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PROCESS FOR REMOVING FINELY DIVIDED SOLIDS FROM RAW LOW TEMPERATURE CARBONIZATION COAL TARS

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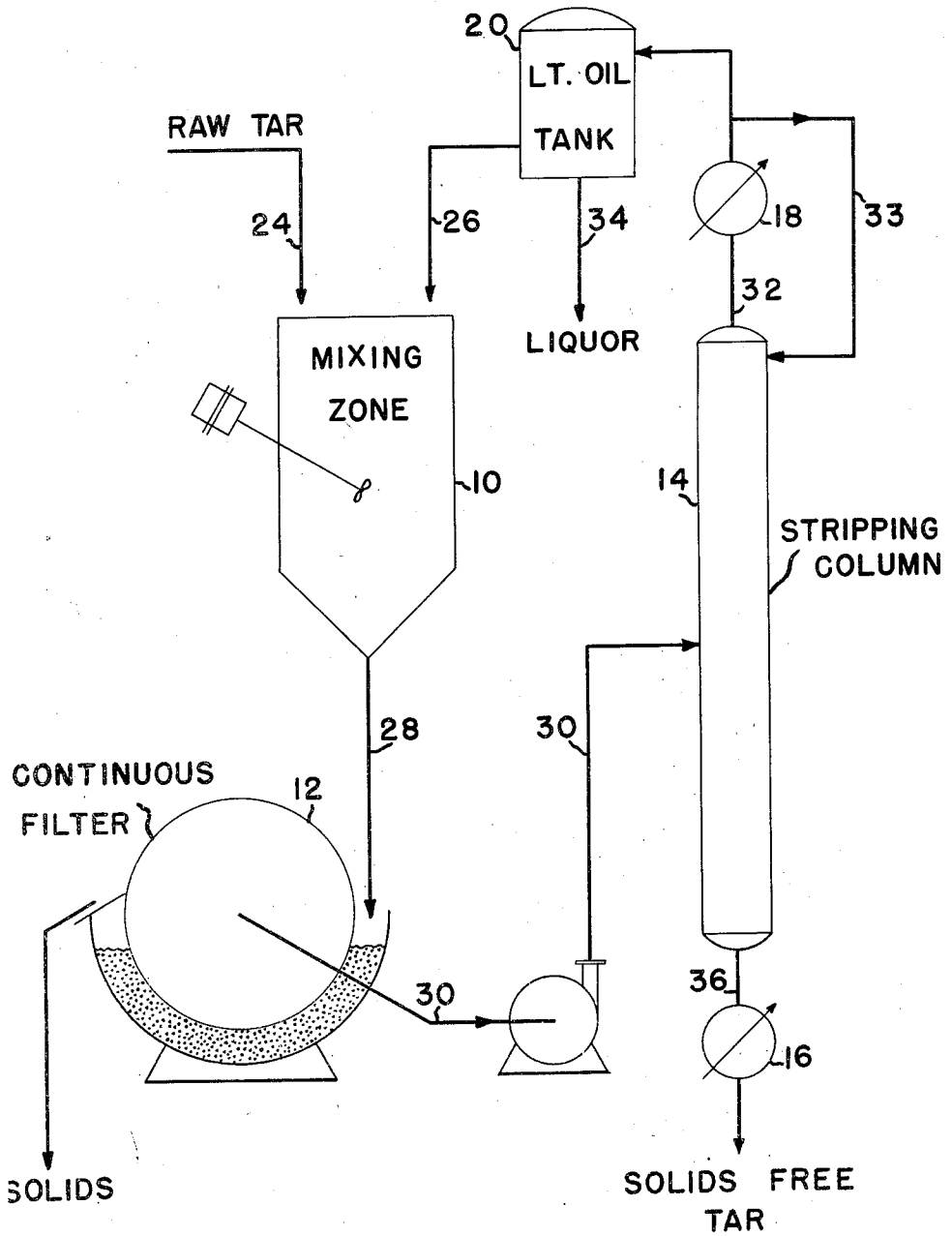

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PROCESS FOR REMOVING FINELY DIVIDED SOLIDS FROM RAW LOW TEMPERATURE CARBONIZATION COAL TARS

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The present invention relates to a process for separating finely divided solids from low temperature carbonization coal tars, and more particularly to a process for effecting this separation by agglomerating the solids with a portion of the tar itself.

The present application is a continuation-in-part of copending U. S. application S. N. 260,265, filed by me on December 6, 1951, now abandoned, and entitled "Process for Removing Finely Divided Solids from Raw Low Temperature Carbonization Coal Tars."

In continuous processes for carbonizing coal at low temperature, the tar product often contains a high concentration of finely divided particles of coal or partially devolatilized solid fuel. The presence of these particles in the product tar is occasioned by entrainment of the particles in the effluent gas and tar vapors from the carbonization process. Some low temperature tars will contain 15 to 25 percent by weight of solids. Frequently more than 50 percent by weight of these solids will pass through a 325 mesh U. S. standard screen. Because of the very fine consistency of these solids, they will not settle out of the raw tar on standing. Moreover, their removal from the tar by filtration is impractical since the particles instantly clog the interstices of any conventional filtering equipment. The high viscosity of the tar and the hard sediment makes continuous centrifuging ineffective for the removal of these solids.

The presence of these solids in the tar seriously reduces the value of the tar. Conventional processing of the solids laden raw tar for recovery of valuable tar acids and oils by such methods as distillation or extraction is difficult. Moreover if the solids laden tar is refined, the solids become even more concentrated in the heavy pitch remaining after the lighter, more valuable constitutents have been removed. Hence the ash content of the residual pitch increases and its value correspondingly decreases.

The primary object of this invention is to recover a solids-free tar from raw low temperature carbonization tar.

Another object of the present invention is to remove the finely divided solids from low temperature carbonization tar.

A further object of my invention is to produce a virtually ash free pitch from low temperature tar.

The term "low temperature tar" as used herein means the normally liquid product from a coal carbonization process operated in the usual low temperature range, i. e., below about 1200° F.

By the term "coal" I comprehend all ranks of coal, including bituminous, sub-bituminous, brown coal, lignite, and the like.

According to the present process, raw tar containing finely divided solids is agitated with a mixture of a predominantly non-aromatic low boiling distillate tar oil containing a controlled amount of low boiling tar acids. For the purpose of this specification, this mixture of low

boiling tar oils and a small amount of low boiling tar acids shall be termed solvent.

The solvent dissolves a major portion of the normally liquid tar and rejects from solution a small amount of the heavy pitch. Droplets of this rejected pitch become coated with the powdery solids from the tar and settle out from the mixture in discrete agglomerated particles which are recovered separately from the liquid tar. The solvent is stripped from the liquid tar and recycled. A significant feature of the present invention is the autogenous production of small amounts of solvent from the raw tar being treated. This feature permits continuous operation of the solids separation process without requiring the addition of extrinsic solvent.

The low boiling tar oils which form the solvent are those low boiling hydrocarbons normally present in low temperature carbonization tars. Those low boiling tar oils represent less than about 5 percent of the weight of low temperature carbonization tars, and usually less than about 2 percent, depending upon the distillation techniques selected. The composition of the low boiling tar oil from a typical low temperature carbonization tar is presented in The Journal of the Institute of Fuel, vol. XX, No. 113, April 1947, at page 111. As set forth in Table IV of the reference, the low boiling oil represents about 2 percent of the total condensed liquid products from low temperature carbonization. Its composition is as follows (in percent):

Crude phenols	12
Saturated hydrocarbons (paraffins and naphthenes)	21.5
Olefinic hydrocarbons	34.5
Aromatic hydrocarbons	30

The exact composition of low boiling tar oils may vary somewhat from this typical analysis, but in all cases, low temperature carbonization tars are predominantly non-aromatic in contrast to the tars resulting from high temperature carbonization.

For the purpose of this invention I prefer to use as solvent the entire low boiling tar distillate fraction having a boiling end point temperature below 200° C. but above 155° C. The initial boiling point of this fraction is generally about 85° C., but may vary somewhat with the nature of the tar from which the low boiling tar oil is derived. While the entire fraction is preferred for ease of operation, nevertheless any narrower fraction thereof may be employed. The low boiling tar oil must in addition contain at least 2 percent by volume of tar acid in order to comprise the solvent of this invention. In some instances the solvent may be a distillate fraction of the low temperature carbonization tar being an end point in excess of 200° C. In other instances the solvent may be a blend of two or more distillate fractions of the tar.

I have discovered that a solvent fulfilling the specifications and suited to the purposes of this invention can be made without the deliberate addition of tar acids by recovering the entire distillate fraction from the low temperature carbonization tar which inherently contains the requisite quantity of tar acids. The distillation end temperature may be selected so as to control the tar acids content quite closely. Those fractions having a distillation end point below about 155° C. will contain virtually no tar acids whereas fractions having a distillation end point of about 200° C. might contain 15 to 30 percent tar acids.

The solvent from low temperature carbonization tar, by itself, is not wholly miscible with a batch of raw tar; instead, the solvent effects a separation of a tacky nonfilterable pitch phase together with the particles of solid fuel contained in the raw tar. The liquid portion of raw low temperature carbonization tars is wholly miscible

with tar acids by themselves; thus tar acids alone will not reject pitch from low temperature carbonization tars.

Nevertheless, if solids-laden tars are treated with low boiling tar oils containing the proper amount of tar acids for the particular raw tar, an optimum quantity of pitch can be rejected from the raw tar to bind virtually all the raw tar solids into readily filterable larger agglomerated particles. Insufficient tar acids in the treating solvent result in excessive pitch rejection and accompanying non-filterability. Excessive tar acids in the treating solvent result in insufficient pitch rejection and very little improvement in the filterability of the raw tar.

The treating solvent should contain at least 2 and preferably less than 20 percent by volume of tar acids, with the balance comprising low boiling tar oils. The exact optimum concentration depends upon the raw tar being treated. Factors controlling the raw tar composition include the type of coal used in the carbonization process, the nature of the carbonization process, the technique of tar recovery and the fraction of solid fuel particles found in the raw tar.

For a better understanding of my invention and its objects, reference should be had to the drawing which is a schematic representation of the preferred embodiment of my invention.

In the drawing, **10** is a mixing vessel, **12** is a continuous filter, **14** is a solvent stripping column, **16** is a cooler, **18** is a condenser, and **20** is a solvent storage vessel.

Raw tar from a low temperature carbonization process is introduced continuously into the mixing vessel **10** through conduit **24**. This raw tar contains all the normally condensible overhead products from a low temperature carbonization process. In addition, the tar contains particles of solid fuel which have been entrained in the vapors leaving the carbonizing apparatus. These particles of solid fuel are coal or partially devolatilized coal or a mixture of both, depending upon the carbonizing apparatus and the starting coal. In the Disco carbonization process,[1] for example, tars are recovered containing up to 25 weight percent of solid fuel particles, which are coal and partially devolatilized fuel, with the coal particles predominating. In other carbonization processes, the solid fuel particles in the tar are almost exclusively partially devolatilized fuel. These fines, of course, possess a high ash composition.

Solvent from vessel **20** is introduced into the mixing vessel **10** through conduit **26**. In general from 0.5 to 3.0 volumes of solvent are employed for each volume of raw tar. Preferably the solvent to raw tar ratio is about 1:1. Low solvent to tar ratios (i. e., less than 0.5:1) produce tacky, non-filterable pitch precipitates. There appears to be little advantage in increasing the solvent to tar ratio above 3:1.

In the mixing vessel **10**, the intermixing of the solvent and the raw tar rejects a portion of the heavy pitch from the liquid phase. Droplets of this rejected, sticky pitch become coated with the powdery solids from the raw tar and settle out as discrete, non-tacky, agglomerated particles.

The mixture of agglomerated particles, tar and solvent passes from the mixing vessel **10** through conduit **28** to a continuous filter **12**. The precipitated pitch and agglomerated solids are collected as a filter cake which can be recovered and briquetted along with additional coal or char to produce a solid fuel briquet. Alternatively, since the process of this invention is integrated with a low temperature carbonization operation, the filter cake can be returned to the carbonization vessel as a feed material. Since the filter cake contains some solvent and tar components, it can be treated to permit recovery of the valuable liquids.

The filtrate from the continuous filter **12** is pumped through conduit **30** to a stripping column where the solvent is distilled overhead. Since the raw tar from the carbonization plant contains low boiling tar oils, as well as low boiling tar acids, there are no solvent make-up problems associated with the present process. Each unit of raw tar being treated supplies a small amount of the low boiling tar oils and tar acids which constitute the solvent. This autogenous solvent production is sufficient to compensate for any reasonable operating solvent losses in the system.

It is significant to note that the solvent and the filtered tar need not be separated immediately. After the initial pitch rejection in the agitation stage, no further separation will occur through the action of the solvent. The solvent (as the term is defined in this application) of this invention has no tendency to react continuously with the heavy components of the pitch. Not all the pitch contained in the raw tar is rejected by the solvent treatment of this invention. Much of the pitch remains in solution after mixing with the solvent and is recovered as a valuable ash-free product.

The composition of the solvent is controlled by regulating the operating conditions of the stripping column which provides an overhead low boiling tar oil product containing the desired tar acids concentration. The lowest boiling tar acid, phenol, has a normal boiling temperature of 180° C. in its pure form. However, small amounts of phenols and other low boiling tar acids form azeotropes and boil along with the low boiling tar oils at temperatures below the normal boiling point of the pure tar acids. In fact I have found that filtrate fractions having a boiling end point temperature of about 160° C. normally contain the proper amount of tar acids required to treat some tars in the agglomerating step of the process. Thus the tar oil distillate fraction boiling below about 160° C. usually contains about 2 to 10 percent tar acids by volume resulting from the azeotropic character of the low boiling tar acids. For most raw tars, this 160° C. boiling end point fraction will be a suitable treating solvent. The discovery that this low boiling tar oil possesses tar acid azeotropes and can be used as treated solvent greatly simplifies the solids removal process.

Solvents with high tar acids concentration precipitate less pitch from the raw tar and hence permit the recovery of slightly greater quantities of liquid product tar. However, when the tar acids concentration in the solvent is too high, no pitch precipitation occurs and the objectionable solids cannot be readily removed from the liquid tar.

The stripped solvent passes overhead from the stripping column **14** through conduit **32** and condenser **18** to the solvent storage vessel **20**. A portion of the overhead solvent is returned as reflux to the column **14** through conduit **33**. Any water in the solvent stream settles in vessel **20** and is withdrawn through a conduit **34**. The water is combined with carbonization plant liquor for treatment.

The bulk of the tar and pitch contained in the initial raw tar is recovered as a bottom product from the stripping column **14** through conduit **36** and cooler **16**. This tar is substantially free of any solid material and can be processed easily in conventional distillation and extraction operations. The pitch contained in the bottom product from the stripping column, because it is essentially ash-free, finds many valuable uses, e. g., as a raw material for the production of electrode carbon.

In order to commence commercial operation of a solids removal system for raw low temperature carbonization tars it is frequently impractical to attempt to collect a supply of low boiling tar oils to be used as solvent. Accordingly for the initial operation of a raw tar solids removal system, commercial low boiling materials may be obtained which will serve the same purpose as the solvent described herein. For example, benzene alone is an excellent material for treating raw tar to effect the desired agglomeration of pitch together with

[1] "Development of the Disco Process of Low Temperature Carbonization" by C. E. Lesher, Mining Engineering 4, 287–99 (March 1952).

dry agglomerated solid particles. The benzene would circulate through the system until replaced by the autogenous solvent of this invention. Foreign solvents such as benzene might be selected which would effect the proper amount of pitch rejection to bind the solids in the raw tar. Benzene, of course, is an unsatisfactory solvent for continued solids removal use because of its expense and because excessive solvent and tar are retained in the filter cakes resulting from operation with benzene.

The pitch rejection step of the present invention is quite effective in causing a particle size accretion of the solids contained in raw tar. In fact it is possible to recover solids-free tar simply by decantation of the liquid remaining above the rejected pitch and solids. Such a system, of course, could be employed in combination with a vacuum drying of the settled solids to recover the liquids associated with the solids. A centrifuging step can be substituted for the filtration step described in connection with the drawing. The presence of the solvent tends to reduce the viscosity of the tar and the increased size of the solids readily permits their centrifugal separation.

Example

The present process was employed to remove solids from a raw tar derived from the low temperature carbonization of Pittsburgh seam coal.

The raw tar contained about 16 percent by weight of finely divided solids which had a differential screen analysis as follows:

Sieve size:	Weight percent
on 48	0.0
100	0.6
200	0.6
325	48.6
through —325	50.2

This tar was unfilterable in its raw state. However, after agitating this raw tar at 24° C. with an equal volume of solvent composed of low boiling tar oils having a boiling end point of 160° C. and containing 6 percent by volume of low boiling tar acids, the mixture was filtered without difficulty.

The liquid filtrate contained virtually no ash and the recovered solvent was a greater volume than that employed in the agitation stage. The solvent stripped tar was about 78 percent by weight of the initial raw tar. The differential screen analysis of the filter cake solids was as follows:

Sieve size:	Weight percent
on 4	4.2
8	15.1
14	13.5
28	25.5
48	23.9
100	10.1
200	4.3
through —200	3.4

If desired, filtration rates for the tar can be increased even further by adding small quantities of coarse char to the raw tar before the solvent treatment.

As seen from the example, the present process can be operated at ordinary room temperatures. Slightly higher temperatures permit operation of the process with a reduced tar acids concentration in the solvent.

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. A process for removing solids consisting essentially of finely divided solid particles from the class of coal and partially devolatilized coal from raw low temperature carbonization tar which comprises mixing the raw tar with 0.5 to 3.0 volumes of a predominantly nonaromatic low temperature carbonization tar distillate fraction containing at least 2 percent by volume of tar acids, separating rejected pitch and agglomerated solids, and recovering the liquids.

2. In the removal from raw low temperature carbonization tar those particles of solid fuel which become entrained in the tar during the carbonization and tar recovery processes, the improvement which comprises mixing said raw tar with 0.5 to 3.0 volumes of a solvent comprising a predominantly nonaromatic distillate fraction from low temperature carbonization tar containing at least 2 percent tar acids by volume, separating from the resulting mixture rejected pitch and agglomerated solids, and recovering the liquids.

3. A process for removing solids consisting essentially of finely divided particles from the class of coal and partially devolatilized coal from raw low temperature carbonization tar which comprises mixing the raw tar with 0.5 to 3.0 volumes of a predominantly nonaromatic low temperature carbonization tar distillate fraction having a boiling end point below 200° C. and containing 2 to 20 percent by volume of tar acids, separating rejected pitch and agglomerated solids and recovering the liquids.

4. A process for removing solids consisting essentially of finely divided particles from the class of coal and partially devolatilized coal from raw low temperature carbonization tar which comprises mixing raw low temperature carbonization tar with 0.5 to 3.0 volumes of a predominantly nonaromatic low temperature carbonization tar distillate fraction having a boiling end point below 200° C. and containing 2 to 20 percent by volume of tar acids, filtering the resulting mixture and recovering the filtrate.

5. A process for removing solids consisting essentially of finely divided particles from the class of coal and partially devolatilized coal from raw low temperature carbonization tar which comprises adding to the raw tar 0.5 to 3.0 volumes of a predominantly nonaromatic low temperature tar distillate fraction having a boiling end point below 200° C. and containing 2 to 20 percent by volume of tar acids, separating rejected pitch and agglomerated solids from the mixture, recovering the liquids, separately recovering from said liquids a distillate fraction having a boiling end point below 200° C. and containing 2 to 20 percent by volume of tar acids, and separately recovering the remaining liquids.

6. A process for recovering ash-free tar and pitch from raw low temperature carbonization tar which comprises continuously agitating each volume of tar along with 0.5 to 3.0 volumes of solvent comprising a predominantly nonaromatic low temperature carbonization tar distillate fraction having a boiling end point below 200° C. and containing 2 to 20 percent tar acids by volume, continuously filtering the mixture of tar and solvent, recovering the filtrate, recovering from said filtrate a distillate fraction having a boiling end point below 200° C. and containing 2 to 20 percent by weight of tar acids, separately recovering the remaining filtrate, and recovering said distillate fraction as solvent.

7. A continuous process for removing solids consisting of finely divided particles from the class of coal and partially devolatilized coal from raw low temperature carbonization tar which comprises continuously mixing each volume of said tar with 0.5 to 3.0 volumes of solvent comprising a predominantly nonaromatic low temperature carbonization tar distillate fraction having a boiling end point below 200° C. and containing 2 to 20 percent tar acids by volume, continuously filtering the mixture of

tar and solvent, recovering the filtrate, recovering from said filtrate a distillate fraction having a boiling end point temperature below 200° C., said temperature being selected so that the distillate fraction will contain 2 to 20 percent by volume of tar acids, separately recovering the remaining filtrate and recovering said distillate fraction to be used as solvent in a cyclic manner.

8. A process for removing solids consisting essentially of finely divided particles from the class of coal and partially devolatilized coal from the raw tar produced by the low temperature carbonization of high volatile bituminous coal which comprises mixing each volume of said tar with 0.5 to 3.0 volumes of solvent comprising a predominantly nonaromatic distillate fraction of low temperature carbonization tar having a boiling end point below 200° C. and containing 2 to 20 percent tar acids by volume, filtering the mixture of tar and solvent, recovering the filtrate, recovering as solvent from said filtrate the distillate fraction having a boiling end point below 200° C. and separately recovering the remaining filtrate.

9. A continuous process for removing solids consisting essentially of finely divided particles from the class of coal and partially devolatilized coal from the raw tar produced by the low temperature carbonization of high volatile bituminous coal which comprises mixing each volume of said tar with 0.5 to 3.0 volumes of solvent comprising a predominantly nonaromatic distillate fraction of low temperature carbonization tar having a boiling

end point below 200° C. and containing 2 to 20 percent tar acids by volume, continuously filtering the mixture of tar and solvent, recovering the filtrate, recovering as solvent from said filtrate a distillate fraction having a boiling end point below 200° C., separately recovering the remaining filtrate, and recycling said distillate fraction to be used as solvent in a cyclic manner.

10. The process of claim 9 in which the high volatile bituminous coal is Pittsburgh seam coal.

11. In the removal from raw low temperature carbonization tar of those particles of solid fuel which become entrained in the tar during the carbonization and tar recovery processes, the improvement which comprises mixing said raw tar with 0.5 to 3.0 volumes of a solvent comprising a predominantly nonaromatic distillate fraction from low temperature carbonization tar having an end boiling point below 200° C. and containing at least 2 percent by volume of tar acids, separating from the resulting mixture rejected pitch and agglomerated solids and recovering the liquids.

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