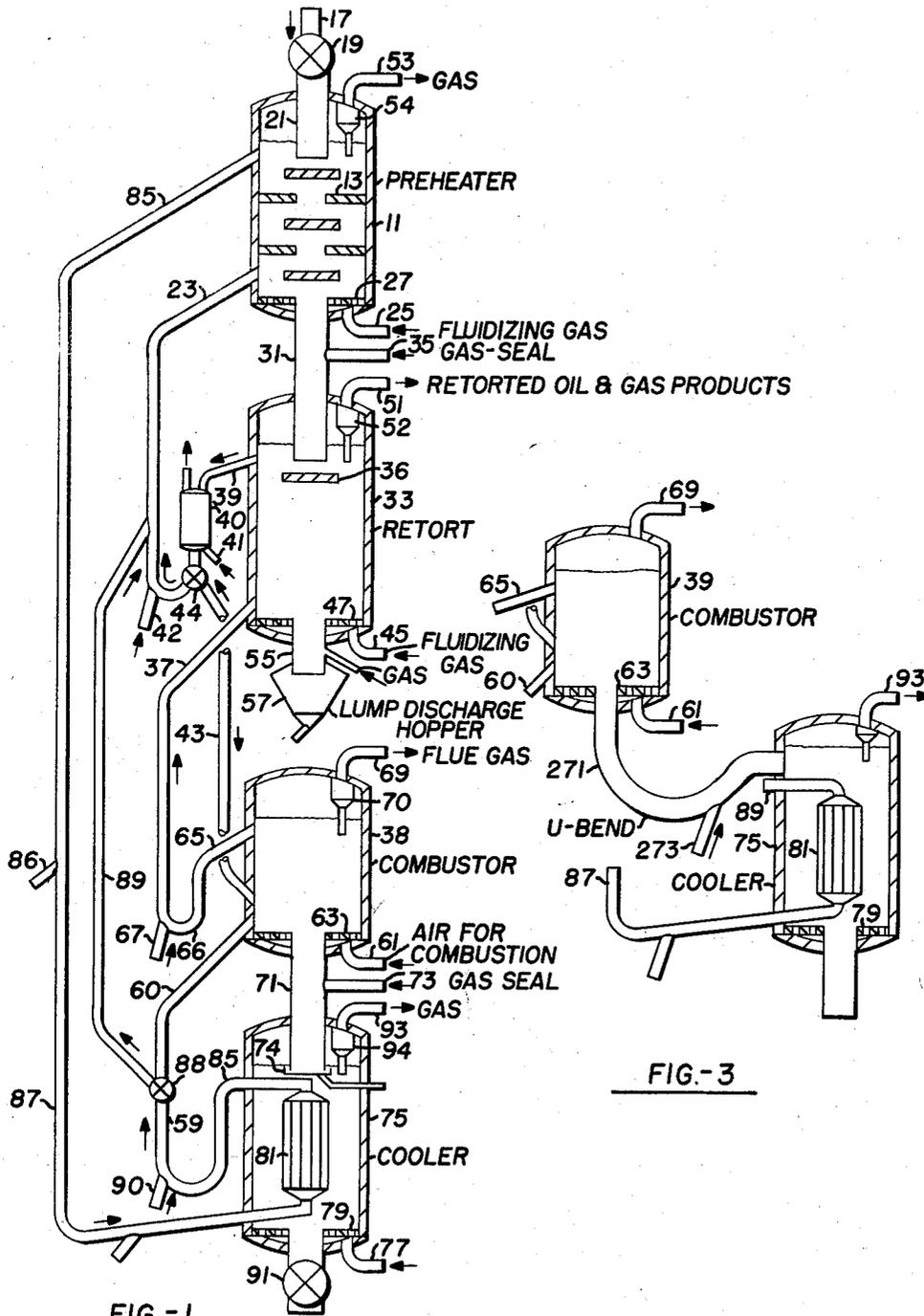


FIG.-1

FIG.-3

Eger V. Murphree Inventor

By Small, Dunham & Thomas Attorneys.

Oct. 13, 1959

E. V. MURPHREE

2,908,617

SYSTEM FOR RECOVERING OIL FROM SOLID OIL-BEARING MATERIALS

Filed Feb. 13, 1956

2 Sheets-Sheet 2

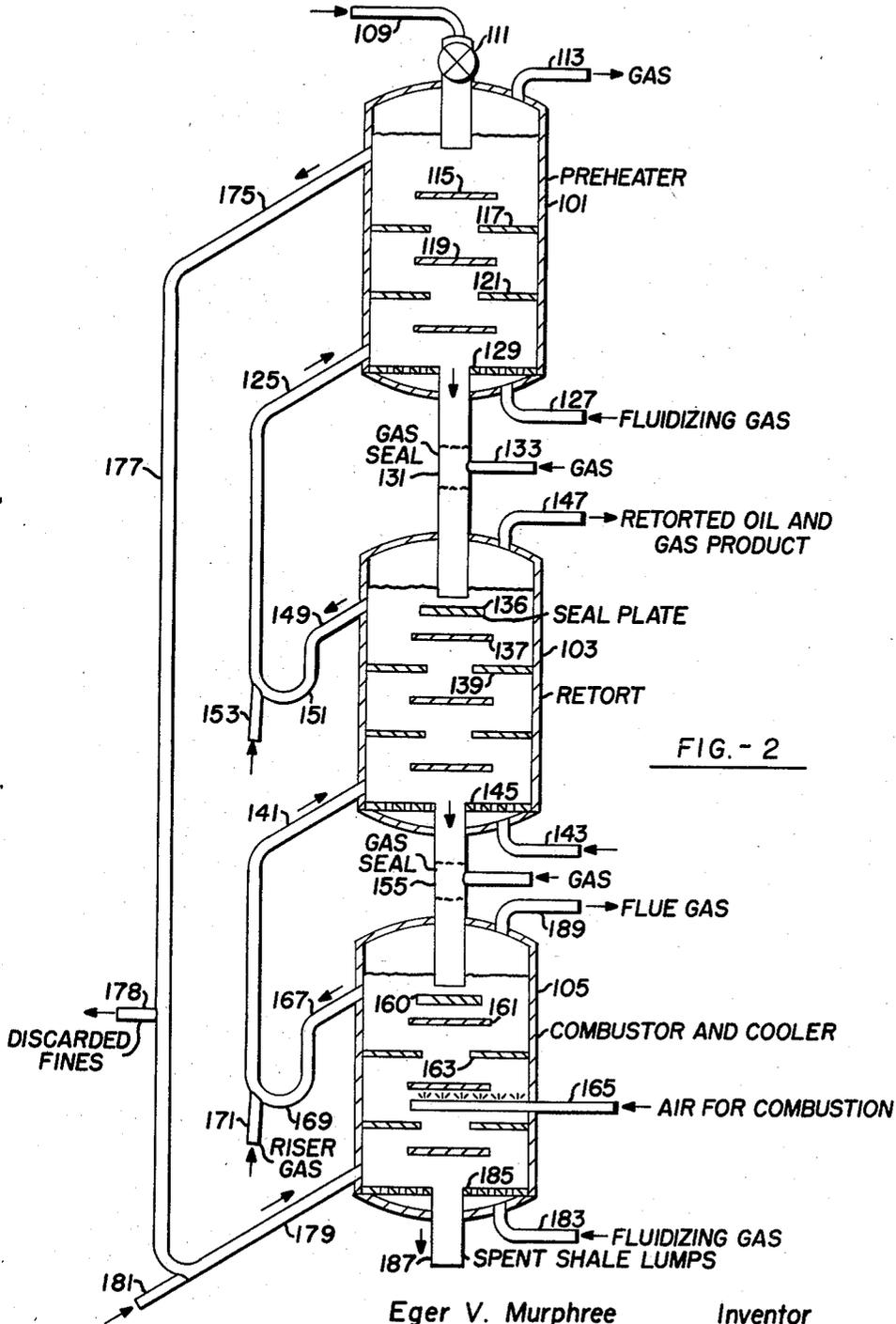


FIG. - 2

Eger V. Murphree Inventor

By Small, Dunham & Thomas Attorneys

1

2,908,617

## SYSTEM FOR RECOVERING OIL FROM SOLID OIL-BEARING MATERIALS

Eger V. Murphree, Summit, N.J., assignor to Esso Research and Engineering Company, a corporation of Delaware

Application February 13, 1956, Serial No. 564,938

2 Claims. (Cl. 202—14)

The present invention relates to an improved system for recovering oil from solid oil-bearing materials. In particular, the invention relates to a system for high temperature retorting of oil shale and other solids containing hydrocarbonaceous material.

In order to recover oil from oil shale and similar oil-bearing solids, it is necessary to retort them in order to break down the solid or semi-solid hydrocarbon or oil-forming materials, such as kerogen. The hydrocarbons, thus broken down to products of moderate molecular weight, are driven off as vapors or entrained liquids. Oil shale, for example, is usually broken into small lumps or particles and then heated to a temperature of 850–1000° F. or more for a sufficient length of time to convert the kerogen and recover the desired oil products. It has previously been proposed to treat oil shale by brushing it, feeding it into the top of a retort in the form of a downwardly moving bed and burning part of the shale or the carbonaceous residue thereof at or near the bottom of the retort. The heat so obtained is transferred to the incoming raw shale by exchange with the combustion and retort gases and this supplies at least part of the heat required for retorting. The present invention involves certain improvements on the process just described which will be explained in detail.

The present invention makes effective use of the highly efficient heat transfer from hot solids to cooler solids made possible by the use of the fluidized solids technique. At the same time it avoids some of the disadvantages of mixing combustion products with the recovered oil. It also avoids some of the difficulties involved in prior processes, wherein spent shale tends to readsorb the recovered oil. Some oil shales are difficult to handle because of extensive decrepitation. As such shales are heated, especially if they have been crushed to small particle sizes to begin with, they may break down to such extremely fine particles, at least in part, that many ultimate particles are carried off in the gases, being almost impossible to separate therefrom. While the present invention is not limited to this latter feature, one important aspect has to do with the handling of such shales without substantially incurring the difficulties just mentioned.

Broadly the invention involves feeding crushed shale, initially of particle size too large to fluidize, downwardly through a system consisting of several superimposed sections. In the uppermost section, the cold raw shale in lump form is preheated by contacting it with a fluidized bed of hot finer particles which are returned from one or more processing steps below. The preheated raw shale then passes by gravity into a retorting section where, in turn, it is contacted with still hotter fine particles from a combustion section below the retorting section. Finally, the spent shale with most of the hydrocarbons removed, but containing carbonaceous deposits, is passed to the combustion section where a combustion supporting gas, such as air or oxygen, is contacted with the spent shale to consume carbonaceous residues associated with the shale and thus to supply heat for carrying out the process:

2

The cooler, finely divided spent shale particles which meanwhile have passed to the top of the preheating section and have released much of their heat are returned, at least in part, to the combustion section. En route they may be used in heat exchange to recover heat from the final spent shale solids.

It will be appreciated that a major object of the invention is the application of the fluidized solids technique to effect heat exchange with raw shale being retorted. Another object is to heat up the shale progressively so as to obtain maximum heat efficiency while at the same time avoiding or at least minimizing readsorption of the released oil on the spent shale.

Other objects are to make a flexible retorting system which, with minor modifications, can be adapted either to a shale which decrepitates extensively or to a shale which maintains its lump form throughout the retorting operation. Other objects will appear more clearly as the description proceeds.

Accordingly, reference will next be made to the accompanying drawings wherein:

Fig. 1 shows a preferred arrangement of a retorting system for shale which decrepitates extensively, and

Fig. 2 shows a modified system particularly adapted to shale which does not decrepitate excessively.

Fig. 3 shows a modification of Fig. 1, using a U-bend seal between two stages of the process.

Referring first to Fig. 1, the system comprises a series of superimposed vessels all of which may be, if desired, included within a single exterior shell. At the top of the figure, a preheater vessel 11 is provided with a series of disc and doughnut baffles 13, 15. These may be perforated, if desired, as is well known in the art. Also, rotary rakes may be used to help the shale to mix and move downwardly from baffle to baffle. These are not shown but are well known in the art.

Raw shale to be processed is fed in through an inlet line 17 and a star-feeder 19 of conventional type. Shale passes downwardly through a line 21 into the preheating section where it comes in contact in counterflow relation with finely divided shale particles supplied to the bottom of section 11 through a line 23. As noted below, this shale is hot but some of it preferably is brought from a heat exchanger and not all of it directly from the retort directly below. Fluidizing gas is introduced at the bottom of section 11 through suitable distributing means, shown herein as a line 25 and a distributing grid 27. This fluidizing gas may be steam, or it may be methane, hydrogen, etc., or some non-condensable components of hydrocarbon products obtained in the retorting section below.

As the preheated shale moves downwardly, settling through the upflowing finer particles, it passes through a conduit 31 into the retorting section 33. In order to prevent undesirable loss of retorting products upwardly through conduit 31, a gas seal should be maintained within the conduit by supplying steam or other suitable sealing gas through line 35 as is well known in conventional moving bed operations. The descending preheated shale flows into the retort section 33. Here a seal plate 36 is provided to distribute the shale, control its flow, and further minimize loss of products up the conduit. In the retort the preheated shale is contacted with upflowing fines supplied through line 37 from a combustor section 38. The latter are at very high temperature, e.g. above 1100° F. or higher, to supply necessary heat. After contacting the preheated solids and imparting enough heat thereto to decompose the kerogen or other hydrocarbons and drive off the oil products, the ascending fines, which have been cooled somewhat in the process, are drawn off from the top of the retorting section through outlet line 39. They are preferably passed

3

through a stripper 40, to which a stripping gas, e.g. steam, is supplied through line 41. After stripping, part of the stripped solids may be caused to flow upwardly through line 23 into the preheating section with the assistance of a supply of riser gas introduced through line 42. The remainder of the fines, or, if desired, all of them, may be taken down to a lower section through line 43 for a purpose to be described later. A 3-way valve 44, or its equivalent, is provided for controlling solids flow out of the stripper 40.

Retorting is carried out by introducing a fluidizing gas into the bottom of the retorting section through a suitable distributor such as line 45 and distributing grid 47. This causes hot fines coming in through line 37 from the combustor 38 to mix with the descending preheated shale and to drive out the oil products therefrom. During this process the shale may break up or decrepitate to a substantial degree but the larger particles thereof continue to flow downwardly countercurrent to the up-flowing fines from line 37. The latter thus ascend to the top of the retorting section and are drawn off through line 39 and stripped as previously described.

The ratio of hot fines to preheated shale in the retorting section is governed in accordance with their respective temperatures to accomplish the desired degree of decomposition of the kerogen or other hydrocarbonaceous ingredients of the shale. The retorting temperature is preferably between 850° and 1050° F. and is usually between about 900° and 1000° F. Contact times are adjusted for optimum production of products. The products, in the form of vapors, are taken through a conventional solids separator, e.g. a cyclone 52, and thence overhead through outlet line 51. From here they are passed to suitable fractionating and recovery equipment, not shown. The gas seal in conduit 31 prevents substantial loss of the vapor products through the preheater section, as previously noted. However, the gases in the preheating section also may be recovered from outlet line 53 at the top of the latter section. A cyclone 54 is shown for separating entrained solids.

The spent shale is now largely free of hydrocarbon materials but contains carbonaceous deposits resulting from decomposition of the kerogen. Remaining lumps descend through outlet line 55 into a hopper section 57. From here they may be discharged. The other part of the spent shale, now reduced in particle size by decrepitation, is carried out through line 39. As noted above, part of it may be taken to the preheater section and the remainder, or all if desired, is passed downwardly through line 43 to the combustor 38. Here they join with solids coming through lines 59, 60, into the lower part of the combustor section.

Air is introduced into the combustor section through an inlet line 61 and a distributing grid 63. This air causes the carbonaceous residues to be burned and raises the temperature of the solids in this section. These solids, after the carbonaceous matter is substantially consumed, are withdrawn from the top of the fluidized bed through line 65 and are passed through a U-bend 66 and thence upwardly through line 37 into the bottom of the retort section. A suitable riser gas such as steam is introduced into line 37 at 67 to lift the solids into the retort section.

The air introduced through line 61 maintains the fluidity of the bed of solids in the combustion zone. The resulting flue gas passes overhead through outlet line 69. It will be understood that suitable solids separating equipment such as cyclone 70, etc. will be used at this outlet, as well as at the outlets 51 and 53 in the retorting and preheating sections previously described.

The finer part of the hot spent shale from the combustor is drawn off in part through line 65, but another and coarser part is withdrawn downwardly through outlet conduit 71. Here, as in the case of conduit 31, a gas seal may be maintained by introducing a suitable gas, such as steam or combustible gas, through line 73. However,

4

to insure a seal, an aerated gas pot 74 is preferably provided to prevent flow of gas up the conduit 71. The descending hot spent shale passes from seal pot 74 into a cooler or heat exchanger section 75. Here it is kept fluidized by a fluidizing gas introduced through an inlet line 77 and a distributing grid 79. A heat exchanger 81 in this section provides means for independently heating cooled shale which is withdrawn from the top of the preheater through outlet line 85. This cooled, finely divided shale, largely spent shale, flows down through standpipe 87 to the bottom of the heat exchanger 81. Fluidizing gas may be supplied to this standpipe by one or more taps 86. The heat from the descending spent shale from conduit 71 raises the temperature of the cooled shale which is kept fluidized and is returned through lines 85 and 59 either into the bottom of the combustor section, or into the preheater section 11, preferably both. Valve 88 and riser 89 convey the shale back to the preheater section where it transfers its heat to the cold raw feed. The cooled spent shale fines are withdrawn from the bottom of the cooling section through a suitable valve, star feeder, or lock hopper arrangement 91 as will be obvious to those skilled in the art. The fluidizing gas introduced through line 77 is taken off at the top through line 93. It can be passed through a cyclone shown at 94 if desired, although it is not essential to remove all the fines therefrom since this gas stream may be recycled to line 77 indefinitely. With this arrangement, the recovery of the ultimate shale fines is facilitated since these may be drawn off by gravity from the outlet 91 previously mentioned.

Referring now to Fig. 2, a somewhat similar system is shown except that it is particularly adapted for the treatment of shale which breaks down into fines to a lesser degree than in the case of Fig. 1. A preheating section 101, a retorting section 103 and a combustor and cooler section 105 are shown as the major components. These all may be included within a single shell for convenience of construction and operation, if desired.

In the apparatus of Fig. 1, only the preheater section is shown with disc and doughnut baffles 13, 15, for promoting contact between the finely divided solids and the lumps of shale being preheated. In the preheater section of Fig. 1, the lumps move downwardly by gravity and to assist in such movement, curved rotating rakes or rabble arms, not shown, may be provided as previously mentioned, to sweep the lumps continuously from each disc or doughnut baffle to the next lower baffle. This can also be accomplished, with some shales, simply by gravity by imparting suitable slopes to the disc and doughnut baffle elements.

In the case of Fig. 2, all three of the sections 101, 103, 105 are equipped with baffles. They likewise may be equipped with rotating rake arms or sweepers, if desired, to cause continuous flow of the lumps to progressively lower levels in the system. On the other hand, they may be designed for gravity flow since the upflowing fluidized fine solids in all three sections help to lift and mobilize the lumps of shale. By the use of perforate baffles, this movement may also be facilitated and they may, of course, have suitable sloping surfaces as will be obvious to those familiar with the problems of moving beds of solids.

Raw shale is introduced to the preheater section 101 through an inlet line 109 and a suitable star feeder 111. If desired, a sealed conduit, so arranged that the gases evolving from the preheater are not lost through the shale inlet, may be used. A separate gas outlet 113 is provided and suitable solids separation equipment, such as cyclones, not shown, may be provided as desired and as described in Fig. 1.

The raw shale in lump form, for example, crushed particles of 0.1 to 1.0 inch or larger, flows downwardly by gravity on to the first baffle section 115 and descends, step by step, over the successive baffles 117, 119, 121, etc. These lumps or relatively large particles are buoyed

5

up, in part at least, by the upflowing fluidized fines introduced from the retort section 103 through inlet line 125 near the bottom of the preheater section. Fluidizing gas is introduced through line 127 and a distributor such as grid 129. The hot fines pass upwardly in counterflow to the descending coarse shale particles. The latter pass from the preheater section through conduit 131 which is provided with a gas seal from a gas supply line 133. The degree of preheat will depend upon relative temperatures and rates of circulation but it is desirable to raise the temperature of the shale several hundred degrees. Preheating to a temperature of 450° to 800° F. is preferred.

The preheated shale passes into the upper part of the retorting section 103 and spreads out over seal plate 136. Here it flows downwardly over baffles 137, 139, etc. in counter flow to the ascending hot fine particles of spent shale which are introduced through line 141 near the bottom of the retort section. The latter are fluidized by gas introduced through inlet line 143 and distributor or grid 145. Relative flow rates of fines and preheated shale are such as to accomplish substantially complete retorting in this section. As a result, the kerogen is decomposed to produce oil and gas products. The products are withdrawn through line 147 at the top of the retorting section and below the gas seal 133. Suitable solids separators, such as cyclones, not shown, should be included in outlet 147 as will be obvious. The retorting temperature, as previously mentioned, is preferably between 900° and 1000° F. although it may be slightly more or less under some conditions.

The upflowing fines are withdrawn from the top of the fluidized bed through outlet 149. They pass through a U-bed or reverse bend of suitable character to effect control of gas flow indicated at 151, as is obvious to those familiar with the art of handling fluidized solids in hydrocarbon conversion operations. The fines are lifted up into the preheater section through inlet line 125 by means of riser gas introduced at 153. The spent shale, largely free of hydrocarbons but containing carbonaceous residues, passes downwardly from the retorting section through an outlet conduit 155. Here a gas seal is maintained by a suitable sealing gas such as steam or hydrocarbon gas introduced through line 157. The descending spent shale passes into the top of the combustor section 105. Here it spreads out over seal plate 160 and then flows down over baffles 161, 163, etc. in counter flow to upflowing fine particles of shale. Air or other combustion supporting gas, such as oxygen, is introduced through a line 165 in the middle part of the combustor and cooler section to heat up the fines so that they can be passed upwardly from outlet line 167 into the bottom of the retorting section through line 141. In so doing, they pass through the sealing bend 169 and are lifted up by riser gas supplied through line 171. The coarser particles continuously descend below the point where air is introduced where they pass in counter flow but in direct contact with cool finely divided shale particles which are withdrawn from the top of the preheater section through line 175, standpipe 177 and inlet line 179. Gas supplied through 181 carries these fines into the bottom part of the combustor and cooler section.

Fluidizing gas is introduced through line 183 and distributor or grid 185 to fluidize the bed of fines within the combustor and cooler section. The descending spent and cooled shale lumps are then withdrawn from the bottom of this section through a suitable valve or lock hopper arrangement 187. Flue gas is taken off at the top through line 189 and part of it may be recycled to assist in fluidizing the lower portion of the bed. In Fig. 3 there is shown a further modification of the lower part of the equipment of Fig. 1. In Fig. 3, a U-bend 271 replaces the simple conduit 71 and seal pot 74 of Fig. 1 to insure a gas seal between the two vessels. Aerating gas may be introduced at 273. In other respects, the operation and the conduit

6

connections are the same as in Fig. 1; hence, they will not be described in detail.

It will be obvious that the respective systems of Figs. 1, 2 and 3 have many features in common and that modifications of each may be added to the other where desired. It will also be apparent that other modifications may be made as will occur to those skilled in the art and it is intended to cover these so far as the following claims and the state of the prior art permit.

What is claimed is:

1. A thermal process for treating raw oil-bearing shale in the form of small lumps which decrepitate when heated, which comprises the steps of first preheating said raw shale by passing it downwardly through a preheating zone in countercurrent contact with an upflowing fluidized bed of heat carrying fine spent shale solids derived from a step later on in the process, passing the thus preheated raw shale downwardly to the upper portion of a retorting zone, countercurrently contacting said preheated raw downwardly moving shale in said retorting zone with a second upflowing fluidized bed of hot spent fluidized fine shale particles therein to supply heat sufficient to retort the oil from said shale, removing vaporous products overhead from said retorting zone as a separate stream substantially free of solids, passing at least a portion of spent fine shale particles withdrawn from the upper portion of said second fluidized bed in said retorting zone downwardly to a combustion zone, burning the carbonaceous residue on said fine spent shale particles in the combustion zone to substantially increase the temperature of the fine spent shale particles, returning the thus heated fine spent shale particles free of combustion flue gases to said retorting zone to form said second upflowing fluidized bed therein, passing another portion of said spent fine shale particles withdrawn from the upper portion of said second fluidized bed in said retorting zone directly to the bottom portion of said fluidized bed of fine spent shale solids in said preheating zone to supply heat thereto as the first-mentioned upflowing fluidized bed of fine spent shale particles, withdrawing spent shale solid particles from the bottom portion of said combustion zone and recovering heat therefrom by indirect heat exchange with fine spent shale particles withdrawn from the upper portion of said first-mentioned fluidized bed in said preheating zone to heat said fine spent shale particles and passing at least a portion of the last-mentioned particles heated in this manner directly to said fluidized bed of fine spent shale solids in said preheating zone to supply heat thereto.

2. A process for retorting shale which comprises, the steps of, downwardly passing relatively coarse fresh shale in direct contact with and through an upflowing fluidized bed of hot, fine spent shale solids in a preheating zone, withdrawing the preheated coarse shale from the bottom of said preheating zone and passing it downwardly through a retorting zone wherein it contacts a second upflowing fluidized bed of fine spent shale solids at a retorting temperature, recovering vaporous products overhead from said retorting zone as a separate stream substantially free of solids, withdrawing hot spent shale from the upper portion of said second upflowing fluidized bed in said retorting zone and passing at least a portion thereof to the lower portion of a combustion zone for admixture with a third upflowing fluidized bed of hot, fine spent shale solids therein and passing the remainder of said last-mentioned hot spent fine shale solids withdrawn from said second fluidized bed in said retorting zone directly to the lower portion of said preheating zone to form said first-mentioned upflowing fluidized bed of hot fine spent shale solids in said preheating zone and to supply thermal energy thereto, introducing air into the lower portion of said combustion zone to burn residual carbon matter on said spent shale solids and to heat the spent shale solids therein, passing hot fine spent shale solids in the absence of flue gas from said combustion zone to the lower portion

7

of said retorting zone to form said second upflowing fluidized bed of fine spent shale solids, downwardly passing burned spent shale from said combustion zone to a shale cooling zone, indirectly contacting relatively cool fine spent shale solids withdrawn from the upper portion of said first-mentioned fluidized bed of solids in said preheating zone with the hot spent shale solids passing down through said cooling zone, passing at least a portion of the thus heated fine spent shale solids from said cooling zone to the lower portion of said preheating zone for addition to said first-mentioned fluidized bed therein and passing the remainder of the thus heated fine spent shale solids from said cooling zone to the lower portion of said combustion zone.

5

10

8

## References Cited in the file of this patent

## UNITED STATES PATENTS

2,471,119	Peck et al. _____	May 24, 1949
2,480,670	Peck _____	Aug. 30, 1949
2,680,091	Barr et al. _____	June 1, 1954
2,725,348	Martin et al. _____	Nov. 29, 1955
2,738,315	Martin et al. _____	Mar. 13, 1956

## FOREIGN PATENTS

668,808	Great Britain _____	Mar. 19, 1952
---------	---------------------	---------------