

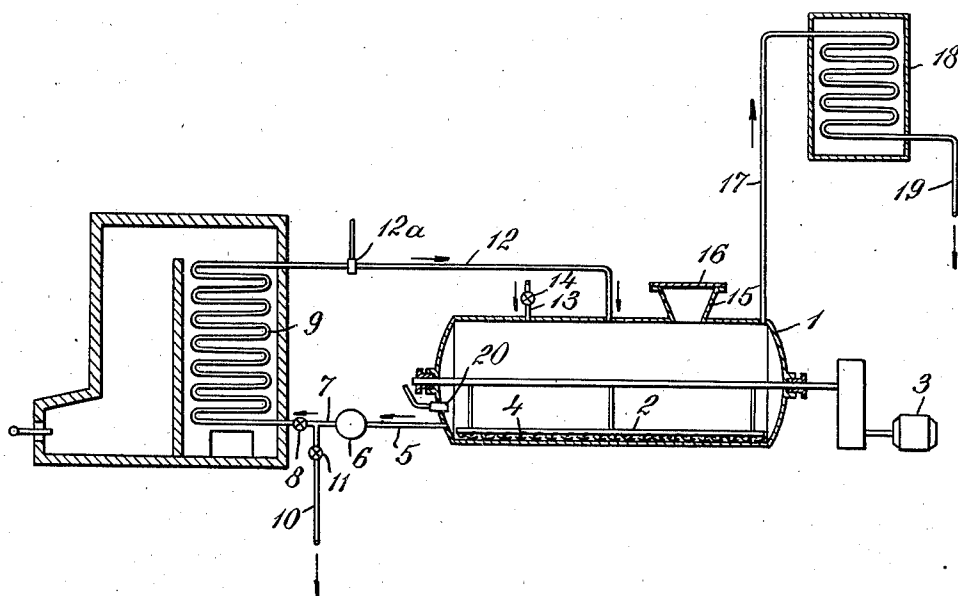
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METHOD FOR DIGESTING SOLID CARBONACEOUS MINERALS

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METHOD FOR DIGESTING SOLID CARBONACEOUS MINERALS

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This invention relates to the manufacture of heat-digestion products from carbonaceous mineral materials such as bituminous coal, cannel coal, shale, and the like under conditions such that a substantial but regulated amount of decomposition of the carbonaceous mineral materials takes place during the digestion.

In the past it has been proposed to prepare such products by introducing the mineral material into a tank containing a body of a hydrocarbon liquid, such as coal tars, high-boiling coal tar oils, and coal tar pitches, or various petroleum tars and oils, and then to heat the tank externally to bring the temperature of the mixture to between 300° and 400° C. Such processes were subject to the disadvantage that since a much higher temperature prevailed at the tank wall surfaces than in the body of liquid, solid material in contact with the surfaces was subjected to more intense heat-treatment than solid material at a distance therefrom and consequently overheating and even charring of the solid material occasionally occurred, and deposit of carbonaceous scale on the walls of the vessel resulted.

Moreover, successful operation of the digestion process requires careful control to effect the desired degree of decomposition of the mineral undergoing digestion, e. g. coal. It has been found that if the digestion is carried out so that no decomposition or only incipient decomposition of the coal occurs, products are obtained of a quite different nature from those desired. If, however, the time and temperature of digestion of a given coal are increased, a relatively sudden change occurs in the consistency of the product together with marked evolution of typical volatile coal-decomposition products and a reduction in the content of volatile combustible matter in the digested mineral.

Commercially desirable products are obtained by carrying the digestion to or beyond the point where these phenomena occur.

On the other hand, if the digestion temperature is too high, excessive decomposition occurs, and the products begin to lose their characteristic properties, such as relatively low susceptibility to temperature change, and approach ordinary pitch.

Accordingly it is essential to control the degree of decomposition of the mineral by controlling not only the time of digestion but the temperature to which it is subjected during digestion. Any process which subjects a portion of the digestion charge to overheating, to that extent

dilutes the desired and characteristic final product with material approaching ordinary pitch in character.

In order to overcome the disadvantages of the direct-fired tank-still process, it has been proposed to circulate the liquid hydrocarbon through a body of coal or other carbonaceous mineral material. In the process thus proposed the hydrocarbon liquid flowed in a circuit involving a heater and a digestion chamber, so that heating of the liquid was accomplished at a point out of contact with the main body of coal which it was desired to subject to the digestion treatment. This process was found to overcome the disadvantages of overheating, excessive decomposition and the formation of carbonaceous scale on heating surfaces. In operation of the process on a large scale, however, it was frequently found that after a run a varying percentage of the coal remained in the digestion chamber in a partially digested condition. Since the properties of the desired product depend to a considerable extent on the content of digested coal, this had two disadvantages:

(1) The properties of the product of the original batch could not be accurately predicted because its digested-coal content was the difference between the coal introduced (less volatile decomposition products) and the varying residue in the digester, and there was no way of determining accurately beforehand the proportion of the coal that would remain as residue;

(2) In formulating succeeding batches it was impossible to make allowance for the varying residue in the digester, part of which would be dispersed in each following batch, for there was no ready means for measuring or weighing the residue in situ.

Still another disadvantage encountered lay in the fact that the partially digested coal possessed a semi-liquid, livery, or jelly-like character such that it formed a more or less resistant protective coating on fragments of undigested coal, and contact of liquid therewith was diminished. As a consequence the digestion was appreciably prolonged.

While the above discussed disadvantages are not of a nature to make the process unworkable, they lead to products of widely variant properties and make it uneconomical for producing products to close specifications.

In accordance with the present invention it has been found that the desired degree of decomposition of the carbonaceous mineral can be effected, while the disadvantages of both the direct-fired

tank-still digestion and the method involving circulation of liquid hydrocarbon through the carbonaceous mineral may be eliminated, by subjecting the mineral in a finely divided condition to heating while suspended in a turbulent stream of the liquid. This is accomplished by mixing the finely divided mineral with the hydrocarbon liquid and passing the mixture at a velocity above its critical velocity through a tubular heater or equivalent heating device.

By the process of this invention it is possible to prepare compositions, suitable for use as paving compositions, road binders, block fillers, roofing compositions, water-proof paints, etc., possessing not only a high degree of uniformity throughout a particular batch but having a minimum of variation between batches.

Apparatus for conducting the process of the present invention is illustrated in the accompanying drawing.

The numeral 1 designates a tank for mixing the carbonaceous mineral material and the liquid hydrocarbon. An agitator 2, driven by motor 3, may be provided for stirring the contents of tank 1. The agitator 2 may be provided with a drag chain 4 for cleaning the walls of the tank, if desired, especially if the tank is arranged with external heating means (not shown) to bring it to reaction temperature. The agitator may either rotate or oscillate, as desired. A pipe 5 leads from tank 1, near the bottom thereof, to pump 6. From pump 6 a pipe 7, having a valve 8, leads to a tubular heating coil 9 arranged to be heated by hot combustion gases. An outlet pipe 10 having a valve 11 is disposed on pipe 7 between the pump and the heating coil. A return line 12 leads from the heating coil back to tank 1. This line is provided with thermometer well 12a for observation of the temperature of the liquid passing therethrough. To avoid formation of vapor bubbles in tubular coil 9, the pipe 12 may be constricted at its entrance to tank 1 thereby maintaining a higher pressure in the coil than in the tank and causing vapors to be "flash" distilled from the heated mixture as it enters tank 1. A greater than necessary constriction should be avoided since this merely serves to increase the power required for circulation.

Tank 1 has an inlet pipe 13 provided with a valve 14 for introducing hydrocarbon liquid and a hopper 15, which has a suitable closure 16, for the introduction of solid carbonaceous mineral matter. If preferred, a star valve or other suitable closure permitting introduction of solid material while avoiding escape of substantial quantities of vapors, may be provided in place of the simple closure 16.

A vapor pipe 17 leads from tank 1 to condenser 18 cooled by water, tar to be used in succeeding digestion, or another suitable cooling medium. Condensate outlet 19 leads to oil storage (not shown).

A thermometer well 20 is disposed in tank 1 to indicate the temperature of the liquid therein. The apparatus may be provided with the customary clean outs, traps, insulation, etc.

The above apparatus may be operated in the following manner:

8000 gallons of topped-tar-and-heavy-tar-oil-mixture having an initial boiling point around 200° C. are charged to tank 1 through inlet 13; valve 14 is then closed. Pump 6 is started as soon as enough of the mixture is introduced to keep the pump supplied. The mixture is circu-

lated through heating coil 9 and recirculated to the extent necessary to heat it to a temperature around 150° C. as indicated by the thermometer in well 20. Finely divided coal, having a particle size not over 0.3 cm. in diameter is then introduced at 15, the agitator being operated to mix the coal with the liquid contents of tank 1. When the desired amount of coal has been added, normally 5% to 45% of the tar-tar-oil-mixture, depending upon the type of product it is desired to produce, the temperature of the mixture in tank 1 may have risen to between 170° and 210° C. and the mixture leaving coil 9 may be at a temperature between 200° C. and 250° C. as recorded by the thermometer in well 12a. Agitation of the contents of the still and circulation of the tar containing suspended coal particles are continued until the desired maximum digestion temperature, usually somewhere between 300° and 320° C., is obtained.

For illustration a tubular heater containing 93 tubes each 2½ inches in diameter and about 8½ feet long connected serially by return bends was found to attain the desired temperature, measured from the time of completing the coal charge, in from 5 to 6 hours. The average linear velocity of the mixture (topped-tar- and heavy-oil-mixture plus 20% of coal particles of less than 0.3 cm. diameter) through the heater was 11 to 12 feet per second, as compared with a critical velocity for the mixture in this apparatus believed in the neighborhood of 1 foot per second. Since the critical velocities of the tar-coal mixtures of commercial importance at the digestion temperature are in the same neighborhood, it may be said that in general the average linear velocity of the mixture within 1¼ inch of the heating surface should be above 1 foot per second. This generalization, however, would not include those cases where turbulence is induced by use of surfaces other than heating surfaces or by use of heating tubes of substantially smaller than 2½ inch diameter or otherwise.

The temperature at 12a at the start may be 60° to 75° or more above that at 20. Fairly satisfactory products have been produced when the mixture has been permitted to absorb heat at about this rate throughout the process and it is possible to maintain a differential of as much as 100° between the temperatures at 12a and 20. However, it is preferred to avoid so high a temperature difference, at least near the maximum digestion temperature. It has been found that a temperature difference of about 20° makes the most satisfactory products.

For an apparatus of the above proportions handling an 8000-8500 gallon charge containing coal which undergoes the desired conversion at about 305° C., the temperatures measured by thermometers at 12a and 20, respectively may correspond as follows:

12a	20
Degrees	Degrees
225±25	190±20
270	230±20
300	280±10
310	290±10
313±3	305±5

The preferred low temperature difference toward the end of the reaction will be maintained automatically if the heating coil is heated by gases that are only a small degree hotter than

the maximum temperature to be attained by the mixture, for the gas-to-liquid temperature difference becomes radically less as the temperature of the liquid rises. In case the gases are at high temperatures on the order of 1000° to 2000° C. the reduction in heating effect as a consequence of reduced temperature difference will be small and to keep the liquid temperature down the liquid may be circulated at an increased rate or the heat supply may be reduced, as by diluting the combustion gases with air or cutting the flow of fuel. In this manner the maximum temperature of the liquid at 12a may be kept within 10° or 20° of the maximum liquid temperature in the tank as recorded at 20.

The following example illustrates the preparation of a coal-digestion product by the process of the present invention:

6889 gallons of a digestion medium consisting of topped high-temperature, bituminous coal tar and heavy creosote oil were charged to tank 1 as above described. The temperature was brought up to somewhat above 150° C. by circulating the tar-oil mixture through heating coil 9 by means of pump 6 from and to tank 1. While the mixture was being circulated, 18,671 pounds bituminous coal, ground to pass a 10 mesh screen, were gradually introduced into tank 1 and there agitated with the tar-oil mixture. The liquid flow through coil 9 was maintained at a constant average rate of 11.60 linear feet per minute during the digestion. Laboratory tests having previously been made to determine suitable digestion temperature for the coal in question to secure the desired degree of coal decomposition, heating and circulation were continued to bring the contents of tank 1 as recorded at 20 to 304° C. over a period of several hours; at the same time the heating of coil 9 was so controlled that the temperature indicated at 12a was at no time more than 100° C. higher than that indicated at 20, and was 315° C. when that at 20 had reached 304° C. The contents of tank 1 were held at 304° C. for an hour and then discharged. During the digestion volatile decomposition products of the coal and distillate from the tar-oil mixture passed off through pipe 17 and condenser 18, condensable constituents being condensed and passed to storage. The product produced in this manner had the following properties.

Melting point	-----°C.	70
Penetration at—		
0° (200 gms., 30 seconds)	-----	14
25° (100 gms., 5 seconds)	-----	30
46.1° (50 gms., 5 seconds)	-----	80
Slide test at 40° C. (7 hours, 30° angle, ½ inch cube)	-----inches	2½

I claim:

1. The method of producing from coal and petroleum tars, pitches of lower temperature susceptibility than ordinary tar pitches of the same melting point, comprising suspending finely pulverized coal in regulated amount in a liquid comprising tar, of the group consisting of coal tar and petroleum tar, or its distillation products,

which liquid is capable of forming pitch on distillation, agitating said liquid and mechanically suspended coal, recirculating said liquid and coal through a heating coil to effect the decomposition of the coal, and continuing the decomposition process until a pitch product of the desired melting point and temperature susceptibility is obtained.

2. The method of digesting bituminous coal in a coal-tar digestion medium, which comprises preparing a mixture of the digestion medium containing the coal suspended therein in finely divided form, withdrawing a portion of the mixture, passing a stream thereof while free from added reagents through a heating zone at a rate such that the average velocity of the mixture within one and a quarter inch of the heating surface is above one foot per second, returning it to the main body of the mixture and mixing it therewith, and continuing said operation only until the temperature of the main body of the mixture has reached but not exceeded a digestion temperature between 300° and 400° C.

3. The method of producing from tar, pitches of lower temperature susceptibility than ordinary tar pitches of the same melting point, comprising suspending finely pulverized coal in regulated amount in a liquid comprising bituminous coal tar or its distillation products, which liquid is capable of forming pitch on distillation, agitating said liquid and mechanically suspended coal, recirculating said liquid and coal through a heating coil to effect the decomposition of the coal, and continuing the decomposition process until a pitch product of the desired melting point and temperature susceptibility is obtained.

4. The method of producing from coal tar, pitches of lower temperature susceptibility than ordinary tar pitches of the same melting point, comprising suspending finely pulverized coal in regulated amount in a liquid comprising coal tar and creosote oil, which liquid is capable of forming pitch on distillation, agitating said liquid and mechanically suspended coal, recirculating said liquid and coal through a heating coil to effect the decomposition of the coal, and continuing the decomposition process until a pitch product of the desired melting point and temperature susceptibility is obtained.

5. The method of digesting bituminous coal in a coal-tar digestion medium, which comprises preparing a mixture of a digestion medium comprising bituminous coal tar and heavy creosote oil containing the coal suspended therein in finely divided form, withdrawing a portion of the mixture, passing a stream thereof while free from added reagents through a heating zone at a rate such that the average velocity of the mixture within one and a quarter inch of the heating surface is above one foot per second, returning it to the main body of the mixture and mixing it therewith, and continuing said operation only until the temperature of the main body of the mixture has reached but not exceeded a digestion temperature between 300° and 400° C.

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