

Oct. 14, 1930.

W. H. HAMPTON

1,778,515

ART OF TREATING SHALE OR THE LIKE

Filed Dec. 16, 1920

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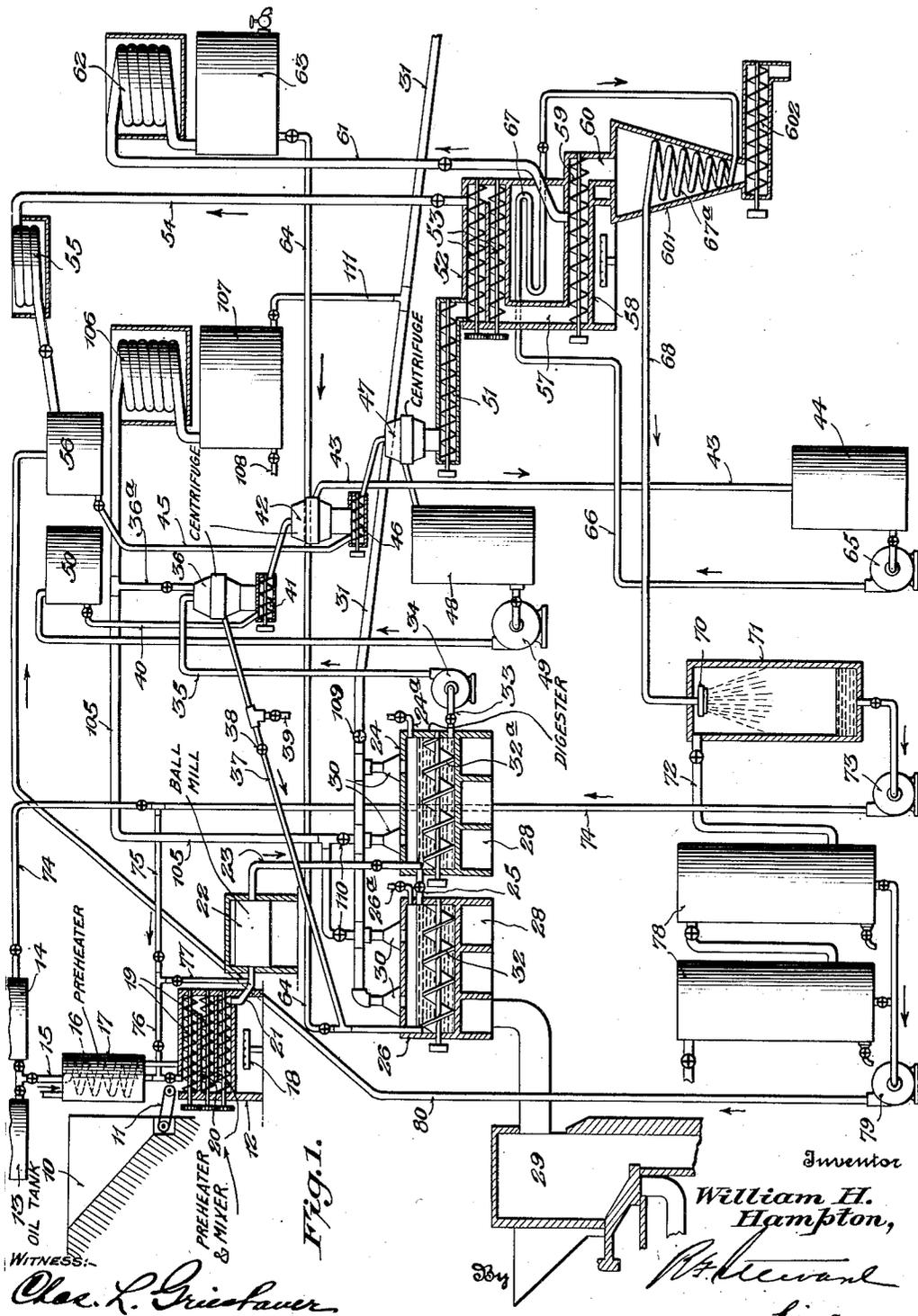


Fig. 1.

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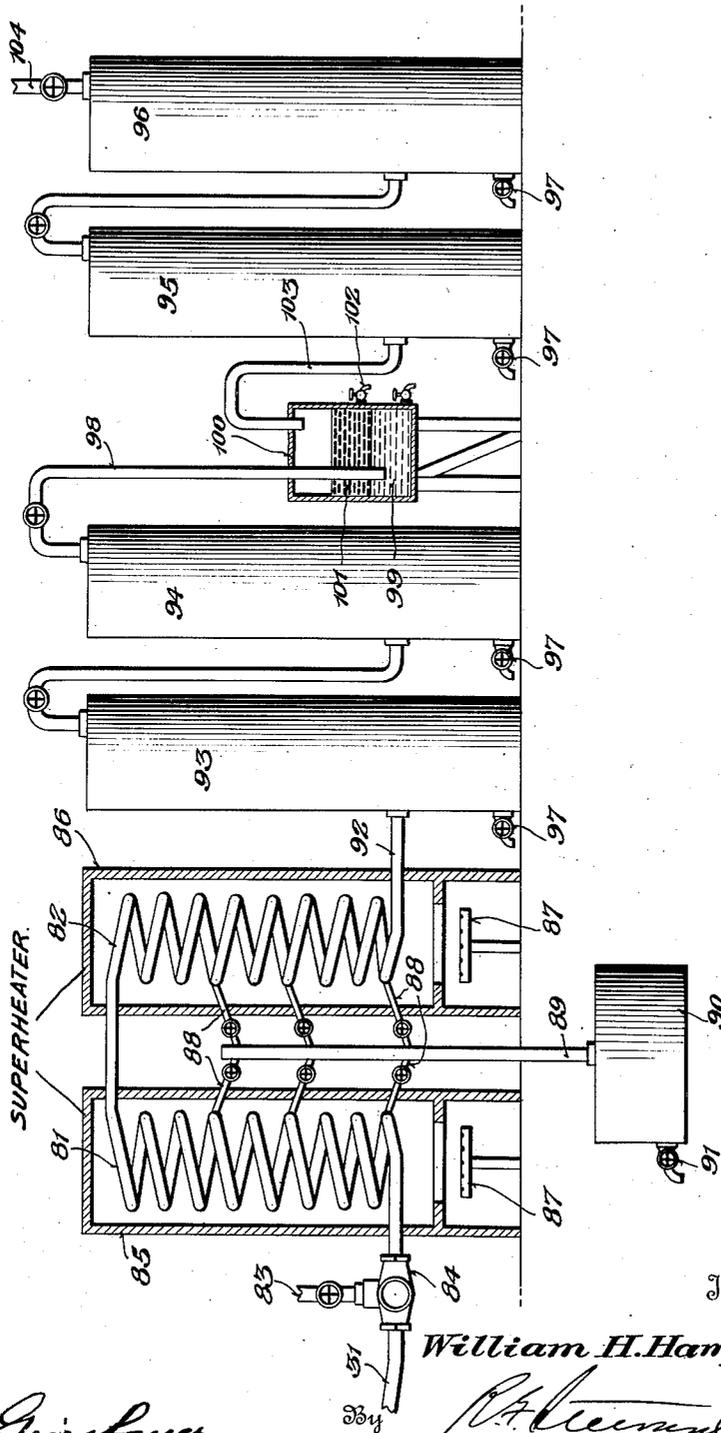
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4 Sheets-Sheet 2

Fig. 1a



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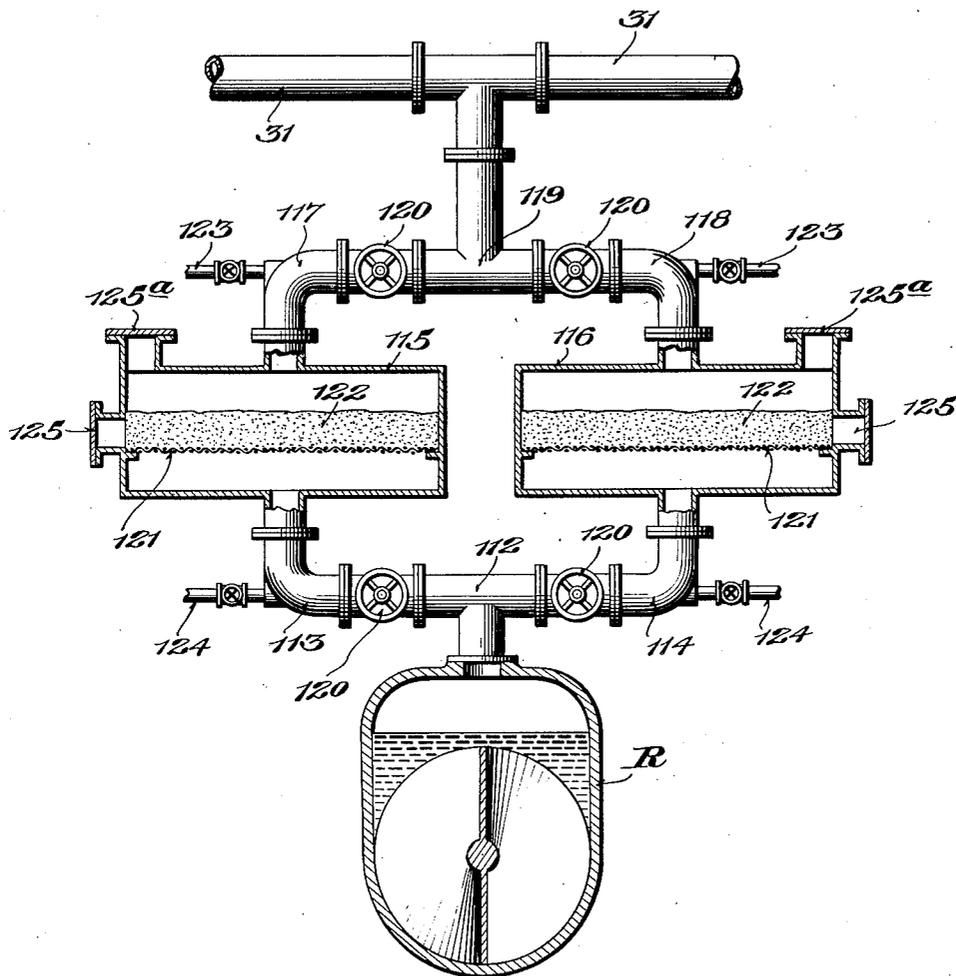
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ART OF TREATING SHALE OR THE LIKE

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4 Sheets-Sheet 3

Fig. 2.



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ART OF TREATING SHALE OR THE LIKE

Filed Dec. 16, 1920

4 Sheets-Sheet 4

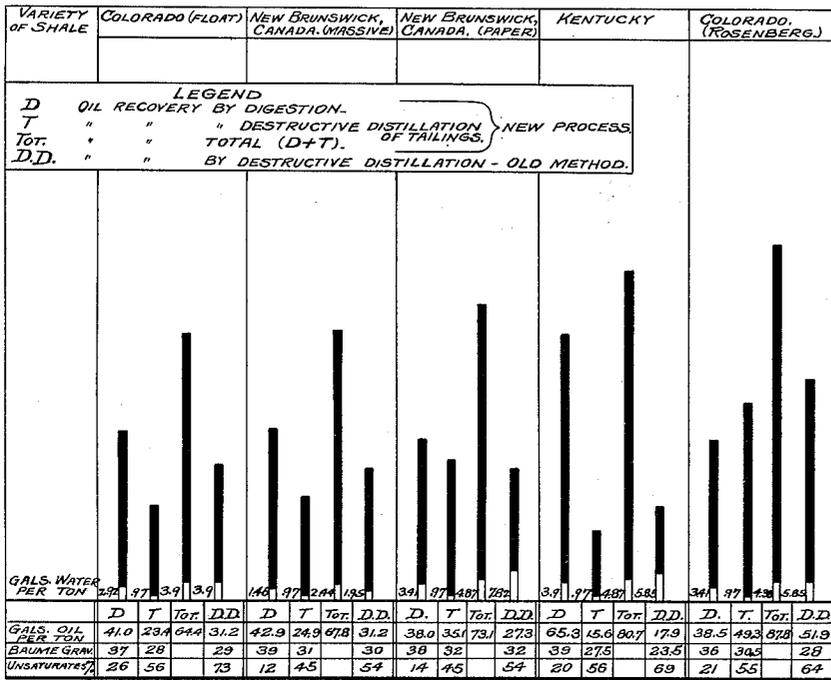
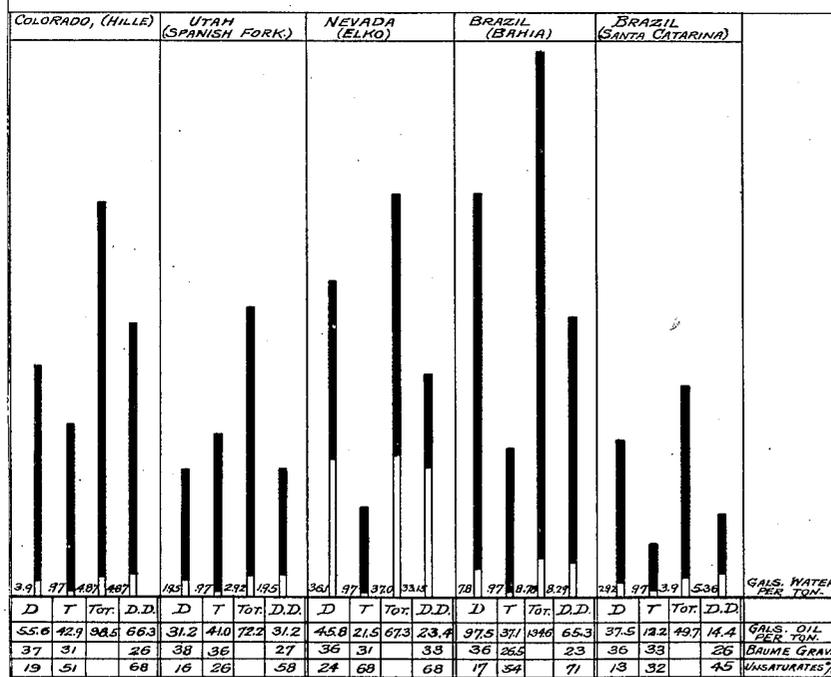


Fig. 3.



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UNITED STATES PATENT OFFICE

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ART OF TREATING SHALE OR THE LIKE

Application filed December 16, 1920. Serial No. 431,188.

This invention relates to art of treating shale or the like. More particularly the invention relates to processes of and apparatus for treating bituminous shales, rocks, sands, 5 coals, and related bituminous mineral substances for the winning of oils and other valuable substances therefrom. The invention also comprises novel products obtainable by said processes.

10 Important objects of the invention are to enable the attainment of substantially enhanced yields of hydrocarbons from bituminiferous minerals, particularly from oil-shales, oil-bearing rocks, sands, and the like; 15 to obtain products of high quality; and to conduct the treating operations in an efficient and economical manner.

In my prior applications Serial Nos. 318,833 and 318,834, filed August 20, 1919, Serial 20 No. 344,016, filed December 11, 1919, and Serial No. 345,485, filed December 17, 1919, of which prior applications the present application is in part a continuation, I have disclosed and claimed certain desirable meth- 25 ods of and apparatus for treating minerals of the character above mentioned, especially oil-bearing shales. In general, said methods involve subjecting the bituminiferous material in relatively finely divided condition to the digesting action of an oil bath, consist- 30 ing wholly or in part of heavy oil fractions, at a temperature sufficiently high to effect substantial liquefaction of the contained bitumens and recovery thereof in various useful 35 forms, the digestion mixture being stirred or agitated during the operation. The present invention relates to subject matter resembling broadly that of said prior applications but involving further novel features of great 40 practical importance.

While in some of its phases the invention is concerned with the treatment of bituminif- 45 erous solids broadly, it has to do in particular with the treatment of bituminous shales; and in this connection it is important to note that a shale is to be sharply distinguished in certain important respects from other bitu- 50 miniferous minerals such as natural asphalts and oil sands, for example. A shale is an aggregate of non-bituminous mineral parti-

cles impregnated and bonded together by bituminous matter of such constitution and character that it is stubbornly resistant to the action of solvents either hot or cold, so that its bonding effect is not destroyed by treat- 55 ment of the shale with solvents as heretofore employed. In other words, a piece of shale, whether large or small, does not disintegrate when treated with a solvent in the ordinary way, even though the solvent may extract 60 some bituminous matter therefrom. An oil sand, on the other hand, is readily attacked by solvents even at relatively low temperatures and promptly disintegrates into its constituent elementary particles with substan- 65 tially complete loss of contained bituminous matter to the solvent. Similarly, by the use of appropriate solvents, in conjunction with proper temperature and time factors, it is feasible to separate asphalt quite completely 70 by known methods from natural asphalt rock or other forms of natural asphalt minerals.

The reasons for the foregoing differences in conduct I believe to be as follows: The kerogen or bitumen of shale is a complex 75 composition consisting largely of high-molecular hydrocarbons of both paraffin base and asphalt base, so intimately associated or alloyed as to give the resistant properties characterizing shale bitumens generally. 80 The shale hydrocarbons (which are often more or less oxygenated or hydrated) forming this combination or alloy comprise a large proportion of normally solid paraffin 85 waxes and asphaltic constituents, which not only resist solvents but are not liquefiable by heat to a substantial extent. The bitumen content of an oil sand, on the contrary, is either liquid or easily liquefiable by heat, 90 and is soluble in common solvents, whether said bitumen content consists of a paraffin base, or an asphalt base, or of both. If it contains both paraffin and asphalt base constituents, there appears to be no complicat- 95 ing association of these into a resistant combination or alloy as in the case of shale. Asphalt as it occurs naturally is free of paraffin base constituents and is not of the complex nature characterizing shale bitumens.

Considering oil shale specifically, there- 100

fore, its treatment for recovery of bitumens is a problem quite distinct from that of other bituminiferous minerals, and this fact is important to bear in mind. It is to be understood, however, that the novel process hereinafter described is also applicable to other bituminiferous minerals, such as those above mentioned.

According to the processes described in said prior applications, shale or the like in a state of relatively fine subdivision or comminution, most desirably in mixture with a heavy oil and moderately heated to say 300 to 400° F., is fed into a digestion bath comprising heavy oil fractions non-volatile under the conditions of digestion, said digestion bath being heated to a substantially higher temperature than that to which the fresh shale is preliminarily heated. I have found that exceptionally favorable results are attainable when the introduction of the fresh shale and oil mixture into the digester is accomplished in such manner that the entering mixture is subjected to a sudden or abrupt rise in temperature. Under these conditions a copious disengagement or evolution of readily condensable hydrocarbons from the digestion mixture takes place, unaccompanied by formation of free carbon and fixed gases, such as methane and hydrogen, to any pronounced extent. The yield of such hydrocarbons is much more pronounced than where the shale is mixed with heavy oil and then gradually heated to the desirable final digestion temperature of say 680° to 700° F. My investigations of various shales show that this method is of advantage in treating practically all bituminous shales where it is desired to obtain a maximum yield of easily condensable fractions volatilizable at the temperature and other conditions of digestion employed; and this is especially so where the kerogen or bitumen of the shale is composed largely of members of the paraffin series, with a lesser proportion of asphaltic or analogous constituents. Without committing myself to any theory in this connection, I may say that there appears to be some chemical reaction between the bitumens of the freshly introduced shale and the heavy oil constituents of the digestion mixture resulting in an abundant yield of readily condensable hydrocarbons volatile under the conditions of digestion prevailing. The sharp increase in temperature experienced by the bitumens of the freshly introduced shale or like material may possibly induce unusual rapidity of such reaction with resultant avoidance of much if any separation of free carbon or formation of fixed gases. At all events, whatever may be the theoretical considerations involved, the observed results are as herein stated when the procedure is carried out in accordance with principles of my invention.

It is also noteworthy that actual observations show that the reaction taking place is apparently exothermic, a further indication of its being chemical in character.

In the best mode of practicing the invention now known to me, the solid mineral matter contained in the digestion mixture is in a state of extremely fine subdivision intimately admixed with residual digestion oil non-volatile under the conditions of operation. The extreme fineness of the mineral matter finally attained in the digester is probably attributable at least in part to the disrupting effect caused by suddenly increasing the temperature of the shale or other mineral treated. The sudden shock of temperature increase seems to have the effect of assisting prompt disruption of the mineral structure and subdivision into elementary particles each consisting of a partly or wholly non-bituminous particle with its bituminous envelope, which latter liquefies and vaporizes to a greater or less extent under the conditions of digestion. Whether or not this is a correct explanation of what takes place, the insoluble or unliquefiable mineral matter persisting in the digestion bath after the digestion is concluded is very finely divided, and separation thereof from the accompanying liquid matter presents some technical difficulty. Separation can be effected, however, in a manner hereinafter set forth; or the residual mixture may be usefully employed without separation for road material and other purposes as described in my prior application Serial No. 318,834. If separation is carried out, it is usually worth while then to treat the separated solids or tailings further to obtain therefrom bituminous matter which resisted the digestion treatment and is still tenaciously held by the mineral particles. According to my observations, the proportion of bituminous matter persisting in the tailings is higher in the case of asphaltic base shales than in the case of paraffin base shales. In practice, I destructively distil the tailings, obtaining (in the case of shales) a yield of shale oil therefrom which, in practically all cases, is almost as large as the total yield obtainable by destructive distillation of the original or untreated shale, and which in some instances is even greater. Moreover a better quality of shale oil is thus obtained, the proportion of unsaturated constituents being considerably lower than in shale oil produced by ordinary destructive distillation processes.

The hydrocarbons volatilized in the digestion operation may be led direct to condenser means for recovery of one or more condensable fractions; or, prior to condensation, they may be subjected to further heat treatment designed to improve the character of the condensates finally obtained. The hydrocarbons volatilized in the digestion include not

only highly volatile condensable fractions but also heavy paraffins which crystallize upon condensation to yield high-melting paraffin wax. These heavy paraffins are vaporized and carried over with the lighter fractions under the conditions obtaining in my process wherein fresh portions of bituminiferous mineral are continuously being fed to the hot digestion bath.

While the process may be successfully carried out in apparatus of various types and arrangements, the novel system illustrated more or less diagrammatically in the accompanying drawings offers a number of important advantages from a practical standpoint.

In these drawings:

Figs. 1 and 1^a, taken together illustrate a complete system in which provision is made for heat treatment of the vapors led from the digestion apparatus, the views being in side elevation, parts being shown in section, and Fig. 1^a being on a somewhat larger scale.

Fig. 2 represents, in transverse section, a digester provided with vapor-filtering means which may be employed to advantage; and

Fig. 3 comprises a chart and table showing results obtained in applying the novel process to various shales, and also comparative results by an old method.

In carrying out the process as applied to treatment of a bituminous shale, for example, and employing the type of apparatus illustrated in the drawings, shale previously crushed to pass say one-half inch mesh or thereabouts is fed from a bin 10 by suitable conveyer means 11 at a controllable rate into the upper part of a combined drier, preheater and mixer indicated generally at 12, preparatory to fine grinding. At the same time, a heavy oil of suitable character is fed from either of the supply tanks 13, 14, through pipe 15 into said mixer and preheater 12 in such manner as to mingle with the crushed shale. In starting operations, this oil may be a cylinder oil or a stripped oil containing practically no fractions volatile below say 700° F., a grade of steam cylinder stock known commercially as Congo cylinder oil being suitable, for example. After the system is operating regularly, the heavy oil used may be derived from the shale itself, as will appear hereinafter. The quantity of heavy oil so introduced may vary to a considerable extent in practice, and depends in part upon the character of the particular shale undergoing treatment; but in the case of a typical Colorado shale normally yielding around 30 gallons of oil per ton by the usual destructive distillation methods, the proportion may be about one volume of oil to two volumes of shale. Richer shales may require relatively less heavy oil, and leaner shales more, for attainment of best results. The piping through which the oil is fed into the apparatus 12 may include a preheating coil 16

housed within an enlargement 17 of the flue or chimney through which pass hot gases from a furnace 18 by which the apparatus 12 is heated.

The shale and oil fed into the apparatus 12 may be thoroughly commingled therein in any suitable manner. In the present example, thorough commixture is effected by a series of screw conveyers 19 which are driven in directions suitable to advance the materials through a series of superimposed tubes 20 arranged to provide a zig-zag path of travel down through the apparatus, the mixture being finally discharged through outlet pipe 21 into appropriate grinding apparatus, here shown as taking the form of a ball mill 22. In passing through the mixer and pre-heater 12, the mixture of shale and heavy oil is gradually heated up to say 300° or 400° F., at which temperatures the shale is relatively soft and friable and is thus in particularly favorable condition to be efficiently acted upon by the grinding apparatus, so that the solid constituents of the mixture can be reduced therein to practically any desired degree of fineness. This heating also serves to drive off hygroscopic moisture from the shale, and even moisture of constitution of the hydrated minerals in the shale. This is desirable in order to avoid complications in the succeeding digestion treatment. In practice it is found desirable to grind or pulverize the shale material in the mill or grinder 22 until 60% or more thereof will pass 200-mesh; but it is not to be understood that this particular degree of fineness is essential. In general it is desirable that the bulk of the mineral matter be at least fine enough to pass 100-mesh. As a rule, the finer the degree of comminution or grinding, the better are the results eventually attainable in recovery of valuable constituents from the shale.

From the mill or grinder 22, the mixture of finely divided shale materials and heavy oil is led continuously in the form of a fluid slurry through pipe 23 into any appropriate form of retort or digester means wherein the mixture is heated, most desirably suddenly, to a materially higher temperature necessary to bring about the breaking down or decomposition of the shale bitumens including liquefaction and partial vaporization thereof, as already set forth, care being taken not to attain a temperature high enough to bring about extensive "cracking" in the usual sense of the term or to coke the material undergoing digestion. By observing such precautions, production of free carbon and fixed gases is reduced to a negligible minimum. In the particular example here illustrated the digester means comprises a digester 24 large enough to contain a digestion bath of which the the volume is great as compared to that of the mixture being fed into it per unit of time. It is thus a simple matter to hold the

digestion bath at a practically constant optimum temperature considerably above that of the material entering through pipe 23, especially in view of the fact that an exothermic reaction seems to occur, as before pointed out. In the arrangement shown, preheated digestion oil is also fed at a controllable rate into the digester 24 through pipe 25 leading from a hot oil reservoir 26 which may conveniently be similar in form to digester 24, both being here shown as of the horizontal cylindrical still type. In practice I find it desirable to feed oil into digester 24 from reservoir 26 at such rate that in the digester the mixture comprises about 3 to 4 parts of digestion oil to 1 part of shale by volume, or about $1\frac{1}{2}$ parts of oil to 1 part of shale by weight. The digester and reservoir are heated by suitable means such as heating flues 28, which are supplied with flame or hot gases from any type of furnace indicated conventionally at 29. For best results, the temperature of the bath in the digester means 24 should be maintained above about 600° F., and most desirably between the approximate limits of 680° and 700° F., this being the optimum range for most effectively operating on the majority of shales in accordance with the invention. Oil vapors collecting in the vapor spaces of the digester 24 and heating reservoir 26 are conducted away through vapor outlets 30 into vapor line 31 for further heat treatment or for disposal in some other manner to be hereinafter set forth. It will be understood that a plurality of digesters 24 may be employed, if desired. Digestion oil continuously supplied to reservoir 26 in a manner to be hereinafter described is continuously agitated and made to progress gradually through the same toward the outlet pipe 25 by means of a helical or screw agitator 32 arranged horizontally in the lower part of said reservoir and so closely adjacent the bottom thereof as to prevent accumulation of caked material thereon. A similar helical agitator 32^a, similarly arranged, serves to agitate continuously the contents of digester 24 and to move them toward the discharge outlet 33.

In the digester 24 a very large proportion of the valuable shale hydrocarbons or bitumens may be evolved under the described conditions of operation in the form of vapors which, though readily condensable and consisting to some extent of fractions normally non-volatile below temperatures as high as 800° or 850° F., are nevertheless given off freely under the conditions of digestion. The yield of such condensable vapors is found to depend in part upon the character of the shale. Shales high in paraffine base content are found to yield much greater proportions of such condensable vapors or "overhead" than are shales in which an asphaltic base predominates. In both cases, however, as before stated, there appears to be

some form of chemical interaction between the heavy non-volatile oil or bitumen constituents of the digestive bath with the oil and other bitumen contents of the fresh mixture fed at a controllable rate into the hot digestion bath under the described conditions wherein the freshly introduced mixture has its temperature suddenly raised to the digestion temperature. This results in an exceedingly large yield of oil fractions vaporizable under the conditions of digestion, these fractions being evolved partly at the expense of the added digestion oil especially where the latter is largely a paraffin base shale oil. Whatever may be the correct theoretical explanation, it has been repeatedly observed in the conduct of the novel process that a very materially larger yield of condensable hydrocarbons volatile at the stated digestion temperatures is obtainable where the described procedure is followed, than is obtainable where the shale is gradually heated up to the digestion temperature without any sharp or sudden rise of temperature at any time. In order to still further enhance vaporization, steam or an inert gas may be introduced into the bodies of oil in the retorts 26, 24, or may be caused to sweep over the surface thereof to facilitate vaporization of certain oil fractions at a lower temperature than would otherwise be required to volatilize them. The retorts are here shown as provided with steam inlets 26^a, 24^a, respectively, whereby the latter procedure may be carried out. Hydrogen may be introduced when it is desired to reduce the percentage of unsaturated constituents in the products. It should be noted that the vaporization of fractions normally nonvolatile at the digestion temperature is also greatly facilitated by continuously feeding into the bath fresh portions of shale whose bituminous content, subjected to sudden temperature increase upon coming into contact with the oil bath, constantly yields large volumes of light vapors (as well as heavier) which aid in sweeping heavier vapors out of the still in a manner analogous to the action of steam. To enhance this effect the introduction of fresh shale mixture may be advantageously distributed or spread over a considerable area of the bath instead of being localized near one end of the bath as shown in Fig. 1 which, as explained before, is to be understood as more or less diagrammatic in character. One way of effecting this is by using a plurality of pipes 23 to introduce the shale mixture into the digester at a corresponding plurality of distributed points, an arrangement obviously not requiring specific illustration here. In this way both the abruptness with which the shale is heated up, and the effective contact and reacting surface between the hot digestion oil and the fresh shale may be greatly increased.

The duration of the digestion may vary, of course, but most advantageously it is long enough to ensure substantially complete stripping from the bath of all fractions vaporizable from it under the conditions prescribed. In practice, I have found that if the operation is so carried on that, as an average, the shale is digested for from 30 to 40 minutes after its entry into the bath, satisfactory results are obtained.

It is apparent that the temperature of the shale may be suddenly raised in various ways, the method hereinbefore described being merely typical. For example, dry pulverized shale, without any accompanying admixed oil, may be fed in controllable amounts directly into the hot digestion bath. This involves certain technical difficulties, however, among which may be mentioned the difficulty of pulverizing most shales by methods ordinarily applicable to solids generally. I have found that many types of shale are very difficult to grind or pulverize unless they are first heated up in mixture with oil to a moderate temperature, say 300° or 400° F. The grinding of very rich shales when dry is attended with difficulty due to softening and gumming up, and also with considerable risk from fire and explosion. The described method of mixing heavy oil with coarsely crushed shale, and then grinding this mixture at temperatures ranging from 300° to 400° F., therefore offers the best solution of the problem now known to me.

Residual solid material arriving at the digestion zone through the action of the screw conveyor 32^a is continuously withdrawn from the digester system, in company with heavy oil and other liquid bitumens, through pipe 33 by a pump 34 which, in the present system, elevates the mixture through pipe 35 and discharges the same, most desirably without substantial reduction in temperature, into the centrifugal separator 36. This centrifugal separator may be of any suitable type adapted to operate continuously to separate the solid from the liquid material and to discharge liquids and solids at different points. An example of a centrifugal separator suitable for this purpose may be mentioned the Elmore type in which the solids collect on a filter screen and are continuously moved to a discharge outlet by a helical scraper; while the liquid passes through the screen and is discharged through another outlet. The separator should be suitably enclosed to prevent air gaining access to the hot oil vapors evolved therein and causing ignition of said vapors. The vapors may be vented from the separator through pipe 36^a to vapor line 105 to be referred to later.

It will be noted that, as here described, the mixture withdrawn from the digester system is fed to the centrifugal separator while still very hot. In this condition, the mix-

ture is highly fluid, can be readily handled by the pump, and can be efficiently treated in the centrifugal separator in such manner as to free the solid matter very largely from the accompanying liquid oily material. While I consider this method of handling the mixture coming from the digester system as particularly advantageous from a practical standpoint, it is to be understood that, within the broad scope of the invention, other procedures may be followed. For example, it is feasible to dilute the digestion mixture with a lighter oil fraction, such as a kerosene fraction for example, and then to pass the diluted mixture through a suitable separator, centrifugal or otherwise, for separation of the solids from the liquid. I consider such a procedure less advantageous, however, in that it is less economical from the standpoint of heat conservation and also because it involves additional steps of treatment which lead to further complications in the separation of the recovered liquid into desired fractions.

Separation by a centrifugal separator offers special advantages in the present process because of the fact that the residual solid mineral matter in the mixture leaving the digester system is in extremely finely divided condition, so that separation by sedimentation or by ordinary filtration can be effected only through liberal dilution with a lighter oil, thus multiplying the operating steps and introducing undesirable complications. Centrifugal separation is especially suitable when the mixture is separated without being cooled down, which procedure is of particular advantage from the standpoint of heat economy.

Oil and other liquid bituminous material separated from the residual solids of the digestion mixture are best conducted from centrifugal 36 back to the digester system with as little reduction in temperature as possible in order to conserve heat units. In the present example, the hot separated oil passes through pipe 37 from the centrifugal 36 to reservoir 26, wherein any unavoidable drop in temperature can be made up before the oil passes into the digester 24. Where the supply of digestion oil thus returned to the digester system is more than sufficient to maintain the digestion mixture at the desired level in the digester 24, the flow through pipe 37 may be reduced by means of valve 38, and a portion of the oil coming from the centrifugal may be diverted to any suitable place of storage or use through valved branch 39. Particularly in the treatment of asphaltic shales, more heavy oil is produced in the digestion and in the subsequent distillation of tailings than is required for use in the digestion bath. The solids or tailings separated in and continuously discharged from the centrifugal separator 36 carry with them some adherent liquid oil not removed in

the centrifugal. In order to remove such adherent liquid material, it is advisable to wash the tailings with a lighter oil such as a kerosene or the like, and then again to centrifugally separate the resultant mixture. To this end, wash oil is fed through pipe 40 to the solids discharged from centrifugal 36, a screw conveyer 41 serving to discharge the mixture into a second centrifugal separator 42, from which the separated wash oil is discharged through pipe 43 to a tank 44. The washed tailings leaving separator 42 may be still further freed from adherent bituminous matter by a second washing with a still lighter oil fraction, such as a light kerosene or even a gasoline fraction, supplied to said tailings through a pipe 45 and mixed therewith with the aid of screw conveyer 46 which feeds the mixture into a third centrifugal separator 47 at a still lower level. From the third separator wash oil is separated and discharged into tank 48, from which it may be elevated by pump 49 to storage tank 50, wash oil being drawn from this tank as required through pipe 40 for washing the tailings discharged from the first separator 36, as already described.

Residual washed tailings discharged from separator 47 may be conveyed by a screw conveyer 51 to suitable means for volatilizing and recovering the adherent light wash oil or solvent, where desired, after which the dried tailings may be subjected to destructive distillation in order to win from them such bituminous content as may have resisted the digestion treatment hereinabove described. In the present example, the conveyer 51 discharges the washed tailings into a drier 52, through which they are advanced by suitable screw conveyers 53, while the resultant volatilized wash oil passes by way of vapor off-take 54 to the condenser 55, the latter discharging into the storage tank 56, from which relatively pure light wash oil is drawn as required through pipe 45 to further wash the tailings discharged from the second centrifugal separator 42, as already described.

The dried tailings are discharged from drier 52 through passage 57 into a retort 58 in which they are subjected to a temperature sufficient to effect destructive distillation, say 850° to 900° F., such temperatures being high enough to complete the distillation when the tailings are agitated during the heating, as in the present example. While undergoing distillation, the residual solid material of the shale is gradually advanced through the retort by screw conveyer 59, and is finally discharged at 60 in a more or less coked condition into a cooler or heat exchanger 601, the cooled material being discharged from the system by conveyer 602. The material thus finally discharged may be utilized, if desired for preparation of road material etc. as described in my prior application Serial No.

318,834. The oil vapors resulting from the destructive distillation may be recovered and utilized in any desired manner, but in the present instance they pass through vapor off-take 61 to a condenser coil 62 discharging into a storage tank 63. The condensate may be conducted wholly or in part through pipe 64 to reservoir 26 where it mingles with oil coming from separator 36, the mixture being heated up in 26 and then flowing into 24. It will be noted that the pipe connection 25 is substantially at the level of the digestion bath in 24, which tends to prevent back-flow of mixture from 24 into 26. It will be noted that the arrangement shown provides for an initial fractionation or stripping of the oil derived from the destructive distillation of tailings in the retort 58, any vapors evolved in reservoir 26 passing into vapor line 31. The tailings distillate collecting in 63 is unlike and is definitely distinguishable from shale oil obtained heretofore by the usual methods of destructively distilling the same original shale, and I believe it to be a novel article of manufacture. As a rule the tailings distillate obtained in my process is of higher Baumé (lower specific gravity) than ordinary shale oil. Moreover it always contains an appreciably lower percentage of unsaturated constituents and has a much milder and better odor than ordinary shale oil which is invariably contaminated with pyridins and other evil-smelling compounds. The new shale oil also contains a substantial proportion of paraffine wax hydrocarbons which crystallize out beginning at about 100° F. and can be easily separated by further cooling.

The first wash oil discharged from the second centrifugal separator 42 contains a considerable amount of heavy oils and other liquid bitumens that still adhered to the tailings discharged from the first separator. This first wash oil, which collects in tank 44 as already described, may be separated into its light and heavy constituents in any suitable manner. In the specific example here illustrated, this oil is drawn from tank 44 by pump 65 and forced by way of pipe 66 through a heating coil 67 arranged in the flues of the combined drier and distilling retort 52, 58, and also through coil 67^a in heat exchanger 601, where the temperature of the wash oil is raised to a suitable topping or stripping temperature, say 700° F., or to such other temperature as is suitable for the particular method of fractionation that may be adopted. As here shown, the heated oil then passes through pipe 68 and is discharged through a rose 70 into a tall chamber or tower 71, the lighter constituents of the oil flashing into vapor which passes off through outlet 72, while heavy constituents that are non-volatile at the temperature prevailing collect in the bottom of the chamber. These heavier

constituents may be withdrawn by pump 73 and forced thereby through pipe 74 to the supply tanks 13, 14. Or such heavy constituents may be sent by the pump through branch pipe 75 and sub-branches 76 and 77 either to the preheater and mixer 12, or ball mill 22, or both, as may be necessary or desirable at any time, the piping being provided with suitable valves, as shown, to enable direction and control of the heavy oil from pump 73 in any desired manner. By sending the oil from chamber 71 directly to the mixer 12 or ball mill 22, or both, the available heat units in the system are still further conserved, and under some circumstances the firing of the mixer by furnace 18 and the preheating of oil in coil 16 may be entirely dispensed with.

The vapors leaving chamber 71 through outlet 72 may be treated for condensation and separation of relatively light oil fractions in any suitable manner. In the present example, said vapors are caused to pass through a series of separating chambers 78, which may be of the well-known Feld type, condensed fractions being withdrawn either separately or together by means of a pump 79 and conducted through pipe 80 to wash oil supply tank 56.

Hydrocarbon vapors leaving the retort system 26, 24, may, within the broad scope of the invention, be disposed of or further treated in any suitable manner. Ordinarily, since these hydrocarbon vapors comprise constituents ranging from relatively heavy hydrocarbons to very light hydrocarbons, it is desirable, especially where a high yield of gasoline-like products is desired, to subject the vapors from the digester system to further treatment in the nature of cracking to increase the proportion of lighter constituents. It is advantageous, however, to avoid in such further treatment the formation of free carbon and non-condensable gases as far as it is practicable to do so. To this general end, the vapors leaving the retort system may be conducted through vapor line 31 into and through superheating coils 81, 82, of which there may be any desired number connected in series. Passage of the vapors through these coils may be assisted and expedited by the injector action of steam introduced in regulatable quantities through valved pipe 83 and injector device 84 inserted in the vapor line 31. If desired the injector may be so operated as to create sub-atmospheric pressure in the retort system 26, 24, and thus to additionally facilitate vaporization. The introduction of steam also has a desirable modifying action on the cracking treatment of the vapors in coils 81, 82, rendering the treatment less drastic and tending to reduce the production of free carbon and fixed gases, and to keep down the percentage of unsaturated products. Ordinarily the employment of substantially atmospheric pres-

sure in the retort system is satisfactory, however, and the description of the other operating conditions in the specific example of the process hereinabove given is based on the assumption that substantially atmospheric pressure is used. It is of course feasible to carry out the digestion under superatmospheric pressure; and indeed this is desirable when a lighter digestion oil such as kerosene is employed. Details of such operation and of suitable apparatus for the purpose are given in my prior application Serial No. 345,485.

The cracking or superheating coils 81, 82, are enclosed in suitable furnaces or retort structures 85, 86, heated by gas burners 87, or the like. Any tarry materials collecting in the superheating coils may be trapped off through connections 88 into pipe 89 discharging into a collecting tank 90. Heavy liquid products collecting in tank 90 may be drawn off through 91 and utilized in any desired manner. For example, they may be introduced into the digester system to serve as a part of the heavy digestion oil for treatment of further portions of shale.

In practice, the temperatures in the superheater coils 81, 82, may attain 900° or 1000° F., or may even be as high as 1300° F. in some cases. The vapors may be under a pressure of, say, from 10 to 30 pounds or thereabouts in the coils, the pressure being controllable in part by the injector. By this treatment, the heavier portions of the volatilized oil fractions undergo to a great extent a cleaving or cracking action resulting in the production of valuable lighter fractions, particularly of the gasoline type. The highly heated vapors leaving the superheater coil 82 are led by pipe 92 into a cooling and condensing system comprising in the present instance two sets of condensing and fractionating towers or chambers 93, 94, and 95, 96, which may be of the Feld type. While the system is here shown as comprising four towers or chambers it may of course comprise as many of these as may be necessary to produce the particular fractions desired. By proper arrangement of these towers, and suitable adjustment of the operating conditions, heavier fractions such as lubricating oils and heavy kerosenes may be condensed in towers, 93, 94, respectively; while lighter fractions, including light kerosenes and gasolines condense and collect in towers 95, 96. The several fractionating towers are provided with draw-off cocks 97, as shown. The condensates obtained in one or more of the towers at the head of the series may be refrigerated and high melting paraffin wax crystallized and pressed therefrom.

I have found it desirable to subject the light kerosene and gasoline vapors passing on beyond tower 94 to a washing treatment prior to their entry into tower 95. In the

present example, the vapors leaving tower 94 pass down through pipe 98 which dips below the surface of water 99 contained in a wash tank 100. This treatment removes resinous and tarry matters which would tend to discolor succeeding condensed oil fractions. A part of the kerosene may also collect in this wash tank as indicated at 101, and may be drawn off through cock 102. After bubbling through the water in the wash tank, the residual uncondensed washed oil vapors leave the wash tank through pipe 103 and are led through the succeeding towers 95, 96, where the lighter kerosenes and gasolines are condensed and recovered as already described, the very small proportion of extremely light vapors and so-called fixed gases leaving the system through valved outlet 104. Such gases may be used for firing the superheater retorts or may be otherwise suitably disposed of. If desired, the heavier fractions obtained from the condensing and fractionating tower system may be employed wholly or in part as digestion oil in the digester system.

Where for any reason it may be desirable or necessary to condense directly any part or all of the vaporized oil fractions leaving the digester system through oftakes 30, rather than to pass such vapors to the superheaters as above-described, this may be effected by by-passing all or any portion of such vapors through pipe 105 to a condenser 106 which discharges into a receiver 107, provided with a draw-off cock 108. In such by-passing operation, valve 109 in the vapor line 31 and valves 110 in the by-pass are of course adjusted as may be necessary to properly direct the flow of oil vapors to the condenser 106. Where desired, liquid condensate in any desired proportion may be run from receiver 107 through valved pipe 111 into the downwardly sloping portion of vapor line 31 and carried by the steam injector 84 into the superheating retorts 81, 82, to undergo superheating and cracking treatment.

In some cases, it is of advantage to filter or dephlegmate the oil vapors evolved in the preheating reservoir 26 and the digester 24, before passing them either to the superheating and refining system or to the condenser 106. To this end I may provide each vapor oftake of each of the retorts 26, 24, with vapor-filtering or dephlegmating means of any suitable type. Most desirably the novel arrangement illustrated in Fig. 2 is employed, where the retort R has its vapor oftake connected by a T-pipe 112 and branch vapor pipes 113, 114, to duplicate filter chambers 115, 116, which are in turn connected in parallel by pipes 117, 118, to T-pipe 119, said pipe 119 leading into vapor line 31. By properly setting shut-off valves 120, vapors from R may be directed through either of the filter chambers or dephlegmators at will, so that either may be temporarily idle for clean-

ing out or repairs without interrupting continuous operation. Each chamber is provided interiorly with a transverse foraminous tray or screen 121, upon which is supported a bed 122 of a porous absorptive filtering medium such as sandy or granular fuller's earth, shale ash, coke, or the like. The steam injector 83, 84, can be operated to pull the oil vapors through such material even though it be in relatively fine condition. The effect is to strain out tarry and imperfectly vaporized matter that is mechanically carried by the vapors leaving the retort, thus aiding to prevent clogging of the superheating and condensing systems to which vapor pipe 31 leads and also improving the quality, color, and odor of the oil fractions recovered. When the filter bed of the particular dephlegmator in service at any given time becomes saturated or appreciably clogged, the flow of vapor may be switched to the other dephlegmator by reversing the setting of the valves 120, and the filter-bed of the first may then be cleaned out or renewed. For example, the filter bed may be washed by means of a suitable solvent introduced at 123 and drained off at 124; while through door 125 the spent filtering medium may be removed, and through door 125^a fresh filtering medium may be charged in. In order to prevent undue drop in the temperature of the vapors in passing through the dephlegmator apparatus, the latter should be covered with suitable heat insulating material, as should also other piping and parts of the complete digester and refiner system at all points where it is desirable to prevent loss of heat units. In addition to the valves specifically referred to in the foregoing description, other valves, indicated conventionally on the drawings, are provided in the piping connections wherever necessary or convenient to enable ready control and direction of vapor or liquid flow in all parts of the system.

Instead of employing the heavy oil from the shale, or other stripped oil, for digestion, it is also feasible to use crude petroleum for this purpose; and in some cases this offers important advantages. Where crude petroleum is used, it undergoes stripping and partial fractionation in the digester and preheater system, 26, 24, while at the same time providing the digestion bath.

The accompanying table (Fig. 3) gives comparative results obtained by treating a number of representative air-dry shales by the process of the present invention and by the usual Scotch destructive distillation method, respectively. This shows in a striking manner the superiority of the present process both as regards quantity and quality of yield. It will be noted that in all cases the total yield attainable by the present process is much greater than that by the old method, amounting to several times as much

in some instances. The table also shows the hygroscopic and constitutional moisture content characterizing the shales in question.

5 The superior results attained in practicing the present invention, as compared to former methods, are apparently attributable to the systematic progressive opening up of the bituminous contents of the shale in such manner as to avoid excessive and localized heating, which latter produce large quantities of free carbon and fixed gases and which are impossible to avoid in the usual methods heretofore in vogue. The products obtained by the present process are practically wholly hydrocarbon oils and the like, commonly amounting to as high as 85 to 95 percent of the hydrocarbon content of the original shale; whereas by the old practice of straight destructive distillation, large quantities of free carbon or coke and fixed gases are inevitably produced, the yield of oil being thus only about 15 to 33 per cent of the hydrocarbons of the original shale and being otherwise disadvantageously affected. Prior proposed modifications of the straight distillation method, involving initial treatment of shale to some extent with a solvent, are also subject to similar drawbacks.

30 While certain preferred forms of my novel process and apparatus have been hereinabove described, it is to be understood that these are for purposes of explanation and illustration merely, and are not intended as restrictive.

35 What I claim is:

1. The process of obtaining valuable products from bituminiferous solid matter of the character described which comprises digesting finely divided bituminiferous solid matter with a suitable oil, and centrifuging the digested mixture, without substantial cooling, to separate it into solid and liquid portions.

45 2. The process of obtaining valuable products from bituminiferous solid matter of the character described which comprises digesting finely divided bituminiferous solid matter with a heavy oil, and centrifuging the digested mixture, without thinning and at a temperature at which the mixture is readily fluent, to separate it into solid and liquid portions.

50 3. The process of obtaining valuable products from bituminiferous solid matter of the character described, which comprises digesting such bituminiferous matter with heavy oil in a digester at temperatures above 500° F. but not substantially exceeding 700° F., centrifugally separating oil from the digestion residue without substantial reduction in temperature, and returning separated oil to the digester while still hot.

65 4. The process of treating solid bituminiferous mineral matter, especially shales and the like, having wax constituents, which

comprise digesting a mixture of such mineral matter with an oil at a temperature above 600° F. below the normal vaporizing temperature of said wax constituents while agitating the mixture, subjecting the mixture to the action of a gaseous carrier medium to effect vaporization of such constituents, and recovering waxy products from the vapors evolved.

70 5. The process of obtaining valuable products from bituminiferous minerals of the character described especially shale and the like, which comprises subjecting such a mineral in the presence of an oil to an abrupt rise in temperature to a point at which a portion of the bitumen content of said mineral is vaporized, and subsequently destructively distilling a residual portion of said mineral to recover additional bituminous matter therefrom.

85 6. Apparatus for treating shale and other bituminiferous solids which comprises, in combination, a digester provided with heating means and stirring means and vapor off-take means, an oil preheater arranged to supply hot oil to said digester, means for feeding comminuted solids into said digester, and a centrifugal separator arranged to receive digestion mixture from said digester and to discharge separated oil to said preheater.

90 7. Apparatus for treating shale and other bituminiferous solids which comprises, in combination, a digestion chamber adapted to contain an oil bath and provided with vapor off-take means, means for charging shale into said chamber, a distilling retort, means for separating residual solid matter from the digestion mixture and delivering such solid matter to said retort, vapor-offtake and condensing means connected to said retort, and means for conducting condensed oil from said condensing means to said digestion chamber.

In testimony whereof I hereunto affix my signature.

WM. HUNTLEY HAMPTON.

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