

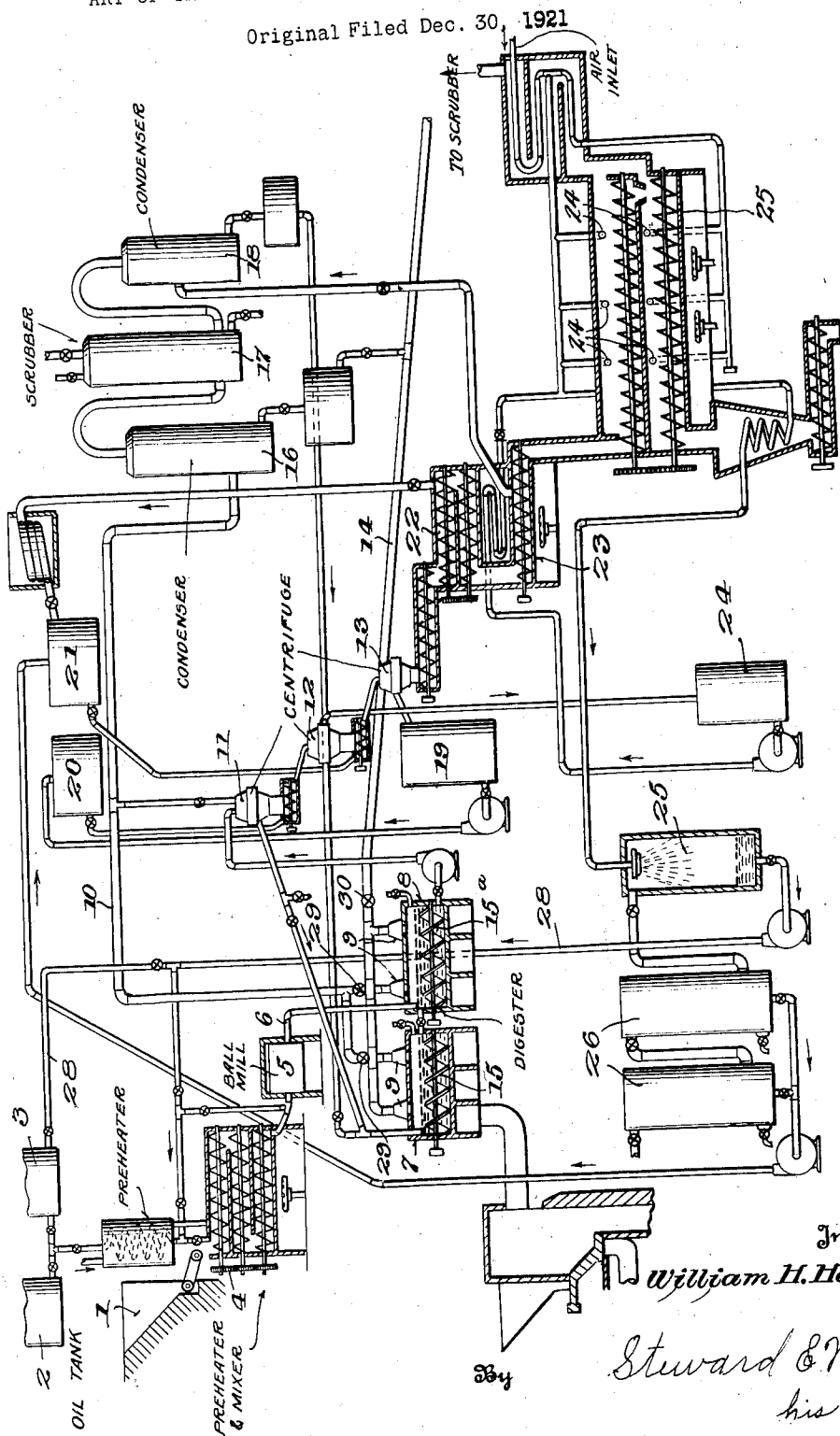
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W. H. HAMPTON

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ART OF TREATING SHALE AND OTHER BITUMINIFEROUS SOLIDS

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Inventor

William H. Hampton

Steward & McKay
his Attorneys.

UNITED STATES PATENT OFFICE.

WILLIAM HUNTLEY HAMPTON, OF PORTLAND, OREGON.

ART OF TREATING SHALE AND OTHER BITUMINIFEROUS SOLIDS.

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This invention relates to art of treating shale and other bituminiferous solids; and in particular the invention has to do with the digestion of shale or the like with a heavy mineral oil, in intimate mixture with a relatively small proportion of an added ammonia-liberating base, such as caustic lime, under conditions of temperature such that complex nitrogen compounds present in the bituminiferous mineral are decomposed at least to a substantial extent with liberation of ammonia which can be recovered by suitable means concomitantly with recovery of valuable hydrocarbon oil fractions vaporized during the digestion process, while at the same time sulfur present in reactive condition is bound or fixed and its evolution as hydrogen sulfid and analogous undesirable volatile sulfur compounds is substantially suppressed.

In prior copending applications Ser. No. 318,833, filed August 20, 1919, Ser. No. 344,016, filed December 11, 1919, Ser. No. 345,485, filed December 17, 1919, Ser. No. 431,188, filed December 16, 1920, I have disclosed and claimed methods of treating shale and other bituminiferous solids by digesting the same in finely divided condition and in fluid admixture with a relatively heavy mineral oil at temperatures preferably ranging from about 600° to 700° F., and recovering hydrocarbon oil fractions vaporized during the digestion, the residual solid mineral matter remaining after the digestion being then most desirably separated from the accompanying unvaporized oil and bitumens and subjected to destructive distillation for recovery of hydrocarbon products from such bituminiferous matter as may have resisted the liquefying and resolving action of the digestion oil. The process thus briefly outlined has proved thoroughly successful but in carrying the same out in practice I have now found it especially advantageous to introduce certain modifications that achieve and increase the efficiency and economy of the process and otherwise favorably affect the results attained. The bitumens present in oil shale and like mineral matter practically always contain appreciable percentages of nitrogen in complex combination. Sulfur may also be present either in organic or inorganic combination, or both. The nitrogen exists partly in combination with hydrogen and carbon, and sometimes also with sulfur, in the form of amido or amido-sulfur compounds.

Under the conditions of digesting shale

with oil in accordance with the procedures disclosed in my prior applications aforesaid, practically none of the nitrogen existing in these complex forms is liberated as ammonia during digestion. The oil fractions vaporized during digestion and recovered as condensates, as well as the residual unvaporized body of oil comprised in the digested mixture, contain nitrogen compounds; and so does the residual solid bituminous matter that has resisted or escaped the breaking-down action of the hot oil bath. The nitrogen compounds present in the various oil fractions cause the oils to darken upon standing and to deposit resinous asphaltic substances insoluble in oils but soluble in certain solvents such as alcohol or benzol. The aforesaid residual solid bituminous matter, upon separation from the digestion mixture and destructive distillation, yields ammonia in free or available form due to pyrogenic decomposition of the bituminous content.

The sulfur content of the original shale or other bituminiferous mineral treated may be present as a constituent of or associated with bitumen complexes, in which form it is highly detrimental because it is largely reactive at the digestion temperatures in question and is evolved as hydrogen sulfid or analogous volatile sulfur compounds when digested at 670° to 700° F. under the conditions of operation set forth in my prior applications aforesaid. On the other hand, sulfur present in the form of iron pyrites, which are carried by some shales, is not evolved during digestion, iron pyrites being substantially inert at the temperatures of digestion. Similarly stable compounds such as sulfates are not affected.

It is therefore a principal object of the present invention to so conduct the digestion treatment of the shale or other bituminous mineral as largely to break down the nitrogen complexes present and to liberate ammonia which can be recovered as a valuable by-product separately from the oil fractions vaporized during digestion, at the same time avoiding formation and deposition of resinous substances of the character above mentioned not only in the lighter oil fractions but also in those not vaporized during digestion. A further object is to bind or fix reactive sulfur in such manner as to suppress its liberation as hydrogen sulfid or in other volatile form while at the same time purifying the hydrocarbon oils produced by the process.

Other objects and advantages of the inven-

tion will become apparent as the description proceeds.

The accompanying drawing shows diagrammatically one system of apparatus for carrying out the novel process.

I have found that the objects of the invention are attained by carrying out the digestion treatment in the presence of a suitable proportion of a base that will react under the conditions of digestion to liberate nitrogen as ammonia, either wholly or to a substantial extent, from the combinations in which it occurs in the mineral; and that will also react to bind reactive sulfur present. Any base capable of reacting to attain these results, can be utilized within the broad scope of the present invention; but for practical purposes it is found advantageous to employ lime as the basic reagent in question, and especially to employ caustic lime (CaO), the hydrated form being usually much less effective. The exact quantity of lime or other basic reagent to be employed in a given instance naturally depends upon the proportions of nitrogen and sulfur contained in the shale in a form which they will react with such base. With the average shale, an addition of 1 to 2 per cent by weight of caustic lime is ordinarily sufficient to accomplish the purposes in view; and it is a very exceptional shale that requires as much as 5 per cent to achieve the results sought.

In order to secure the best results in carrying out the invention, it is of great importance to ensure that the caustic lime or other basic reagent is brought into proper reacting relation with the shale. For maximum effectiveness, both the shale and the lime should be finely pulverized and very intimately commingled. This is best accomplished by grinding the lime and shale together, the shale having been previously dried if necessary so that the lime undergoes little or no hydration during the mixing or blending operation. In a particularly desirable way of accomplishing this grinding in practice, the shale which has been previously coarsely comminuted by rough crushing, is delivered, together with the necessary amount of added caustic lime, from the bin 1 into the agitating means shown at 4. The heavy oil to be used in the digestion mixture is supplied from the tank 2. The mixture is stirred and preheated to say 300° or 400° F., at which temperatures the shale becomes comparatively soft and friable and is thus in particularly favorable condition to undergo fine grinding in suitable grinding machinery, whereas without such preheating it is very much more difficult to pulverize. The mixture thus prepared and preheated as described may be run into a ball mill or other suitable grinding device 5 and the solid constituents of the mixture reduced with comparative ease to a fineness such that substantially all of the solids

will pass a 100-mesh screen, and in practice it is found desirable that the grinding or pulverizing be continued until 60% or more of the solids will pass 200-mesh. This treatment achieves a most intimate commixture of the caustic lime with the bituminous mineral, thereby favoring efficient reaction of the lime upon the decomposable nitrogen compounds of the mineral during the subsequent digestion with liberation of ammonia on the one hand, and binding of reactive sulfur as calcium sulfid (CaS) on the other. Furthermore, fine grinding effectively exposes the refractory bitumens of the shale to the liquefying and decomposing action of the heavy digestion oil.

The oil used for the digestion bath may vary considerably in character but it should desirably consist wholly or in substantial part of oil fractions that do not vaporize extensively at or below 700° F. In starting operations, this oil may be a stripped oil, a grade of steam cylinder stock known commercially as Congo cylinder oil being suitable, for example. After the process has been operating for a sufficient period, the digestion oil used may be the heavier fractions of oil derived from the shale itself, said oil being supplied through pipe 28 and tank 3. In some cases it is advantageous to employ crude petroleum for making up the digestion bath. The amount of heavy oil so commingled with the shale and lime may vary considerably depending upon the character of the particular shale to be treated. In the case of a typical Colorado shale that normally yields about 30 gallons of oil per ton by the ordinary Scotch distillation method, mixing about one volume of heavy oil with two volumes of crushed shale gives good results. Richer shales require relatively less heavy oil, and leaner shales more. The quantity of caustic lime used is advantageously somewhat in excess of that theoretically required to effect the desired ammonia liberation and sulfur fixation, especially since the breaking down of some of the oxygenated bitumens during the digestion apparently effects hydration of the lime to some extent and thus reduces its activity at this stage of the process, although this hydration is of advantage at a later stage, as will hereinafter be pointed out. As a rule, the use of two per cent by weight of caustic lime, figured on the weight of the shale, is sufficient, and in many cases one per cent is enough.

The finely ground mixture prepared as above described and of slurry-like consistency, is led through pipe 6 into the digester means shown at 7 and 8. The temperature of digestion should be high enough to bring about the desired liquefaction and breaking down of the shale bitumens in the oil digestion bath. At the same time the temperature should not be allowed to go high enough

to cause the far-reaching decomposition of the oil hydrocarbons with deposition of free carbon and formation of coke which characterizes what is commonly termed "cracking".

5 In practice it is found desirable to maintain the digestion bath at above 500° F., a range of from 600° to 700° F. being suitable, and the optimum range being about 680° to 700° F. The fluid mass should also be thor-
10 oughly agitated continuously throughout the digestion to cause constant rubbing of the mineral particles upon each other and thus expose fresh surfaces to the hot oil bath. It may be noted here that the action of the
15 hot oil bath on the shale bitumens is not merely a liquefying or solvent action, but involves a chemical breaking down and decomposition of said bitumens into lighter products. The heavy oil added to the shale
20 in making up the digestion mixture is also in its turn broken down to yield lighter products, due apparently to chemical interaction between said oil and the shale bitumens under the conditions of digestion.

25 During the digestion, ammonia is liberated and is conducted with the oil vapors and the steam generated in the reaction, through vapor oftakes 9 into vapor line 10. No sulfuretted hydrogen is evolved the reactive sulfur
30 being bound by the lime. The oil vapors may be fractionally condensed as shown at 16 to produce commercial distillates and the ammonia scrubbed out at 17 or otherwise recovered according to known methods. The
35 unvaporized portion of the digestion mixture is treated, as by centrifuging at 11, 12 and 13, or by dilution with a lighter oil and sedimentation, to separate residual solid matter or "tailings", the oil separated from such
40 tailings being amenable to treatment for production of valuable lubricating oils, for example. When treating the unvaporized portion of the digestion mixture by the centri-
45 fuging process just mentioned the continuous flow of wash oils is supplied to the successive centrifuging units by means of the tanks 19, 20, 21 and 24, together with the circulating pumps and flow pipes. In this
50 manner, the heavy oils and other bitumens adhering to the tailings discharged from the separators are completely washed out. The wash oil from the first unit 11 is returned to the digester 7; that from the third unit 13
55 is returned through 19 to the tank 20; while that from the second unit 12 passes through 24 and is separated into its light and heavy constituents by circulating through retort 23, towers 25 and 26, the respective fractions
60 being returned to the tanks 21 and 3. The oils, both heavy and light, obtained as described, have much less tendency to darken in color, and remain much clearer than when lime is not added to the mixture. Moreover they do not deposit resinous matter upon
65 standing.

If it is desired to subject the vapors leaving the retort system 7, 8, to further cracking to obtain a high yield of gasoline products, the valves 29 are closed and valve 30 opened and the vapors are delivered through vapor
70 line 14 to suitable superheating coils as described in my previous application, Serial No. 431,188. The ammonia may similarly be recovered in such a system by the usual
scrubbing means.

75 It should be noted that carbonates of lime and magnesia, which are often carried by shales, do not function usefully in the present process and do not produce the results
80 sought.

The digestion can be carried on in any
suitable digester as at 7 and 8 equipped with
stirring means 15 and 15*, and provided with
vapor oftakes 9 leading to a condenser system 16 and 17. The stirring means may ad-
85 vantageously serve to advance the fluid digestion mixture in a systematic manner from a point of feed to a point of discharge. Apparatus of this general type being known
90 in the art, no detailed description thereof is necessary here.

The residual solids or tailings from the digestion having been washed successively with a light oil in the centrifugal separators and
95 dried, while passing by means of screw conveyors through the drier 22, may be destructively distilled in retort 23 to obtain further hydrocarbon oils from such bituminous matter therein as resisted or escaped the action
100 of the hot oil bath, and also to obtain more ammonia. The character of the tailings is such that this can be effected at temperatures ranging from 700° F. initial to 900° F. final, the final temperature being obviously much
105 lower than is required in the Scotch process. This is because the prior digestion has rendered the residual bitumens less refractory and more amenable to heat treatment. As regards the ready liberation of ammonia, the
110 partially hydrated lime serves to supply the steam needed at the higher temperatures of destructive distillation to aid in the ammonia-forming reactions. It is to be noted in this connection that as a result of the prior
115 digestion the lime is present in peculiarly intimate commixture with the residual solids and can thus react most effectively. The distillation is carried to coke, the hydrocarbons driven off being condensed in tower 18 and the ammonia recovered in the scrubber 17.
120

The total yield of oils from shale treated by the method hereinabove described is far greater than by the ordinary Scotch destructive distillation of raw shale, and the ammonia recovery is also larger and is obtained
125 at much lower temperatures.

The invention has been described more particularly with reference to treatment of bituminous shale, for the sake of a concrete
130 example illustrating the broad principles in-

volved and also because the invention at present finds its most important practical application in that field. Moreover, the treatment of shale is a problem distinct from the treatment of other bituminiferous solids owing to the peculiarly refractory and resistant character of the bitumens contained in shale which has baffled many attempts to extract said bitumens by means of solvents. However, the principles of the invention are also applicable to other bituminiferous solids such as coals, peat, lignite and the like, which can to advantage be commingled in finely divided condition with lime and a heavy oil, digested as before described, and the tailings destructively distilled to coke, the process yielding valuable hydrocarbon oil fractions, ammonia and coke by the rational and relatively low-temperature treatment set forth.

In the treatment of shale and peat, where the coky residue from destructive distillation of the tailings is usually of too low calorific value for direct use as fuel, there may be a third stage in the ammonia recovery, as follows: The fixed carbon of the aforesaid coky residue, and whatever carbon compounds have survived the final heating to 900° F., are in highly active condition at the close of the distillation and will take fire readily if exposed to air. By admitting such air through inlets or tuyères 24 into contact with the coky residue in regulated quantity in retort 25, partial combustion may be effected whereby the temperature is considerably raised and further ammonia liberated and recovered. By proper control of the air admission, a type of producer gas can also be obtained.

What I claim is:

1. In the treatment of solid bituminiferous mineral matter to obtain valuable products therefrom, the process which comprises heating such bituminiferous matter in intimate fluid commixture with an ammonia-liberating base and a mineral oil at temperatures not substantially exceeding about 700° F., and recovering volatilized products.

2. In the treatment of solid bituminiferous mineral matter to obtain valuable products therefrom, the process which comprises digesting, at temperatures not substantially exceeding about 700° F., such bituminiferous matter in finely divided condition and in intimate fluid commixture with finely divided caustic lime and a mineral oil, and recovering volatilized products.

3. In the treatment of solid bituminiferous mineral matter to obtain valuable products therefrom, the process which comprises heating such bituminiferous matter in intimate fluid commixture with an ammonia liberating base and a mineral oil at temperatures not substantially exceeding about 700° F., the mixture being agitated and maintained fluid throughout the digestion, recovering volatilized products during digestion, separating

residual solid matter from the still fluid mixture after digestion, and distilling such separated solid matter to coke with recovery of distillate.

4. The process as defined in claim 3 further characterized by conducting the coking distillation at temperatures from about 700° F. up to about 900° F.

5. The process as defined in claim 3 further characterized by subjecting the resultant coke, without cooling, to controlled combustion, and recovering ammonia from the combustion gases.

6. The process of treating solid bituminiferous mineral matter to obtain valuable products therefrom, which comprises digesting an intimate commixture of such bituminiferous matter and an ammonia liberating base, both in finely divided condition, in a mineral oil bath, at temperatures above 500° F. but not substantially exceeding 700° F., and recovering volatilized products.

7. The process of treating solid bituminiferous mineral matter to obtain valuable products therefrom, which comprises digesting an intimate fluid commixture of finely divided bituminiferous matter and a finely divided ammonia liberating base with a heavy mineral oil, at temperatures within the approximate range of from 600° to 700° F., to liberate ammonia and volatilize certain hydrocarbon oil fractions.

8. The process of treating solid bituminiferous mineral matter to obtain valuable products therefrom, which comprises digesting a finely ground mixture of such bituminiferous matter and not exceeding about 5 per cent of its weight of caustic lime with a heavy mineral oil at temperatures approximating 680° to 700° F., to liberate ammonia and volatilize certain hydrocarbon oil fractions.

9. The process of treating solid bituminiferous matter of the shale type, to obtain valuable products therefrom, which comprises digesting an intimate mixture of such bituminiferous matter and an ammonia liberating base with a mineral oil at temperatures sufficiently high to liberate ammonia but insufficiently high to cause substantial deposition of carbon, and also recovering valuable hydrocarbons from said mixture.

10. The process of treating solid bituminiferous matter of the shale type, to obtain valuable products therefrom, which comprises finely grinding together such bituminiferous matter and lime, digesting the ground material at temperatures within the approximate range of from 600° to 700° F. with sufficient heavy mineral oil to provide a fluid digestion mixture, and recovering both liberated ammonia and volatilized hydrocarbons.

11. The process of treating bituminous shale or the like to obtain valuable products therefrom, which comprises preparing a mixture of pulverized shale or the like with caus-

tic lime and enough heavy mineral oil to give the mixture a fluid consistency, digesting said mixture with the aid of agitation at temperatures sufficiently high to liquefy a substantial portion of the shale bitumens but insufficiently high to cause substantial carbon deposition, said mixture remaining fluid during the digestion, recovering ammonia liberated and hydrocarbons volatilized during digestion, separating residual solid matter from the digestion mixture, and destructively distilling such separated solid matter.

12. The process of treating bituminous shale or the like which comprises heating and agitating a fluid mixture of finely ground shale, finely ground caustic lime and a heavy mineral oil, at temperatures above 500° F. but not substantially exceeding 700° F., and recovering liberated ammonia and volatilized hydrocarbons.

13. The process as defined in claim 12 in which approximately 1 to 2 per cent of lime is employed in the mixture.

14. The process as defined in claim 12 char-

acterized by the further steps of destructively distilling the residual solid matter from the digestion to obtain coke and further volatile matter including ammonia.

15. The process of treating solid bituminiferous mineral matter which comprises digesting such matter in finely divided condition, at temperatures above 500° F. but insufficiently high to effect substantial cracking, in admixture with mineral oil and a basic reagent capable of binding sulfur present in reactive state under the conditions of operation, and collecting a distillate.

16. The process of treating bituminous shale or the like which comprises digesting, at temperatures above 500° F. but not substantially higher than 700° F., a fluid mixture comprising finely divided shale, a heavy mineral oil, and a relatively small proportion of caustic lime, and collecting distillate from the digestion.

In testimony whereof I hereunto affix my signature.

WILLIAM HUNTLEY HAMPTON.