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PROCESSES FOR THE RECOVERY OF OIL FROM SHALES

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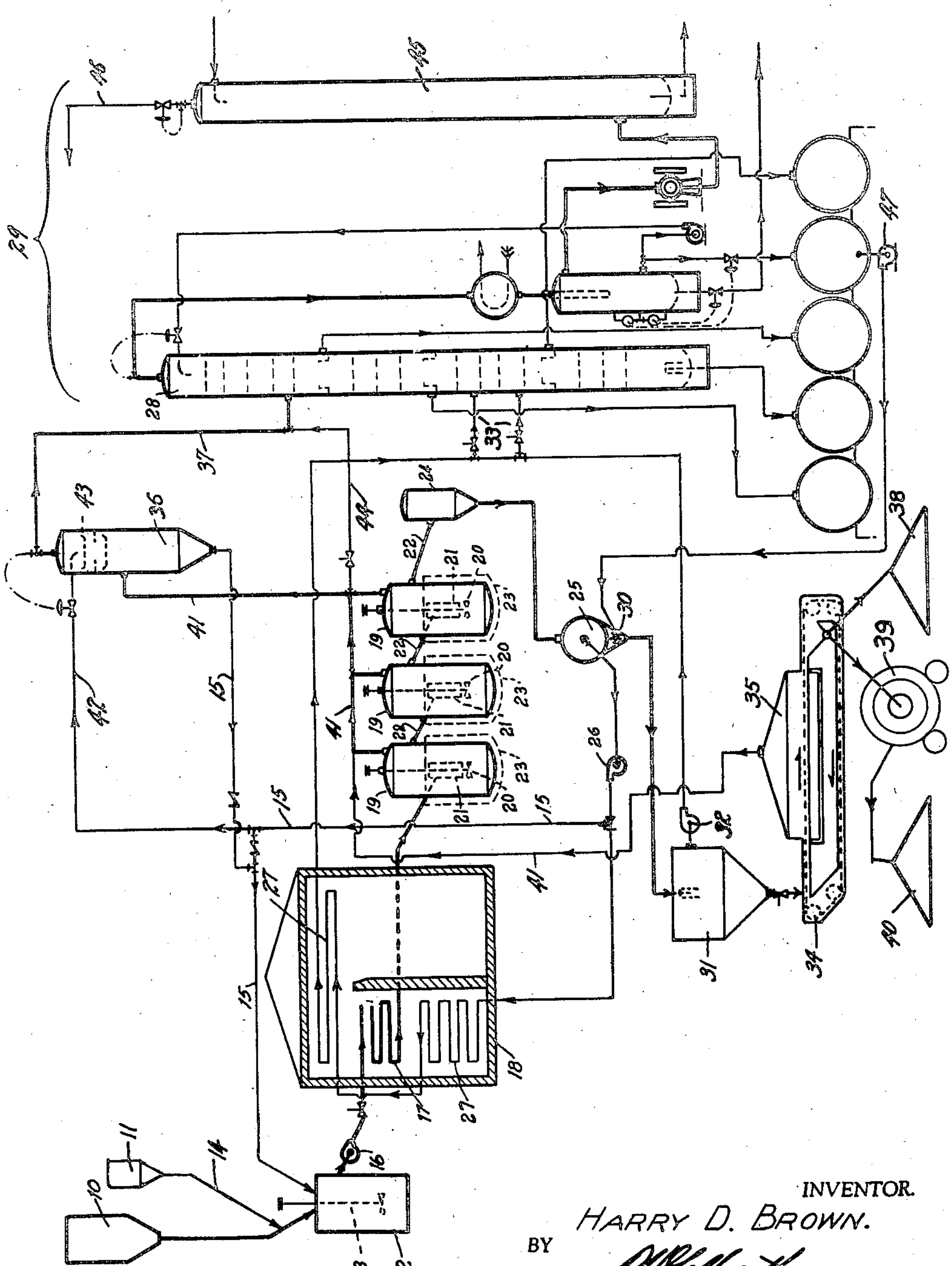

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PROCESS FOR THE RECOVERY OF OIL FROM SHALES

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2 Claims. (Cl. 196—14)

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This invention relates to a method and means for the processing of oil shales and other pyrobituminous materials for the recovery of oil therefrom.

The processing of oil shale has presented a difficult problem. The quantity and character of the evolved oil has been infinitely variable, depending upon the method of retorting and the temperature at which the destructive distillation was carried out. The presence of air in a retort is usually detrimental and the carry-over of dust with the vapor interferes with the refining operations which must follow.

The principal object of the invention is to provide a continuous method and means for the complete recovery of oil from oil shale at a low temperature whereby the "kerogen" is transformed into a soluble group of hydrocarbons in which the character and quality of the recovered oil will be uniform.

Another process is to provide a method or process for this purpose in which the bitumen will not be subjected to destructive distillation so that the highest obtainable recovery of oil will be effected.

A further object is to provide a process in which the residue of the shale will have exceptional value as a soil conditioner and fertilizer and in which the same residue may be prepared to form a highly active adsorbent for stabilizing gasoline distillates.

Other objects and advantages reside in the improved means and the method of use thereof. These will become more apparent from the following description in which reference is had to the accompanying drawing which forms a part hereof.

The drawing illustrates a diagrammatic flow sheet of the process.

Briefly, the method contemplates a removal of the oil from the shale by digestion under the influence of heat in the presence of an oil recycle stock in which the liberated hydrocarbons are soluble aided by a suitable catalyst.

Referring to the drawing, the shale to be treated, having been dried and ground to pass a ten mesh screen (or coarser, if mechanical separation of the pulp can be prevented), is fed from a fine ore bin 10 at a uniform rate to a pulp conditioner 12 provided with any suitable agitating mechanism 13. A catalyst, such as aluminum chloride (anhydrous), is added to and agitated with the shale in the conditioner 12 from a catalyst storage hopper 11 through a catalyst line 14. If aluminum chloride is used as the catalyst, it

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should not exceed three percent of the dry shale weight.

Sufficient vehicle oil, which will be herein designated the "recycle stock," is fed into the conditioner 12 from a recycle stock piping system 15 to form a pulp with the ground shale which is sufficiently fluid to be pumped. The recycle stock is obtained as a product of the improved method as will be later described.

The fluid pulp, after thorough intermixing, overflows from the conditioner 12 at a point well above the bottom thereof and flows to a pulp pump 16 by means of which it is forced through a pre-heating coil 17 in a suitable furnace 18 where it is heated to not more than 250° C.

The hot pulp flows from the furnace to a series of digestion cells 19 provided with any suitable mechanical agitators 20. The pulp is introduced into each cell through a feed sleeve 21 above and about the agitator of that cell and flows from each cell to the next successive cell through a overflow pipe 22. Each digestion cell 19 is provided with a suitable heating jacket 23 capable of maintaining a temperature of 200° C. at the vapor outlet of each cell.

As the digestion progresses in the cells 19, the "kerogen" is converted to soluble hydrocarbons and fixed gases. The light fractions of the former are volatilized and expelled with the fixed gases through the vapor outlets of the cells to a vapor line 41.

Exfoliation of the shale particles above grain size along the plane of original laminations occurs under the conditions of the digestion and reduces the shale to a very fine carbonaceous residue. This assures intimate contact with solvent and complete removal of the oil therefrom.

The density of the pulp overflowing the final cell is adjusted by control of the amount of recycle stock introduced at the conditioner 12 to a consistency of approximately 50% solids. The overflow from the final cell is conducted to a receiver or surge tank 24 from whence it flows to a continuous, totally enclosed, vacuum filter 25 where substantially all of the remaining oil is removed and/or separated from the residue.

The separated oil is then forced by means of a pump 26 through re-heating coils 27 in the furnace 18, thence through feed lines 33 to a primary fractionating column 28 of conventional design which forms a part of a standard refinery, designated in its entirety by the numeral 29.

The filter cake from the continuous filter 25 is repulped in a suitable mill 30, positioned directly under the filter 25, with a sufficient amount of gasoline or light naphtha, furnished by a solvent pump 47, to dissolve out the remaining oil. The dissolved oil and solvent flow to a settling tank 31, the clear overflow of which is pumped by means of a pump 32 into the fractionating column 28 through the lines 33.

The thick sludge from the tank 31 is conveyed by means of the totally enclosed, refuse chain conveyor 34 through a heater 35 in which the temperature of the residue is elevated to not less than 200° C. to volatilize the remaining solvent and any residual aluminum chloride.

The dried residue is cooled and stock piled at 38 ready for market as a soil conditioner. If the residue is to be used as an adsorbent in petroleum distillation, it is discharged from the conveyor 34 directly into a suitable rotary kiln 39 and heated to 500° C. at which temperature the carbon escapes as carbon dioxide (CO_2). A light tan colored decarbonized ash is produced, indicated at 40, which is useful as the adsorbent previously mentioned. The carbon dioxide will pass to the atmosphere or, if desired, may be used in saturating the caustic liquors in the recovery of phenols from the oils of the process.

The vapors and fixed gases originating in the digestion cells 19, and the vapors from the heater 35 together with the aluminum chloride sublimed at these points, are conducted through the vapor line 41 to a dephlegmator or partial condenser 36 where the aluminum chloride is condensed and the solvent vapors and fixed gases are expelled through a vapor line 37 of the fractionating column 28. A portion of the recycle stock is diverted from recycle piping 15 through a reflux line 42 to the top part of the dephlegmator above trays 43 therein. The reflux cools the vapor to approximately 175° C. so as to remove the aluminum chloride. A small portion of the light fractions volatilized from the cells 19 will also be condensed and this condensate plus the oil reflux will form a slurry with the aluminum chloride which is returned from the bottom of the dephlegmator to the recycle stock piping system 15.

An intermixture of the slurry from the dephlegmator 36 and oil from the pump 26 forms the recycle stock which is employed in the conditioner 12. Thus a closed circuit for the catalyst is obtained. Mechanical losses and losses by decomposition of the aluminum chloride due to the presence of water are low and the additional amount of aluminum chloride necessary to maintain a definite reagent concentration of not more than three percent during operation is exceedingly small.

The uncondensed vapors and fixed gases flow from the top of the dephlegmator 36 through the vapor line 37 to the primary fractionating column 28. A by-pass line 44 is provided for use with catalysts other than aluminum chloride, thus eliminating the partial condenser 36 which is intended for aluminum chloride recovery only.

The non-condensable gases from the process are conducted to an absorber 45 in the refinery 29 in which the very light hydrocarbons will be recovered. The gases thus stripped are discharged from the top of the absorber through a gas line 46 and pass to a suitable gasometer for use for heating purposes in the plant.

It will be noted that the oil recycle stock and the catalyst are acting directly on the raw natural shale and not on any products of destructive distillation. Therefore, the recovery is much more direct and more simplified than prior methods. Specific laboratory tests substantiate the above process in every detail.

The oil recycle stock is only a portion of the unvaporized oil from the digestors as separated from the residue on filter 25. The oil not so used passes on to the refinery thru the furnace 18. It will be recalled that the digestors remove only the light hydrocarbons in the form of vapor along with the fixed gases and aluminum chloride. The endpoint of gasoline is about 200° C., therefore, only crude gasoline has been expelled at the digestion cells. The initial boiling point of the hydrocarbons in solution in the recycle stock, also the recycle stock itself, is 200° C. The unvaporized oil from the digestors will, therefore, contain the fractions starting with kerosene and ending up with lubrication oils and pitch. After primary fractionation these oils are refined to their respective marketable products. Then too, when equilibrium is reached in the process, the amount of recycle stock will be constant and the hydrocarbons derived from the fresh shale being introduced will be over and above that amount used as recycle stock.

While preferred forms of the invention have been described in some detail together with the theories which it is believed to best explain its success, it is to be understood that the invention is not limited to the precise procedure described nor is dependent upon the accuracy of the theories which have been advanced. On the contrary, the invention is not to be regarded as limited except in so far as such limitations are included within the terms of the accompanying claims in which it is the intention to claim all novelty inherent in the invention as broadly as is permissible in view of the prior art.

Having thus described the invention, what is claimed and desired secured by Letters Patent is:

1. A process for the recovery of oils from shales comprising: intermixing the shale with sufficient vehicle oil to form a fluid mixture; pumping the mixture through a pre-heater to a digesting cell; heating the mixture in said cell under the influence of agitation to expel the fixed gases and vaporize the lighter fractions; overflowing the fluid mixture from the digesting cell; filtering the latter overflow to separate the sludge from the oil in the remaining mixture; pumping a portion of the latter oil through a heater to a fractionating column; fractionating the latter portion to obtain fractions therefrom; intermixing the remainder with additional shale for introduction into the process; repulping the sludge from the filtering step with a gasoline fraction; settling the solids from the pulp; and pumping the fluid residue to said column.

2. A process for the recovery of oils from oil shales comprising: intermixing the shale with a hydrocarbon oil product of the process having an initial boiling point of about 200° C., adding aluminum chloride to said mixture; maintaining the mixture as a pulp by mechanical agitation in a digestion zone at a temperature of 200° C. for a time sufficient to convert all kerogen of the shale to hydrocarbons and to vaporize aluminum chloride and hydrocarbons boiling below about 200° C.; withdrawing resulting hydrocarbon vapors, fixed gases and aluminum chloride vapors as an overhead product from the digestion zone; condensing the aluminum chloride vapors and at least some of the hydrocarbon vapors to form a slurry of aluminum chloride in liquid hydrocarbons and returning the slurry to the initial mix-

ing step; removing non-volatilized oil and shale residue from the digestion zone; separating the non-volatilized oil from the shale residue; recycling a suitable quantity of the non-volatilized oil to the initial mixing step as the hydrocarbon oil product having an initial boiling point of about 200° C.; discharging the remainder of the non-volatilized oil to a primary fractionating system and recovering a gasoline fraction therefrom, repulping the shale residue with the gasoline fraction for recovery of the oil still retained in the shale; separating the repulped shale residue into a solid shale residue and a liquid oil fraction; and recovering by distillation any gasoline hydrocarbons remaining in the solid shale residue.

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