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METHOD FOR REMOVING FINELY DIVIDED SOLID PARTICLES
FROM LOW TEMPERATURE CARBONIZATION TARS

Filed Dec. 22, 1958

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3,010,893

3 Sheets-Sheet 1

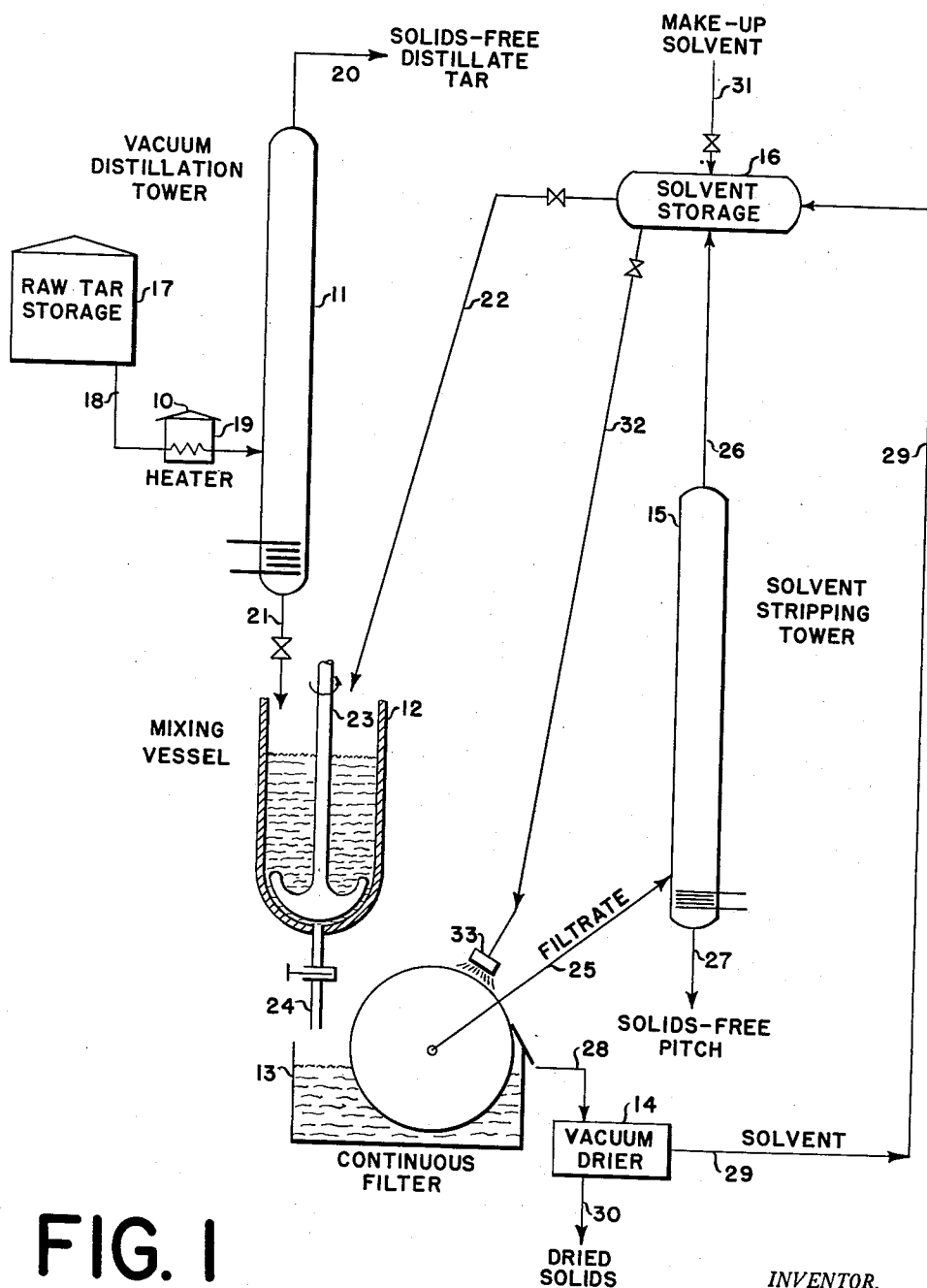


FIG. 1

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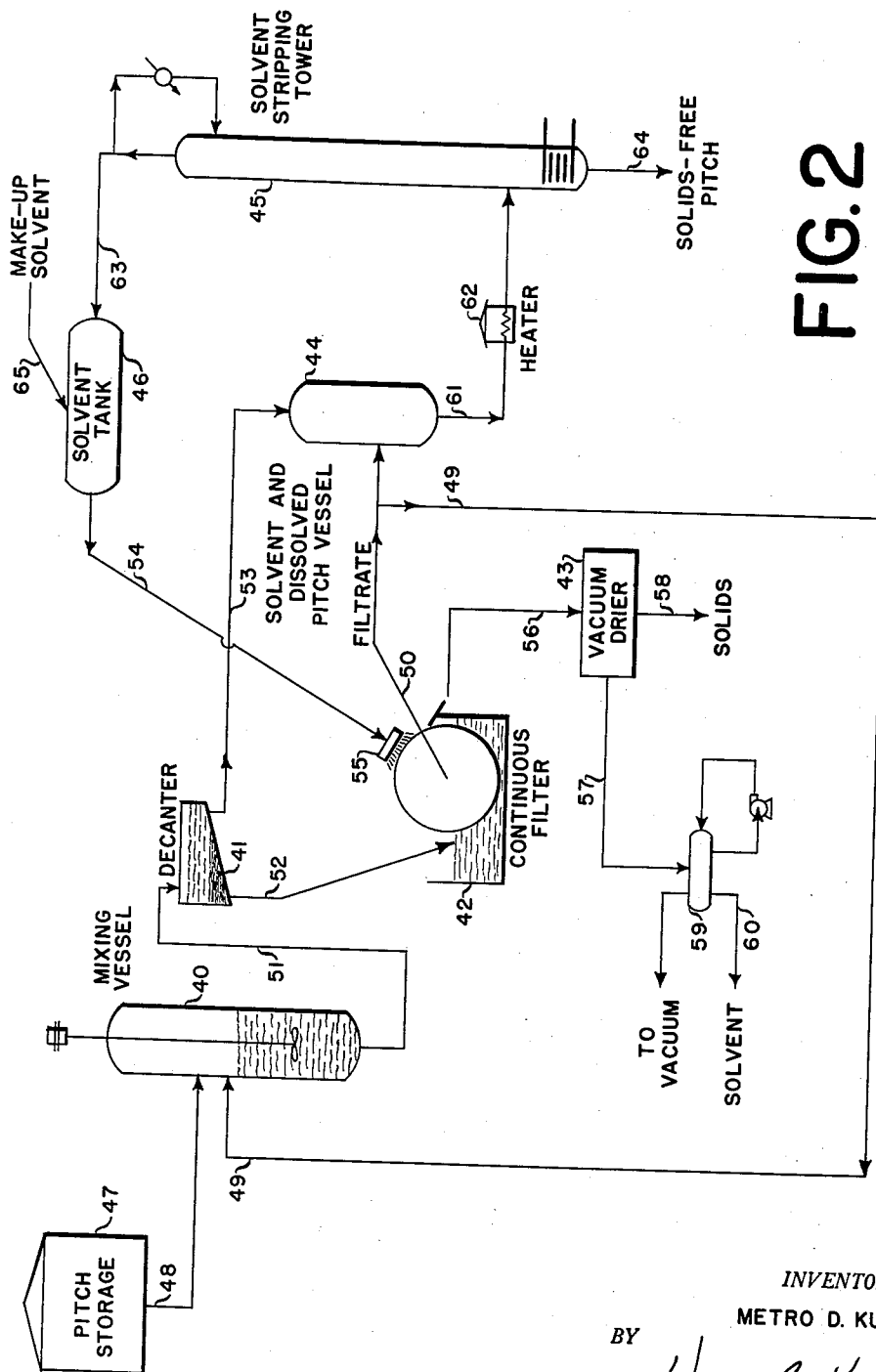
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3 Sheets-Sheet 3

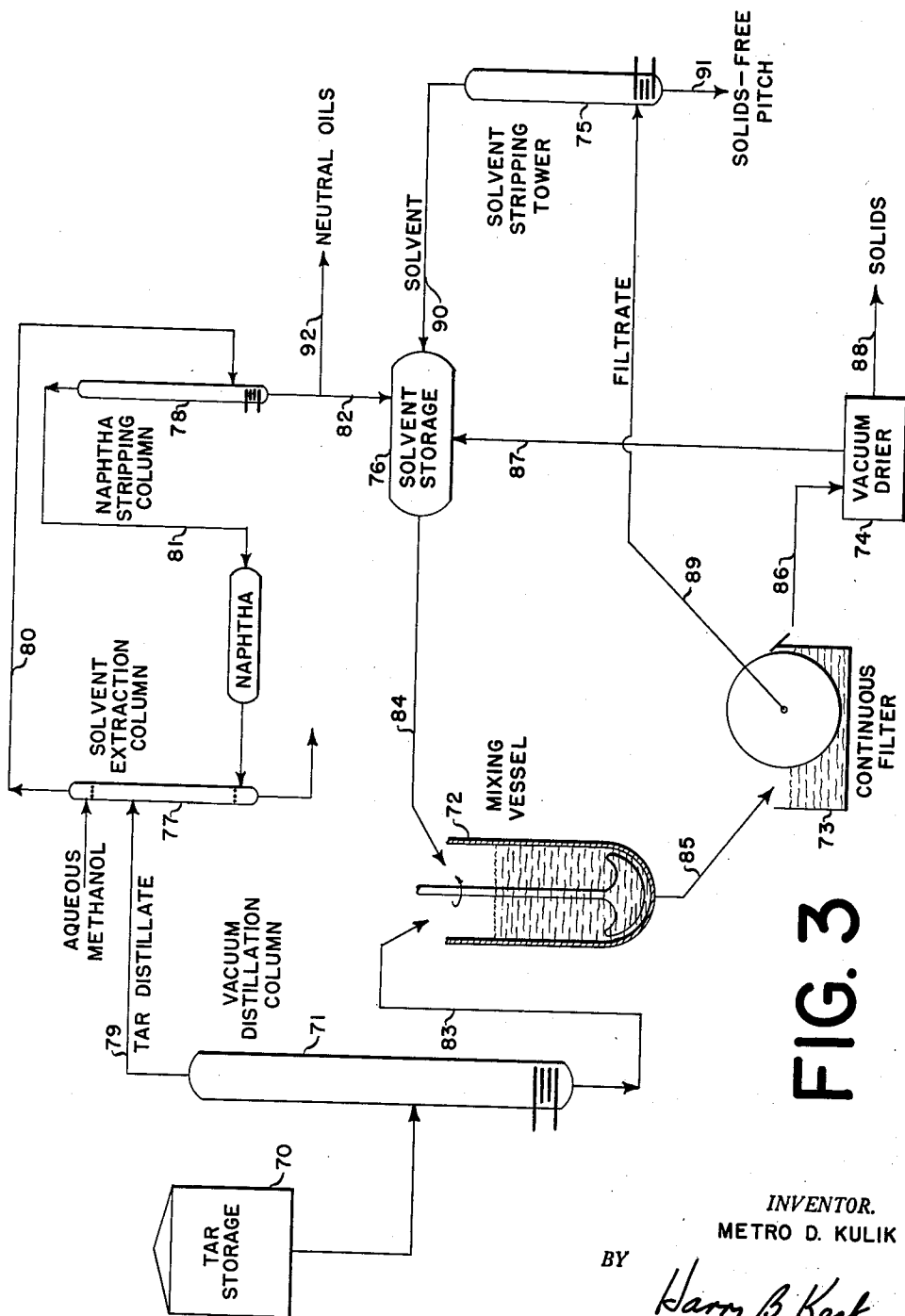


FIG. 3

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3,010,893

METHOD FOR REMOVING FINELY DIVIDED SOLID PARTICLES FROM LOW TEMPERATURE CARBONIZATION TARS

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18 Claims. (Cl. 208-8)

The present invention relates to a method for removing finely divided solid particles from tars obtained by low temperature carbonization of naturally occurring carbonaceous solid fuels, such as coal and lignite. More particularly, it is directed to removing such particles from the pitch residue obtained in the processing of the tar.

This application is a continuation-in-part of my copending application Serial No. 695,006, filed November 7, 1957, and since abandoned.

When bituminous coal is subjected to low temperature carbonization, i.e., below 1500° F., the product tar is collected as a vapor. Subsequent condensation of the vapors produces a highly viscous liquid tar product that is variously designated as raw, crude, unprocessed or unrefined tar. This condensed tar contains virtually all of the condensable ingredients in the carbonization vapors along with the finely divided particles of coal and partially carbonized coal entrained therein. Separation of these abrasive finely divided particles from the condensed tar cannot be accomplished by the usual mechanical separation techniques at ordinary temperatures (filtration, centrifugation, settling) because of the fine state of subdivision of the solid particles and because of the high density and viscosity of the liquid. At ordinary temperatures the low temperature carbonization tar is not free-flowing. At the elevated temperatures required to reduce the liquid viscosity to an operable value for the usual mechanical separation techniques, pressurized equipment is required to prevent loss of the lower boiling constituents of the liquid through evaporation. Even at the elevated temperatures (reduced viscosity), however, the usual separation techniques are inadequate since the extremely finely divided solid particles actually enter the interstices of conventional filtration equipment to blind the filter septum; the low apparent density of these particles prevents their separation from the viscous liquid through settling and resists even centrifugal separation.

Where the tar is obtained by fluidized low temperature carbonization, the difficulty is intensified for two reasons. First, the finely divided particles of coal and partially devolatilized coal contained in the tar are unusually small in size and are present in greater quantity because of the extremely turbulent conditions prevailing within a fluidized low temperature carbonization processing vessel. Second, the tars obtained from fluidized low temperature carbonization processes tend to be of a more primary character, i.e., the constituents tend to be closely related in structure to the constituents of the coal employed because there is little opportunity for cracking the constituents prior to recovery. Hence these tars tend to be more highly viscous than other types of low temperature carbonization tars.

Tars produced by low temperature carbonization of coal may contain up to twenty-five percent and more by weight of finely divided particles of coal and partially carbonized coal. Where these tars originate from fluidized low temperature carbonization processes, the suspended solid particles are almost universally capable of passing through a 325 mesh Tyler screen. The presence of these abrasive solids in the tar seriously reduces the value of the tar. Processing of the solids-laden raw tar for recovery of valuable liquid constituents by conven-

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tional processing methods such as distillation and extraction is difficult.

In U.S. Patent 2,774,716 I have disclosed a process for recovering these finely divided solid particles from raw low temperature carbonization tar by mixing the raw tar with a distillate fraction obtained from the low temperature carbonization tar itself and containing at least two percent by volume of tar acids. This process effects a selective precipitation of pitch constituents which combine with the finely divided solid particles to form larger agglomerates which can be filtered readily. This process proved adequate for treating most low temperature carbonization tars. However where tars obtained by fluidized low temperature carbonization are to be treated, the process permits filtration only at low rates that are commercially unacceptable.

In order to provide a method for removing the extremely finely divided particles of coal and partially carbonized coal from fluidized low temperature carbonization tars, I developed a solvent treatment process described in copending application Serial No. 515,647, filed June 15, 1955, now U.S. Patent 2,871,181. According to the process of the said copending application, I have provided a heating and cooling cycle which serves to form discrete agglomerate particles of sufficient size to permit rapid filtration. While this process provides the only known method for filtering the finely divided solids from fluidized low temperature carbonization tars at commercially desirable filtration rates, nevertheless, the requirements for heating and cooling the raw tar introduces expensive processing treatments.

Subsequently I discovered that if the freshly prepared raw tar obtained from a fluidized low temperature carbonization process is aged in storage at ambient climatic temperatures for about six months, it may be filtered at commercially acceptable rates by the process disclosed in my earlier issued U.S. Patent 2,774,716, previously mentioned. The heating and cooling cycle process described in my copending application Serial No. 515,647 appears therefore to be a type of artificial aging process.

It would appear that the aging of the freshly prepared raw tar, such as by storage for a period of six months, introduces some phenomena which render the raw tar more readily susceptible to treatment by the process described in U.S. Patent 2,774,716 (supra).

These phenomena may include polymerization of the tar, or oxidation of the tar, or flocculation of the suspended solids. Without attempting to define precisely the nature of the phenomena, the gross benefits resulting from aging are of value in permitting removal of the finely divided solid particles. However, the commercial impracticability of storing tar for a period of six months is apparent. Furthermore, the only other known process, namely that described in my copending application Serial No. 515,647, now U.S. Patent 2,871,181, involves expensive processing treatments. The pressing commercial need therefore exists for a process whereby freshly prepared raw tar obtained from a fluidized low temperature carbonization process may be refined by conventional processing methods.

Accordingly, it is an object of the present invention to provide a method for removing finely divided particles of coal and partially carbonized coal from the tar product resulting from low temperature carbonization processes.

Another object of this invention is to recover in high yield the liquid constituents of low temperature carbonization tar separately from entrained particles of coal and partially devolatilized coal.

A further object of this invention is to provide a method whereby freshly prepared raw tar obtained from

a fluidized low temperature carbonization process may be refined by conventional processing methods.

Yet a further object of this invention is to effect the described separation by employing as a solvent a low boiling hydrocarbonaceous distillate fraction autogeneously produced from the tar itself.

An additional object is to provide a method for selecting a preferred solvent system for effecting the desired separation.

A still further object is to provide a method for removing finely divided solids from the distillation bottoms fraction of fluidized low temperature carbonization tar that has first been distilled prior to removal of the solids.

According to the present invention, tar obtained by a low-temperature carbonization process, and containing finely divided solid particles derived from the process, is distilled under reduced pressure prior to the removal of the solid particles. Thereby the low boiling tar constituents are recovered as a solids-free distillate fraction. The higher boiling tar constituents are recovered as a distillation bottoms product containing all of the finely divided solid particles from the original tar. This distillation bottoms product henceforth is referred to as "pitch" throughout this specification. The solids-laden pitch thereafter is agitated with a low boiling distillate fraction preferably obtained from the tar itself and preferably containing at least two percent by volume of tar acids. Such solvents are more fully described hereinafter. The solvents selectively reject from the solution certain of the pitch constituents which combine with the finely divided solids to form larger agglomerates which are readily filterable.

The process of this invention finds particular and specific utility in the treatment of freshly prepared raw tars obtained by the fluidized low temperature carbonization of caking bituminous coals. This process is of further commercial importance in that it may be readily integrated into an over-all scheme for the processing of tar. As a further specific feature of this invention, the solvency power of the solvents used may be readily controlled and varied thereby obtaining desired preselected distributions of the pitch constituents.

When pitch derived from a bituminous coal is treated with the desired solvent system, the resulting products comprise a dissolved solids-free pitch and a filter cake containing the finely divided solid particles of coal and partially carbonized coal together with a small quantity of pitch and some occluded solvent. In most cases the pitch which appears in the filter cake is less than about five percent of the total liquid constituents of the raw tar feedstock. Substantially all of the occluded solvent contained in the filter cake can be recovered. The remaining solids may be employed as a solid fuel or, if desired, may be reintroduced into the low temperature carbonization process for further treatment. The separation described may be effected in a single stage or, preferably, in a plurality of stages. The actual mechanical separation of the particulate agglomerates from the solvent solution of pitch may be accomplished by filtration, settling or centrifugation.

For a more complete understanding of the present invention, its objects, features and advantages, reference should be had to the following detailed description and accompanying drawings in which:

FIGURE 1 is a schematic flow diagram illustrating apparatus adapted to the practice of the present invention;

FIGURE 2 is a schematic flow diagram illustrating apparatus adapted to the practice of a preferred embodiment of the present invention; and

FIGURE 3 is a schematic flow diagram illustrating apparatus adapted to the practice of an alternative embodiment of the present invention.

Referring to FIGURE 1, the apparatus illustrated schematically includes a heater 10, a vacuum distillation tower 11, a mixing vessel 12, a continuous filter 13, a

vacuum dryer 14, a solvent stripping tower 15 and a solvent storage tank 16.

The low temperature carbonization tar is contained in a storage tank 17. In a preferred embodiment, the tar is a freshly prepared raw tar obtained from fluidized low temperature carbonization of bituminous coal and contains substantial quantities of finely divided particles of coal and partially devolatilized coal. The tar in storage tank 17 is maintained at a temperature above its softening temperature to permit its pumping through a conduit 18 into the heater 10. Preferably the heater 10 is of a pipe still construction in which the tar passes at high velocity through a series of heated pipes. Coking of the raw tar within the heater 10 should be avoided. High velocity pipe still heaters are generally satisfactory for this purpose. The tar is heated to a temperature of about 700° F. and is introduced through a conduit 19 into the vacuum distillation tower 11. The vaporizable constituents are recovered by distillation under reduced pressure, preferably by being flashed overhead as a vapor through a distillate recovery conduit 20 and recovered as a solids-free tar distillate having a 95 percent distillation point in the range of 300 to 450° C. The liquid phase distillation residue, i.e., pitch, collects in the bottom of the vacuum distillation tower 11 with the finely divided particles of coal and partially devolatilized coal concentrated therein. The distillation residue is recovered from the vacuum distillation tower 11 through a conduit 21 either intermittently or continuously. The distillation residue has a 5 percent distillation point in the range of 300 to 450° C.

The distillation residue is introduced from the conduit 21 into the mixing vessel 12 which is maintained at a temperature above the melting point of the distillation residue. For each volume of distillation residue introduced into the mixing vessel 12, from about 0.75 to about 3.0 volumes of solvent are introduced into the mixing vessel 12 from the solvent storage vessel 16 through a solvent conduit 22. The mixing vessel 12 preferably is maintained at a temperature below the initial atmospheric boiling point of the solvent. If this requirement conflicts with the previous requirement that the temperature be maintained above the softening temperature of the distillation residue, then a closed mixing vessel 12 should be used to avoid solvent evaporation. Agitating means such as a rotating anchor stirrer 23 are provided within the mixing vessel 12 to maintain the contents under agitative conditions. With more efficient mixing devices, less hold-up time would be required for the liquid phase within the mixing vessel 12. Less efficient mixing devices will require a greater hold-up time. With highly efficient mixers, a hold-up time of several seconds should be sufficient to accomplish the desired agglomerate formation. As an alternative for the mixing vessel 12 as shown in FIGURE 1, it would be acceptable to provide a length of pipe through which both solvent and pitch are moved under highly turbulent conditions resulting in efficient liquid-to-liquid contacting.

A dilute slurry of soluble pitch in solvent with solid agglomerates is recovered from the mixing vessel 12 through a conduit 24 and introduced into the basin of the continuous filter 13. A rotating drum filter has been illustrated schematically. The filtrate comprising solids-free solution of soluble pitch and solvent is recovered through a filtrate conduit 25 and introduced into the solvent stripping tower 15 whence the solvent is vaporized and recovered overhead through a conduit 26 for storage in the solvent storage tank 16. Preferably there is a wide boiling range difference between the solvent and its dissolved pitch to permit ready stripping of the recycle solvent.

The solids-free and solvent-free pitch is recovered as a bottoms stream from the solvent stripping tower 15 through a pitch conduit 27. The material has a low hydrogen-to-carbon ratio, and is an excellent starting

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material for preparing carbon black. It may be hydrogenated to produce valuable low boiling hydrocarbons.

Reverting to the continuous filter 13, the filter cake, comprising agglomerate masses of coal and partially devolatilized coal bound by insoluble pitch, is recovered and conveyed through a conduit 28 (which may be a conveyor belt, for example) to a vacuum dryer 14. Solvent retained in the filter cake is recovered from the vacuum dryer through a conduit 29 for storage in the solvent storage tank 16. The vacuum dryer 14 is operated under relatively mild temperature conditions such that only the lower boiling solvent is recovered. The pitch retained within the filter cake is not normally recovered.

The solvent-free agglomerate masses are recovered from the vacuum dryer 14 through a conduit 30 for further treatment or use. By returning these agglomerates to the carbonization process whence they originated, the pitch constituent will be vaporized and in part converted to lower boiling liquids through mild cracking under the thermal conditions of carbonization. The coal constituents will be further devolatilized to yield greater liquid products.

Make-up solvent, if required, is introduced into the system through a make-up solvent conduit 31 associated with the solvent storage tank 16.

The make-up solvent, preferably, is autogenously produced in the present process as a distillate fraction of the raw tar distillate recovered through the conduit 20.

Further improved recovery of the soluble portions of the pitch can be effected by spraying the filter cake solids on the continuous filter drum with fresh solvent from a conduit 32 through a spray 33. The additional solvent used in this manner traverses the filter cake dissolving in transit additional quantities of soluble pitch which are recovered along with the added solvent as filtrate through the filtrate conduit 25. Thus a slight improvement in recovery of soluble pitch can be achieved at the expense of greater solvent inventory and increased solvent stripping facilities in the embodiment illustrated in FIGURE 1.

This same improvement of recovery of soluble pitch can be achieved by the system illustrated in FIGURE 2 without increasing the solvent inventory of the process and without increasing the solvent stripping facilities. According to the embodiment illustrated in FIGURE 2, the separation of solids from liquid tar and solvent is accomplished in two stages. A first stage employs a simple decantation to recover the bulk of dissolved pitch and solvent from a dilute slurry of solids in pitch and solvent. The residue, a concentrated slurry, then is subjected to continuous filtration with solvent washing of the filter cake on the continuous filter. The solvent employed in the first stage is not a fresh solvent but instead contains dissolved pitch. This first stage solvent is obtained as filtrate from the filtration stage. Fresh solvent is employed to wash the filter cake on the continuous filter. Thus with the same amount of solvent, an increased recovery of soluble pitch is effected.

Referring to FIGURE 2, there is illustrated a mixing vessel 40, a decanter vessel 41, a continuous filter 42, a vacuum dryer 43, a solvent and dissolved pitch storage vessel 44, a solvent stripping tower 45, and a solvent storage vessel 46.

A high boiling distillation residue obtained from raw low temperature carbonization tar is obtained by distillation as described in connection with FIGURE 1. This distillation residue which contains finely divided particles of coal and partially devolatilized coal, is introduced into the mixing vessel 40 from a pitch storage vessel 47 through a pitch conduit 48. A solution of solvent and dissolved pitch is introduced into the mixing vessel 40 through a conduit 49. The solvent and dissolved pitch flowing through the conduit 49 originates as filtrate through a filtrate conduit 50 from the continuous filter 42 as will be hereinafter described. From about 0.75 to

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about 3.0 volumes of solvent and dissolved pitch are employed for each volume of pitch entering the mixing vessel 40. When sufficient mixing has occurred in the mixing vessel 40 to cause agglomeration of the finely divided particles of coal and partially devolatilized coal with insoluble portions of the pitch, the entire contents of the mixing vessel 40 are introduced through a conduit 51 into the decanter vessel 41. The agglomerated particles of solids are allowed to settle to the bottom of the decanter vessel 41 whence they are drawn off through a slurry conduit 52 for filtration treatment to recover solids-free solvent and dissolved pitch. The solids-free, supernatant liquid from the decanter vessel 41 is withdrawn through a conduit 53 as a solution of solvent and soluble pitch. This solution is introduced into the solvent and dissolved pitch storage vessel 44 for further processing.

Referring to the continuous filter 42, the slurry of agglomerates in solvent and dissolved pitch enters the filter basin through slurry conduit 52. Solids-free filtrate passes through the filter and is recovered through a filtrate conduit 50 for storage in the solvent and dissolved pitch storage vessel 44. A filter cake comprising the agglomerated solids forms on the drum surface of the continuous filter 42 with a small quantity of entrained solvent and soluble pitch. Fresh solvent from the solvent storage tank 46 is introduced through a conduit 54 and is sprayed through a spraying device 55 onto the filter cake. In traversing the filter cake, the fresh solvent dissolves some of the soluble pitch retained in the cake for recovery from the continuous filter 42 as filtrate through the filtrate conduit 50. The filter cake, substantially free of any residual soluble pitch, is recovered through a filter cake recovery conduit 56 and introduced into the vacuum dryer 43 whence entrained solvent is vaporized and recovered through a solvent recovery conduit 57. The agglomerated solids, substantially free of solvent, are recovered from the vacuum dryer 43 through a conduit 58. The solvent vapors from conduit 57 are allowed to condense in a condensate vessel 59. The condensed solvent is withdrawn through a conduit 60 for reuse in the process. The condensed solvent from conduit 60 can be returned to the continuous filter 42, or to the mixing vessel 40 or to the solvent storage tank 46.

The recovered solids-free filtrate and supernatant decanted solutions are combined from conduits 50 and 53 in the solvent and dissolved pitch storage vessel 44. The contents of this vessel are withdrawn continuously or intermittently through a conduit 61, heated in a heating device 62 and introduced into the solvent stripping tower 45 whence the solvent is recovered for recirculation in the process through an overhead solvent recovery conduit 63. Solvent-free pitch, free of solids, is recovered as product from the bottom of the stripping tower 45 through a pitch recovery conduit 64. Additional fresh solvent may be introduced into the system through a conduit 65 to compensate for any processing losses.

The filtrate recovered from the continuous filter 42 through the filtrate conduit 50 comprises the solvent which is used in the mixing vessel 40. This stream contains both solvent and dissolved pitch. I have found that the dissolved pitch contained in the solvent does not interfere with the formation of agglomerate particles in the mixing vessel 40. By recirculating the fresh solvent, first, for washing the filter cake in the continuous filter 42, I am able to increase the overall recovery of soluble pitch from the starting material without increasing the solvent inventory required in the process and without enlarging the solvent stripping facilities.

A decanter vessel 41 has been illustrated and described for the preliminary recovery of a solvent solution of dissolved pitch. If desired, other separation techniques may be employed such as filtration or centrifugation. However, because of its simplicity, decantation is preferred for the preliminary separation.

Referring to FIGURE 3, I have illustrated there a

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flow diagram of the present invention showing the embodiment previously illustrated in FIGURE 1 in combination with facilities for autogenously generating the required solvent from the raw low temperature carbonization tar itself.

FIGURE 3 includes a raw low temperature carbonization tar storage vessel 70, a vacuum distillation column 71, a mixing vessel 72, a continuous filter 73, a vacuum dryer 74, a solvent stripping tower 75, a solvent storage vessel 76, and typical facilities for treating the distillate fractions obtained from the raw low temperature carbonization tar. These typical facilities include a double solvent extraction column 77 and a stripping column 78 for recovering naphtha used in the double solvent extraction column 77. The double solvent extraction column 77 and stripping column 78 are the essential portions of a recovery system of the type described in U.S. Patent 2,666,796 by Everett Gorin and Martin Neuworth and assigned to the assignee of the present invention. According to this process, a mixture containing low temperature carbonization tar distillate including tar acids and neutral oils can be separated efficiently by countercurrent extraction with an aqueous methanol solvent and a low boiling naphtha (such as hexane). The tar acids are recovered in the aqueous methanol solvent and the neutral oils are recovered in the low boiling naphtha.

Thus the raw low temperature carbonization tar containing particles of finely divided coal and partially devolatilized coal is distilled in the vacuum distillation column 71 to produce an overhead distillate fraction through conduit 79 comprising low boiling tar acids and neutral oils. As before, the distillate fraction in the conduit 79 has a 95 percent distillation point in the range 300 to 400° C. Some contaminants such as carboxylic acids, sulfur compounds and tar bases may also be present. These materials, however, do not concern the present process. The distillate tar, or preferably a distillation fraction thereof (e.g., boiling below about 230° C.) is subjected to a solvent extraction treatment as described in U.S. Patent 2,666,796 supra in the double solvent extraction column 77. The tar acids are recovered from the bottom of the extraction column 77 in aqueous methanol solution. The subsequent treatment of this solution is immaterial to a discussion of the present invention.

The neutral oil constituents are recovered overhead from the extraction column 77 through a conduit 80 as a solution in low boiling naphtha. The low boiling naphtha is removed from the solution in the stripping tower 78 and is recovered for recirculation in the process through a naphtha recycle conduit 81. The neutral oils obtained from the raw tar distillate are recovered free of low boiling naphtha as a bottoms product from the stripping column 78 through a conduit 82. Normally this neutral oil stream will contain a small percentage of tar acids as contaminants. The presence of some tar acids is required if the neutral oil stream is to be employed in the solvent in the present process. In the event the quantity of tar acids existing as contaminants in the neutral oil stream flowing through conduit 82 is inadequate, additional tar acids may be added to provide the desired mixture, i.e., from about 2 to about 20 percent by volume of tar acids. Thus it appears that each portion of raw low temperature carbonization tar introduced from the storage vessel 70 provides autogenously quantities of the solvent required in the solids removal process which forms the present invention.

A flow of materials through the remainder of the apparatus in FIGURE 3 corresponds to that described in connection with FIGURE 1. Briefly, the distillation residue from the distillation column 71 is introduced into the mixing vessel 72 through a conduit 83. Solvent is introduced into the mixing vessel 72 from the solvent storage vessel

76 through a conduit 84. The materials are agitated in the mixing vessel 72 until the desired agglomerates are formed. A slurry of agglomerates and solvent and dissolved pitch is withdrawn from the mixing vessel 72 through a slurry conduit 85 and introduced into the continuous filter 73. The filter cake comprising the agglomerates of finely divided particles of coal and partially devolatilized coal is withdrawn as a filter cake through a filter cake conduit 86 and treated in a vacuum dryer 74 for recovery of any solvent retained therein. The solvent is returned to the solvent storage vessel 76 through a solvent conduit 87. The solvent-free solids are removed through a conduit 88.

Filtrate from the continuous filter 73 containing solvent and dissolved pitch is withdrawn through a filtrate conduit 89 and stripped of solvent in the solvent stripping tower 75. The stripped solvent is recovered overhead through a conduit 90 and returned to the solvent storage vessel 76. The solids-free pitch, having been separated from its solvent, is recovered as a product through the pitch recovery conduit 91 at the base of the solvent stripping tower 75.

Normally only a small portion of the neutral oil stream in conduit 82 will be required to provide the additional solvent to compensate for processing losses in the solids-removal process of the present invention. The bulk of the neutral oil stream accordingly can be withdrawn from the conduit 82 through a product conduit 92. Alternatively, where a particularly low boiling solvent is desired, the entire stream flowing through the conduit 82 may be distilled and a low boiling distillate recovered therefrom for use in solvent preparation.

As a further alternative, the tar acid oil which enters the double solvent extraction column 77 through the distillate conduit 79 may be preliminarily distilled and a low boiling fraction thereof employed in preparing the solvent of this invention. Such distillates usually will contain sufficient quantities of tar acids as azeotropes to meet the solvent specifications. The low boiling character of such solvents greatly simplifies the solvent stripping requirements in the solvent stripping tower 75.

The integrated process shown in FIGURE 3 also may be combined with the two-stage solids-removal process shown in FIGURE 2.

STARTING MATERIAL

The starting material in the present invention may be any tar derived from the low-temperature carbonization of a naturally occurring bituminous material, the tar containing finely divided solid particles derived from the carbonization process. By effecting preliminary fractionation of the tar and concentrating the finely divided solids into a distillation bottoms fraction, the size of required processing equipment is considerably reduced. The present process is particularly advantageously employed when the starting material is a freshly prepared raw tar obtained by the fluidized low temperature carbonization of a bituminous coal. Such tars possess a high density and a high viscosity. They contain suspended therein substantial quantities of finely divided particles of coal and partially carbonized coal. These solid particles are almost universally capable of passing through a 325 mesh Tyler standard screen and may comprise up to about 25 percent and more of the total weight of the tar. The liquid components of the tar have an initial boiling point of about 150° C. and a final boiling point in excess of about 450° C. In addition to hydrocarbons, the liquid constituents include oxygenated compounds as well as nitrogen- and sulfur-containing compounds. A typical tar produced by low temperature carbonization of caking bituminous coal showed a specific gravity of 1.117 (with solids). This tar contained 13.04 percent by weight of

finely divided solids. The solids-free tar had the following boiling range distribution.

Fraction:	Weight percent
IBP, 230-----	14.0
230-300-----	9.9
300-350-----	11.5
350-400-----	11.4
Above 400-----	53.2

The ring and ball softening temperature (ASTM E-28-51T) of the solids-free pitch remaining after distillation of those materials boiling below 400° C. was 130° C. Thus the solids-free pitch is a solid material at room temperature. About 99 percent of the solid particles of coal and partially carbonized coal in the tar were capable of passing through a 325 mesh Tyler standard screen.

PRELIMINARY TAR DISTILLATION

According to the present invention, the raw solids-laden low temperature carbonization tar is first subjected to a distillation under reduced pressure to permit recovery of the more valuable low boiling constituents as a solids-free distillate. Preferably the preliminary distillation is accomplished by a vacuum flashing technique to avoid heating the tar to excessive temperatures at which coking might occur. Heating the raw solids-laden tar to a temperature of about 200 to 350° C. followed by flashing under vacuum conditions results in vaporization of about 30 to 50 percent of the raw tar. A distillation residue containing those constituents boiling above a cut-temperature in the range of 350 to 450° C. can be obtained in this manner. The flashed tar vapors are recovered as a solids-free distillate and, if desired, can be fractionated while still in the vapor form. The distillation residue, i.e., the pitch, has concentrated therein the solid particles of coal and partially devolatilized coal.

It is considered an essential feature of this invention that tar containing the fine particles of carbonaceous material dispersed therein is first separated into the pitch and distillate fractions prior to any processing of the tar by use of an agglomerating pitch-solvent. Thus despite the increased concentration of the fine particles in the pitch compared with the tar, separation is thereby more readily accomplished. Where the tar is a freshly prepared raw tar obtained by the fluidized low temperature carbonization of a caking bituminous coal, this preliminary separation is essential for the obtaining of commercially acceptable rates of filtration.

SOLVENT

Throughout the present specification, the term "solvent" is employed to designate the treating reagent of the present invention. The solvent has the property of dissolving a major portion of the liquid constituents of the pitch and selectively avoiding solution of a small portion of the high boiling pitch constituents. A preferred solvent comprises low boiling hydrocarbons preferably obtained from distillate fractions of the low temperature carbonization tar itself along with a small quantity (in the range of 2 to 20 percent by volume) of phenols. Such a light oil-phenol solvent can be autogenously generated from the low temperature carbonization tar.

Those portions of the tar boiling below about 160° C. comprise principally neutral hydrocarbons. Fractions boiling between about 160 and 230° C. comprise principally neutral hydrocarbons and tar acids including phenol, cresols, xylenols and ethyl phenols. Fractions boiling between about 230 and about 300° C. comprise principally neutral hydrocarbons and high boiling tar acids. The neutral hydrocarbons in the tar boiling below about 300° C. are suitable as the hydrocarbon constituents of the solvent in the present process.

The solvent should possess a boiling range well below that of the pitch undergoing treatment to facilitate separation and recovery of the solvent for reuse in the process.

Generally, the bulk of the solvent comprises essentially non-aromatic hydrocarbons; in addition the solvent contains from about 2 to 20 percent by volume of tar acids such as phenol, cresols, xylenols and monoethyl phenols.

One preferred solvent is the entire distillate fraction from low temperature carbonization tar boiling up to about 160° C. This fraction comprises predominantly neutral hydrocarbons with a small, but sufficient quantity of tar acids which appear in the distillate as the result of azeotropic phenomena. Depending upon the tar acid content of the raw tar, suitable distillate fractions may include those having a distillation end point below about 200° C. Those low boiling neutral hydrocarbons from low temperature carbonization tars are predominantly paraffinic and naphthenic, i.e., they are not predominantly aromatic. Hence they differ from the so-called "light oils" of coke oven tars which are principally benzene, toluene and xylene. Indeed the low temperature carbonization tars are remarkably free of benzene, toluene and xylene.

Another preferred solvent is the neutral oil obtained when a distillate fraction of raw low temperature carbonization tar boiling from about 160 to about 230° C. (termed tar acid oil) is refined by a double solvent extraction process as described in U.S. Patent 2,666,796. In such a refining process, the tar acid oil is separated by countercurrent contact with aqueous methanol and a low boiling paraffinic solvent. The neutral constituents of the tar acid oil are extracted in the low boiling paraffinic solvent along with a small contaminating quantity of tar acids. After recovery of the low boiling paraffinic solvents, the remaining neutral oil fraction is a satisfactory solvent. Usually this neutral oil fraction will contain sufficient tar acids for use. Additional tar acids may be added if desired.

The solvents of this invention may be conveniently referred to as agglomerating pitch-solvents because of their effect on the finely dispersed particles contained in the pitch residue. Those hydrocarbon solvents having kauri-butanol values between about 65 and 75 are particularly preferred.

KAURI-BUTANOL SOLVENCY

While I prefer to use the light oil-phenol solvent autogenously produced from the tar itself, other solvents may also be advantageously employed, for example, those derived from petroleum hydrocarbons. Furthermore, I have found that hydrocarbon solvents having different chemical compositions and aromaticity contents may be used provided they have comparable boiling ranges and the same solvency power, as determined by their kauri-butanol numbers. Thus a petroleum solvent blend of solvents having the same kauri-butanol number and a comparable boiling range may be used interchangeably with the light oil-phenol solvent.

The kauri-butanol test method is a standardized procedure (ASTM designation: D1133-54T) for determining the relative solvent power of hydrocarbon solvents used in paint and lacquer formulations. Thus the kauri-butanol value of a solvent is the volume in milliliters at 25° C. of the solvent, corrected to a defined standard, to produce a defined degree of turbidity when added to 20 grams of a standard solution of kauri resin in normal butyl alcohol. For kauri-butanol values of 60 and over, the standard is toluene and has an assigned value of 105. In general, the more aromatic the solvent the greater is its kauri-butanol value. However, phenolic solvents, such as tar acids, have extremely high kauri-butanol values, far in excess of their aromatic content alone.

I have further found that a significant correlation exists between the kauri-butanol value of a solvent, the filtration value of the dissolved pitch and the percentage recovery of the pitch. Thus solvents with kauri-butanol

values above about 70 to 75 gave increased solvent hold-up in the filter cake, lower filtration rate, decreased solids agglomeration and increased blinding of the filter cloth. When solvents with kauri-butanol values lower than 65 were used, poor tar recovery and tacky filter cakes were obtained. Thus a preferred range of kauri-butanol values for the hydrocarbon solvents of this invention lies between 65 and 70.

The kauri-butanol value of a solvent or blend of solvents may be approximated by determining the total aromaticity present by use of the fluorescent indicator adsorption method (ASTM designation: D1319-55T). With a known tar acid content, the kauri-butanol number of the solvent system is found by the formula:

$$K-B \text{ No.} = \text{percent aromatics (total)} + 0.6\% \text{ tar acids}$$

The tar acid coefficient is based on the determination that tar acids are approximately 1.6 times more effective than benzene in raising the kauri-butanol number.

SOLVENT AGGLOMERATING TREATMENT

The distillation residue, containing coal and partially devolatilized coal, is agitated with about 0.75 to 3 times its volume of the herein-described solvent. The materials are maintained at a temperature above the melting point of the pitch during this treatment. Preferably the agitation is conducted below the atmospheric boiling point of the solvent to avoid the need of pressurized apparatus to confine the solvent. The following table sets forth the ring and ball softening temperatures of the whole raw tar and several distillation residues.

Tar Fraction:	Ring and ball softening temperature, °C.
A. Whole raw tar ¹ -----	8
B. Distillation residue boiling above—	
230° C. ¹ -----	20
300° C-----	37
380° C-----	68
400° C-----	80
440° C-----	150

¹ ASTM E-28-51T procedure followed at lower temperatures to provide common basis for comparison of tar fractions. Conventional procedure is not intended for use below 35° C. Results of such determinations have been quite reproducible.

Continuing contacting of the pitch and solvent under agitated conditions achieves solution of most of the pitch in the solvent. Some of the tacky pitch constituents, however, are insoluble in the solvent and are disposed in a distinct viscous liquid phase throughout the solution. Agitation of the material effects contacting of the insoluble tacky pitch droplets with the finely divided solid particles of coal and partially carbonized coal. The solid particles adhere to the insoluble tacky pitch droplets to form larger agglomerates. With a highly efficient agitation system, the solid particles can be agglomerated in this fashion in a matter of seconds.

The resulting material comprises a solution of most of the pitch in the solvent along with agglomerate masses formed from the coal and partially carbonized coal. By varying, within desired limits, the kauri-butanol value of the solvent used, the relative proportions of dissolved pitch may be thereby varied.

ELIMINATION AND RECOVERY OF AGGLOMERATED SOLIDS

These agglomerated masses of solid particles can be removed from the solution by settling and decantation, by filtration, by centrifugation and the like. Filtration is preferred to improve the quantitative recovery of soluble pitch and solvent. The filtrate comprising the solvent and soluble pitch is recovered. The solvent is stripped from the filtrate by distillation for reuse. The boiling range of the solvent under preferred conditions is well below that of the pitch. The pitch is recovered as a solids-free material.

The filter cake is recovered as discrete agglomerate particles moistened by the solution of solvent and soluble pitch. Thermal drying of the filter cake permits recovery of the solvent retained therein. The dry filter cake comprises those particles of coal and partially carbonized coal originally in the tar together with the insoluble pitch serving as a binder for the agglomerates. The dry filter cake can be used as a fuel or may be returned to the carbonization process whence it originated for further processing.

The following examples illustrate this invention, but are not intended as limitations thereof.

Examples

Example 1.—A sample of freshly prepared raw low temperature carbonization tar was obtained from a fluidized low temperature carbonization process operated with caking bituminous coal. The raw tar contained 13.04 percent by weight of solid particles which were capable of passing through a 325 mesh Tyler standard screen. This freshly prepared tar was contacted with 1.5 volumes of a solvent consisting of neutral oil boiling from 160–180° C. obtained from the low temperature carbonization tar itself. The solvent contained in addition 2 percent by volume of tar acids. Upon agitation of the raw freshly prepared tar and the solvent, a gummy tacky semi-liquid phase separated out. A clear supernatant liquid was recovered comprising a solution of the solvent and soluble portions of the whole tar. The gummy, tacky second phase could not be recovered by filtration. It contained excessive quantities of viscous pitch.

Thus it appears that freshly prepared tar from low temperature carbonization of caking bituminous coal via fluidized processes produce a reject phase which is virtually unfilterable and which contains excessive quantities of valuable pitch.

Example 2.—The same low temperature carbonization tar described in Example 1 was allowed to sit in storage at room temperature for a period of six months. The tar then was treated with the neutral oil solvent (containing phenol) described in Example 1. The mixing of the solvent and whole raw tar resulted in the formation of agglomerate particles which were non-tacky and readily filterable. Thus it appears that one way to remove the finely divided particles of coal and partially devolatilized coal from raw low temperature carbonization (obtained by a fluidized process) is to allow the material to stand for an extended period and thereafter to treat the aged tar in the manner described in my prior patent, U.S. 2,774,716.

Example 3.—The same raw low temperature carbonization tar described in Example 1 was distilled under vacuum to remove as distillate those constituents having a normal 95 percent boiling temperature of about 440° C. The residue from this distillation contained the tar constituents having a five percent boiling temperature of about 440° C. and in addition the particles of coal and partially devolatilized coal existing in the raw tar. When this distillation residue was treated with about 1.5 volumes of the solvent described in Example 1, agglomerate particles of non-tacky consistency were formed. Filtration was readily accomplished.

Example 4.—The same procedure as described in Example 3 was repeated except that the solvent employed was the entire neutral oil fraction recovered by double solvent extraction of tar acid oil boiling from 160 to 300° C., according to U.S. Patent 2,666,796 supra. Again non-tacky agglomerate particles were formed which were readily filterable.

Example 5.—The procedure described in Example 3 was repeated except that the solvent employed was a low temperature carbonization tar neutral oil free of tar acids. A tacky liquid phase was formed containing the solid particles of coal and partially devolatilized coal. This tacky phase was unfilterable. Thus it appears that

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small quantity of tar acids is required in the treating solvent to effect the desired recoverability of agglomerate solids. However, in lieu of addition of tar acids, addition of an aromatic solvent in sufficient amount to form a blend of equal kauri-butanol value, and also comparable boiling range, may also be resorted to.

Example 6.—A sample of raw low temperature carbonization tar obtained from a fluidized low temperature carbonization process employing caking bituminous coal was obtained. The tar contained 19.6 percent by weight of solid particles which were capable of passing through a 325 mesh Tyler standard screen. The tar was vacuum distilled to recover those constituents having a 95 percent boiling temperature about 440° C. The distillate fraction comprised about 55 percent of the tar by weight. The remaining 45 percent of the tar was recovered as a distillation bottoms product having a ring and ball softening temperature of about 140° C. This distillation residue was introduced into a mixing vessel along with an equal volume of solvent. The solvent contained 88 percent by weight of neutral oils obtained from low temperature carbonization tar boiling from 150 to 220° C. The remainder of the solvent comprised 12 percent by weight of tar acids. Thus, based on 100 parts of raw low temperature carbonization tar 45 parts of pitch and 45 parts of solvent were introduced into the solvent treating process.

The materials were mixed at a temperature of about 150° C. which was below the boiling temperature of the solvent and above the softening temperature of the distillation residue. Agglomerate particles of solid materials and insoluble pitch were formed and the overall mixture was recovered as a slurry and introduced into a vacuum filter operated at 150° C. Recovered were 59.1 parts of filtrate containing 21.7 parts of dissolved pitch and 37.4 parts of solvent. A moist filter cake containing 30.9 parts included 7.6 parts of solvent 3.7 parts of pitch and 19.6 parts of solid materials. The cake was subjected to a vacuum drying treatment at 140° C. and 20 mm. mercury pressure. From the vacuum drying treatment 7.6 parts of solvent were recovered. The dried filter cake contained 23.3 parts including 3.7 parts by weight of pitch and 19.6 parts by weight of solids. The solids and tar were in the form of dry, free flowing granular particles. The solids would not pass through a 325 mesh Tyler standard screen.

Based on the 100 parts of initial low temperature carbonization tar, the 80.4 parts by weight of liquid components were recovered as follows: 55 parts by weight as distillate, 21.7 parts by weight as filtrate. The overall liquid recovery was

$$\frac{76.6}{80.4} = 95.5$$

percent. The recovery of high boiling pitch was 21.7 parts by weight of the original 25.4 parts by weight appearing in the distillation residue or

$$\frac{21.77}{25.4} = 85.5$$

percent recovery based on pitch alone. Solvent recovery throughout the process was virtually quantitative.

Example 7.—A sample of raw low temperature carbonization tar was treated for removal of solid particles according to the system illustrated in FIGURE 2, with one variation, i.e., filtration was substituted for the illustrated decantation treatment. The raw tar contained 80.4 parts by weight of liquid constituents and 19.6 percent by weight of solid particles capable of passing through a 325 mesh Tyler standard screen. The raw tar was distilled to recover those constituents having a 95 percent boiling temperature of about 440° C. The distillate fraction comprised about 55 parts by weight, based on 100 parts by weight of raw tar. The distillation residue comprised about 45 parts by weight includ-

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ing 25.4 parts by weight of pitch and 19.6 parts by weight of solids.

The distillation residue was mixed with 49.1 parts by weight of second stage filtrate including 47.5 parts by weight of solvent and 1.6 parts by weight of pitch. The ingredients were mixed at 150° C. and the resulting slurry was filtered. This slurry contained 94.1 parts by weight including 47.5 parts by weight of solvent, 27.0 parts by weight of tar and 19.6 parts by weight of solid. The filtrate was recovered and the filter cake was washed with 45 parts by weight of fresh solvent comprising 88 percent of neutral oil (derived from low temperature carbonization tar) boiling from 150 to 220° C. and 12 percent by weight of tar acids. The mixture of fresh solvent and filter cake as a slurry was filtered once more. The resulting filtrate comprised 49.1 parts by weight including 47.5 parts by weight of solvent and 1.6 parts by weight of soluble pitch. This filtrate corresponds to that employed as the solvent in the first stage mixing treatment. The filter cake contained 26.8 parts by weight including 5.1 parts by weight of solvent, 2.1 parts by weight of pitch and 19.6 parts by weight of solids. Following the vacuum drying at 140° C. and 20 mm. mercury pressure, a dried cake comprising 21 parts by weight including 19.6 parts by weight of solids and 2.1 parts by weight of pitch was recovered. The 5.1 parts by weight of solvent contained in the filter cake were flashed overhead for recirculation. The first stage filtrate included 39.9 parts by weight of solvent (recovered for recycle) and 23.3 parts by weight of solids-free and solvent-free pitch.

The overall liquid recovery included the 55 parts by weight of tar recovered as distillate and the 23.3 parts by weight of pitch recovered as bottoms from the stripping treatment or

$$\frac{78.3}{80.4} = 97.4$$

percent recovery. The recovery based on pitch alone was

$$\frac{23.3}{25.4} = 91.7$$

percent.

Thus the overall loss of liquids from the raw low temperature carbonization tar can be reduced from about 4.5 percent (according to Example 6) to about 2.6 percent (according to Example 7) by adopting the method illustrated in FIGURE 2. This improved liquid recovery is manifested in processing of any low temperature carbonization tars whether obtained from fluidized processes or otherwise.

Example 8.—A sample of 25 grams of pitch obtained as a tar bottoms product that had been topped at 440° C. was mixed with two volumes of solvent at 150° C. and filtered on a 72-mm. diameter Buchner funnel through No. 1 Whatman paper. The pressure differential of the filter was 710 mm. Hg. Filtration time was taken as the time it took the liquid to pass through the filter to the first appearance of the solid cake. The cake was then immediately covered with an additional volume of solvent heated to 150° C. After filtration was complete, air was allowed to pass through the filter cake for approximately 2 minutes. The cake was removed and weighed and dried at 160° C., 25 mm. Hg for 1 hour for solvent removal and reweighed for determination of solids and occluded pitch. Filter cake solids were determined as 10.1 grams and the ash-free available pitch as 14.9 grams. Blinding was estimated by comparison of the blackness of the filter papers from the individual runs.

A blend consisting of a low temperature carbonization light oil having a kauri-butanol value of 85 and a petroleum naphtha having a kauri-butanol value of 34 was prepared. The final solvent blend had a kauri-bu-

tanol value of 70. Using this blend as solvent, a filtration time of 3 seconds and pitch recovery of 87.3 percent were obtained.

A commercially available hydrocarbon solvent (Amsco D (W-1) of American Mineral Spirits Co.) having an aromatic content of 72.0 percent was also used. This solvent distilled over the range 155-207° C. It had a kauri-butanol value of 72. Using this latter solvent, a filtration time of 3 seconds and pitch recovery of 85.2 percent were obtained.

Another commercially available hydrocarbon solvent (Picco T-30, Pennsylvania Industrial Chemical Corp.) having a kauri-butanol value of 70 gave a filtration time of 3 seconds, a pitch recovery of 85.9 percent. This solvent has an aromaticity of 70 percent, consisting principally of highly alkylated benzene and naphthalene compounds and alkylated cycloparaffins. Its boiling range is 155-278° C. with its 95 percent point at 260° C. Thus despite the differences in composition and derivation among the three solvents, all had essentially the same kauri-butanol values and gave substantially identical results.

According to the provisions of the patent statutes, I have explained the principle, preferred construction, and mode of operation of my invention and have illustrated and described what I now consider to represent its best embodiment. However, I desire to have it understood that, within the scope of the appended claims, the invention may be practiced otherwise than as specifically illustrated and described.

I claim:

1. The method of processing a low-temperature carbonization tar containing finely divided particles of carbonaceous solids difficultly removable therefrom, which comprises distilling said particle-containing low-temperature carbonization tar to form a solids-free distillate fraction having a 95 percent boiling temperature range of 300 to 450° C. and a pitch residue containing said particles, agitating the solids-laden pitch residue with an agglomerating pitch-solvent selected from the class consisting of (1) a predominantly non-aromatic low temperature carbonization tar distillate fraction containing at least 2 percent by volume of tar acids and (2) a hydrocarbon solvent having a kauri-butanol value between about 65 and 75 to form a pitch solution containing particulate agglomerates with a minor amount of undissolved pitch, and separating the resulting agglomerates from the solids-free pitch solution.

2. The method of claim 1 wherein said tar is a freshly prepared raw tar derived from the fluidized low temperature carbonization of a bituminous coal.

3. The method of claim 2 wherein said pitch-solvent is at least a portion of said distillate fraction containing from 2 to 20 percent by volume of tar acids.

4. The method of claim 1 wherein said pitch-solvent has a kauri-butanol value between about 65 and 75.

5. The method for removing finely divided particles consisting essentially of naturally occurring carbonaceous solid fuels and partially devolatilized naturally occurring carbonaceous solid fuels from a tar containing said particles, said tar being derived from the low temperature carbonization of naturally occurring carbonaceous solid fuels, which comprises heating said tar under vacuum to separate therefrom a solids-free distillate fraction having a 95 percent boiling temperature range of 300 to 450° C., thereby concentrating said particles in the unvaporized pitch residue, agitating the solids-laden pitch residue with 0.75 to 3.0 times its volume of a pitch-solvent selected from the class consisting of (1) a predominantly non-aromatic low temperature carbonization tar distillate fraction containing at least 2 percent by volume of tar acids and (2) a hydrocarbon solvent having a kauri-butanol value between about 65 and 75 at a temperature above the softening temperature of the pitch residue whereby the bulk of said pitch residue becomes dissolved

in said pitch-solvent and the said particles and undissolved pitch form particulate agglomerates, separating the resulting agglomerates from the pitch-solvent solution of pitch, recovering the said pitch-solvent from said solution and recovering the residue thereof as solids-free pitch.

6. The method of claim 5 wherein said tar is a freshly prepared raw tar.

7. The method for removing finely divided particles consisting essentially of coal and partially devolatilized coal from a tar containing said particles, said tar being derived from the low temperature carbonization of bituminous coal, which comprises heating said tar under vacuum to separate therefrom a solids-free distillate fraction having a 95 percent boiling temperature range of 300 to 450° C., thereby concentrating said particles in the unvaporized pitch residue, agitating the solids-laden pitch residue with 0.75 to 3.0 times its volume of a pitch-solvent selected from the class consisting of (1) a predominantly non-aromatic low temperature carbonization tar distillate fraction containing at least 2 percent by volume of tar acids and (2) a hydrocarbon solvent having a kauri-butanol value between about 65 and 75 at a temperature above the softening temperature of the pitch residue whereby the bulk of said pitch residue becomes dissolved in said pitch-solvent and said particles and undissolved pitch form particulate agglomerates, separating the resulting agglomerates from the pitch-solvent solution of pitch, recovering the said pitch-solvent from said solution and recovering the residue thereof as solids-free pitch.

8. The method according to claim 7 wherein said pitch-solvent consists essentially of non-aromatic hydrocarbons containing at least 2 percent by volume of tar acids.

9. The method according to claim 7 wherein said pitch-solvent has a kauri-butanol value between about 65 and 75 and is selected from the group consisting of (1) essentially non-aromatic hydrocarbons containing at least 2 percent by volume of tar acids and (2) a mixture of hydrocarbons predominantly of an aromatic nature.

10. The method according to claim 7 wherein said pitch-solvent has a kauri-butanol value between about 65 and 75 and is a mixture of hydrocarbons predominantly of an aromatic nature.

11. The method for removing finely divided particles consisting essentially of coal and partially devolatilized coal from a tar containing said particles, said tar being derived from the low temperature carbonization of bituminous coal, which comprises heating said tar under vacuum to separate therefrom a solids-free distillate fraction having a 95 percent boiling temperature range of 300 to 450° C., thereby concentrating said particles in the unvaporized pitch residue, agitating the solids-laden pitch residue with 0.75 to 3.0 times its volume of a pitch-solvent comprising at least a portion of said tar-derived solids-free distillate fraction at a temperature above the softening point of the pitch residue whereby the bulk of said residue becomes dissolved in said pitch-solvent and the said particles and undissolved pitch form particulate agglomerates, separating the resulting agglomerates from the pitch-solvent solution of pitch, recovering the said pitch-solvent from said solution and recovering the residue thereof as solids-free pitch.

12. The method of claim 11 wherein the tar-derived pitch-solvent has a distillation end point below about 200° C. and contains 2 to 20 percent tar acids by volume.

13. The method of claim 11 wherein said tar-derived pitch-solvent has a kauri-butanol value between about 65 and 75.

14. The method for removing finely divided particles capable of passing through a 325 mesh Tyler standard screen and consisting essentially of coal and partially devolatilized coal from a tar containing said particles, said tar being derived from the fluidized low temperature carbonization of bituminous coal, which comprises heating

titles in the unvaporized pitch residue, agitating the solids-laden pitch residue with 0.75 to 3.0 times its volume of a pitch-solvent selected from the class consisting of (1) a predominantly non-aromatic low temperature carbonization tar distillate fraction containing at least 2 percent by volume of tar acids and (2) a hydrocarbon solvent having a kauri-butanol value between about 65 and 75 at a temperature above the softening temperature of the pitch residue whereby the bulk of said pitch residue becomes dissolved in said pitch-solvent and the said particles and undissolved pitch form particulate agglomerates capable of being retained on a 325 mesh Tyler standard screen, separating the resulting agglomerates from the pitch-solvent solution of pitch, recovering the said pitch-solvent from said solution and recovering the residue thereof as solids-free pitch.

15. The method of claim 14 wherein said distillate fraction is separated from said tar by flash vaporization under vacuum and wherein the agglomerates are separated from the pitch-solvent solution of pitch by filtration.

16. The method for removing finely divided particles consisting essentially of coal and partially devolatilized coal from a tar containing said particles, said tar being derived from the low temperature carbonization of bituminous coal which comprises heating said tar under vacuum to separate therefrom a solids-free distillate fraction having a 95 percent boiling temperature range of 300 to 450° C., thereby concentrating said particles in the unvaporized pitch residue, agitating the solids-laden pitch residue in a mixing zone with 0.75 to 3.0 times its volume of a pitch-solvent solution comprising pitch dissolved in a pitch-solvent which itself comprises low-boiling essentially non-aromatic hydrocarbons containing at least two percent by volume of tar acids, conducting the agitating treatment at a temperature above the softening temperature of the pitch residue whereby the bulk of said pitch residue becomes dissolved in said pitch-solvent and the said particles and undissolved pitch form particulate agglomerates, separating a first solids-free solution of pitch-solvent and pitch, contacting the said agglomerates with a pitch-free pitch-solvent to dissolve therein additional quantities of pitch, recovering a second solids-free solution of pitch-solvent and pitch separately from said agglomerates, combining said first and second solutions, recovering said pitch-solvent therefrom by distillation, and recovering a solids-free pitch product.

17. The method for removing finely divided particles consisting essentially of coal and partially devolatilized coal from a tar containing said particles, said tar being derived from the low temperature carbonization of bituminous coal, which comprises heating said tar under vacuum to separate therefrom a solids-free distillate fraction having a 95 percent boiling temperature range of 300 to 450° C., thereby concentrating said particles in the unvaporized pitch residue, agitating the solids-laden pitch residue in a mixing zone with 0.75 to 3.0 times its volume of a recycle pitch-solvent solution comprising pitch dissolved in a pitch-solvent which itself comprises

said tar under vacuum to separate therefrom a solids-free distillate fraction having a 95 percent boiling temperature range of 300 to 450° C., thereby concentrating said par- a low-boiling essentially non-aromatic distillate fraction derived from said tar and containing at least two percent by volume of tar acids, conducting the agitating treatment at a temperature above the softening temperature of the pitch residue whereby the bulk of said pitch residue becomes dissolved in said pitch-solvent and the said particles and undissolved pitch form particulate agglomerates, allowing said agglomerates to settle from suspension and recovering a substantial portion of the solids-free supernatant pitch-solvent solution and dissolved pitch, recovering the settled agglomerates in a slurry of said solution, filtering said slurry to recover a first solids-free filtrate comprising pitch-solvent and pitch, washing the agglomerates with fresh pitch-solvent to dissolve additional pitch contained therein, recovering a second solids-free filtrate comprising said pitch-solvent and pitch, combining said first and second filtrates as a combined stream for use in part as the said recycle pitch-solvent solution, and recovering the remainder of said combined stream together with said supernatant solutions.

18. The method for processing a freshly prepared raw tar derived from the fluidized low temperature carbonization of bituminous coal, said tar containing finely divided particles capable of passing through a 325 mesh Tyler standard screen and consisting essentially of coal and partially devolatilized coal, which comprises heating said tar to flash vaporize under vacuum a solids-free distillate fraction having a 95 percent boiling temperature in the range 300 to 450° C., thereby concentrating said particles in the unvaporized pitch residue, recovering from said distillate fraction a pitch-solvent consisting of a low-boiling predominantly non-aromatic hydrocarbon solvent containing between 2 and 20 percent tar acids by volume and having a distillation end point below about 200° C. and a kauri-butanol value between about 65 and 75, agitating the solids-laden pitch residue with 0.75 to 3.0 times its volume of said pitch-solvent at a temperature above the softening temperature of the pitch residue whereby the bulk of said pitch residue becomes dissolved in said pitch-solvent and the said particles and undissolved pitch form particulate agglomerates, thereafter separating the resulting agglomerates from the pitch-solvent solution of pitch by filtration, recovering for reuse the said pitch-solvent from said solution by distillation therefrom and recovering the residue thereof as a solids-free pitch product.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,010,893

November 28, 1961

Metro D. Kulik

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 6, line 57, for "filterate" read -- filtrate --; column 8, line 66, for "car" read -- tar --; column 9, line 4, for "IBP, 230" read -- IBP -230 --; column 12, line 40, for "neutrol" read -- neutral --; line 45, for "finly" read -- finely --; lines 46 and 47, after "carbonization" insert -- tar --; column 15, line 32, for "of" read -- for --; line 72, for "kuari-" read -- kauri- --; column 18, lines 1 to 3, strike out "said tar under vacuum to separate therefrom a solids-free distillate fraction having a 95 percent boiling temperature range of 300 to 450° C., thereby concentrating said par-" and insert the same before "ticles in the" in line 1, column 17; column 18, line 49, after "product." insert the following claim:

19. The method of claim 5 wherein said pitch solvent has a kauri-butanol value between about 65 and 75.

in the heading to the printed specification, line 9, for "18 Claims." read -- 19 Claims. --.

Signed and sealed this 24th day of April 1962.

(SEAL)

Attest:

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