This invention relates to a coke oven by-product recovery process, and more particularly to a process by which pyridine bases and tar bases can be recovered from coke oven gases.

In the destructive distillation of coal and other carbonaceous materials such as peat, lignite and the like, various valuable substances are given off as hot gases. Among these are the so-called "pyridine and tar bases." The term "pyridine and tar bases" is used to indicate compounds normally recovered from coke oven gases which have a basic reaction. Among these compounds, the principal ones are pyridine, picolines, lutidines, colidines, and quinolines.

Specific pyridine and tar base compounds which have been isolated from coke oven gases include pyrrole, pyridine aniline, 2-methyl pyridine, ortho-toluidine, 2,3-dimethyl pyridine, indole, 1,2,3,4-tetramethyl pyridine, quinoline, iso-quinoline, 2-methyl quinoline, 1-methyl iso-quinoline, 1-naphthylamine, 2,8-dimethyl quinoline, carbazole, acridine, phenanthridine, hydroacridine, 2-methyl carbazole, and benzo-carbazole.

The total amount of pyridine and tar bases recovered and the relative proportions of individual compounds, will depend on the nature of the carbonaceous material and the conditions of carbonization.

For many years, not much thought was given to the recovery of pyridine and tar bases as such. Recently, however, these compounds have grown in importance to the chemical industry because of their increased use, for example, in the manufacture of waterproofing materials, sulpha drugs and other medicinal products, organic chemicals, acrylic fibers, and insecticides, with the result that the recovery of pyridine and tar bases has become an increasingly important part of coke oven by-product recovery practice.

In the normal coke oven by-product recovery plant, the hot gases coming from the ovens are generally first cooled and treated to remove tar therefrom. Subsequently, they may be treated with a mineral acid, such as sulphuric acid to remove ammonia with production of an acid ammonium liquor, such as an ammonium sulphate liquor.

Particularly advantageous types of such recovery processes are described in detail in the copending applications of Gerald L. Eaton, Serial No. 161,325, filed May 11, 1950, and Serial No. 186,655, filed September 19, 1950; of Thomas G. Reynolds Serial No. 186,886, filed September 26, 1950, now Patents Numbers 2,649,403; 2,649,405; and 2,649,404, respectively; and in my own copending application, Serial No. 354,542 filed on even date herewith.

In recovery processes of this nature, basic compounds of the type described are ordinarily found both in the tar and in the acid ammonium liquor resulting from the ammonia-removal treatment.

Conventionally, that portion of the basic compounds separated from the coke oven gases with the tar is called "tar bases," while that portion separated with ammonia is referred to as "pyridine bases." This terminology will be used throughout the present specification and claims. It will be understood that in general the same compounds appear in both the tar bases and the pyridine bases, although the proportions of individual compounds may be different in each group.

In the acid ammonium liquor, the pyridine bases are present as salts of the mineral acid used, e.g., as pyridine sulphate where the mineral acid is sulphuric acid. In the tar, the tar bases are mixed with tar acids and neutral oils. In view of the dissimilar natures in which the tar bases and the pyridine bases are found, it might be expected that different methods would be used for their recovery, and, generally speaking, each has hitherto been processed separately. Two recovery systems involve duplication of apparatus with higher initial costs and higher labor expenses.

It is an object of the present invention to provide a more efficient means for recovering tar bases and pyridine bases from coke oven gases.

It is another object to provide an improved method for recovering tar bases from a mixture of other tar components.

It is a further object of the present invention to provide a method for coke oven by-product recovery wherein tar bases may be recovered along with the pyridine bases.

Other objects of the invention will appear from a consideration of the following specification and claims.

According to the present invention, impure tar bases are directly mixed with acid ammonium liquor containing salts of pyridine bases so that the acid liquor reacts selectively with the tar bases to form the corresponding salts which may then easily be separated from other tar components. These tar bases and pyridine bases are concentrated in a single stream in the same form, i.e., as salts, and may be recovered in one operation.

The drawing is a flow sheet of a coke oven by-product recovery process, embodying the novel tar base recovery process.

As shown in the drawings, in one form of coke oven by-product recovery process, hot gases generated in coke oven 1, first pass into a main 2, where they are contacted with an aqueous flushing liquor injected as at 3. By means of this liquor, the coke oven gases are reduced in temperature to between about 60° C. and about 100° C., ammonia is absorbed, and tar contained in the gases is condensed. The condensed tar containing tar bases, and the foul flushing liquor with its absorbed ammonia, pass through downsomer 4 into flushing liquor decanter 5.

The coke oven gases flow from downsomer 4 to primary cooler 6 where they are again contacted with an aqueous liquor drawn in this case from circulating liquor decanter 7.

By means of the circulating liquor in primary cooler 6, the temperature of the coke oven gases is further decreased to from about 20° to about 40° C. The circulating liquor used in primary cooler 6 is withdrawn and returned to circulating liquor decanter 7.

The coke oven gases passing overhead from primary cooler 6, are charged to a naphthalene scrubber 7a where they are contacted with an absorber oil for the removal of naphthalene. Passing out of naphthalene scrubber 7a, the gases flow through an electrostatic precipitator 8, where residual tar, present as a "fog," may be further removed.

The gases are then compressed in booster 9 to a pressure which is dependent upon the demand requirements and upon the pressure drop of downstream apparatus, but is preferably above about 4 p. s. i. g.

The compressed gases are then delivered to an ammonia saturator 10 where they are contacted with a mineral acid, preferably with sulphuric acid.
In the saturator 10, the ammonia present in the gases is absorbed as the salt of the mineral acid employed, for example, ammonium sulphate. At the same time pyridine bases are absorbed as salts of the acid, for example, pyridine sulphate. The ammonium sulphate may be delivered as a slurry to centrifuge 11, where the crystals are separated, leaving an acid liquor comprising ammonium sulphate, pyridine base sulphates, and sulphuric acid. The coke over gases now freed of ammonia pass through an acid catcher 12, to remove any acid which may have been picked up in the saturator 10, and then to a final cooler 13 where they are contacted with water to reduce their temperature to between about 20° C. and about 40° C.

From the final cooler 13, the gases pass into a light oil scrubber 14 where they are again contacted with an absorber oil, in this case to remove light oils. The gases, on leaving light oil scrubber 14, may be charged to fuel lines or burners.

Turning now to decanters 5 and 7, the tar removed from the gases forms a bottom layer in these decanters, leaving an aqueous upper layer containing ammonia. The tar comprises a great many constituents, including pitch, creosote oils, naphthalene, tar acids, tar bases, and light oil. The tar bases may comprise between about 0.4% and about 0.7% of the weight of the tar. To separate these components, the tar is charged to tar and light oil distillation plant indicated generally as 15. The particular process by which the tar is distilled is not a part of this invention, but, advantageously, the distillation procedure shown in my said copending application S. N. 354,542 (from which the section labeled 15 in the present drawing is derived) or in the copending applications of Gerald L. Eaton, Ser. Nos. 161,325 and 185,665; or in the copending application of Thomas G. Reynolds Ser. No. 186,886, may be used.

As indicated in the figure, in the tar distillation plant 15, the tar coming from decanters 5 and 7 may first be processed to free it from water, as in dehydrator 16, then preheated as in heater 17, and charged to a distillation column 18.

In the distillation column 18 an overhead steam may be taken off which comprises tar acids, tar bases, and neutral materials such as naphthalene and light oils. Higher boiling components removed from distillation column 18 as at 18a, may be processed for further separation. For details of such further processing, reference may be had to my said copending application 354,542. According to the invention, the stream taken overhead from the fractionator 18, usually containing between about 1.4% and about 5.5% by weight tar bases, say about 2.5%, as well as tar acids and neutral oils, is charged to a weak caustic settler 19 where it is contacted with a dilute alkaline solution, for example, with dilute sodium hydroxide, in this case drawn from a strong caustic settler 20. Preferably the dilute alkaline solution charged to weak caustic settler 19 will contain between about 5% and about 30%, usually about 10% sodium hydroxide. Other soluble bases such as potassium hydroxide may be used. By means of the alkaline solution in settler 19, the tar acids from fractionator 18 are neutralized and form a water layer at the bottom of the settler, containing sodium carbonate and like salts of tar acids. An upper layer forms in the settler 19 comprising the tar bases and the neutral oils. This upper layer is drawn off through line 21.

In the settler 19, now to the saturator centrifuge 11, as pointed out above, the acid liquor from the centrifuge contains the ammonium salt of the acid and more importantly, pyridine bases as salts of the acid employed. In general, when sulphuric acid is used, the acid liquor will contain by weight from about 3% to about 15%, preferably about 6% H2SO4, from about 45% to about 50% (NH3)2SO4, usually about 47%, and from about 1% to about 8%, usually about 3% pyridine base sulphates.

According to the invention, this acid liquor is now mixed with the tar base-neutral oil layer drawn from weak caustic settler 19 and the mixture is charged to acid settler 22. The acid mixture from the saturator reacts with the tar bases from settler 19 neutralizing those bases and forming the corresponding salts. Thus, if the mineral acid used in the saturator 10 is sulphuric acid, salts such as pyridine sulphate will be formed in settler 22 from the tar bases drawn from settler 19. The salts form in an aqueous lower layer which also contains the ammonium and pyridine base salts from the saturator, leaving an upper layer comprising the neutral oils, and such tar acids as were not removed in the weak caustic settler 19 and which are sprung by the acid in the acid settler.

The lower layer in acid settler 22, containing the acid salts of the pyridine and tar bases, is drawn off and further processed to spring the pyridine and tar bases and recover them as described below.

The upper layer in settler 22 is drawn off and charged to the strong caustic settler 20, in admixture with an alkaline such as sodium hydroxide entering through line 20a. By this means residual tar acids are neutralized and collected in a lower aqueous layer leaving an upper layer of neutral oil. The lower layer from settler 20 is drawn off and recycled to the weak caustic settler 19 as noted above.

The neutral oil drawn off through line 20b may be returned to the distillation plant 15.

Referring now to the ammonia liquor which forms the upper layer in flushing liquor recanter 5, this is charged to a conventional ammonia still 23 having a lime leg 24 for the separation of fixed ammonia.

In the still 23 ammonia is removed from the aqueous flushing liquor and is taken overhead through line 25. The steam of ammonia from line 25 passes through a pyridine-tar bases stripper 26 whose purpose will be described below, and the overhead from stripper 26, rich in ammonia, is charged to a springer 27, where it contacts the acidic pyridine-tar bases mixture drawn from the settler 22. The ammonia reacts with the pyridine-tar bases mixture to spring the pyridine and tar bases from their combination with the acid. The reactant mixture passes into a receiver 28 where volatile constituents are allowed to pass overhead as at 28a. If desired, such constituents may be returned to the foul gas line (not shown). The liquid mixture from receiver 28 is then charged to a settler 29 where the pyridine and tar bases form as an upper layer, leaving a lower layer consisting principally of an aqueous ammonium-acid salt solution. The lower aqueous layer 35, 54, 54c is returned through line 26 to the distillation plant 15 where it is contacted with steam entering at 26a and with the steam of ammonia from line 25, to remove any residual pyridine-tar bases which may have been retained in the aqueous layer in separator 29.

It must be emphasized that the upper layer in settler 29 contains substantially all the pyridine and tar bases present in the coke oven gases. Thus, by utilizing the saturator liquor to separate the tar bases from other tar components, I have at the same time succeeded in concentrating both the tar bases and the pyridine bases in a single recovery stream.

It will be understood that the coke oven by-product recovery process described may be modified or changed to a very considerable extent without departing from the invention, and that the figures given are for illustrative purposes only.

In general, my method may be employed with advantage in any coke oven by-product recovery process wherein

In the basic compounds referred to are removed from coke oven gases partially with tar and partially in an acid-ammonia removal treatment.

Although sulphuric acid is the acid generally employed in removing ammonia, the present method may easily be adapted to processes employing other acids such as phosphoric acid.

What I claim is:

1. In a coke oven by-product recovery process wherein
hot coke oven gases are treated to remove tar containing tar bases therefrom, and wherein said gases are subsequently treated with a mineral acid to remove ammonia and pyridine bases therefrom with the production of an aqueous acid liquor containing salts of said pyridine bases, an ammonia salt and the free acid, the steps of mixing the tar bases with said aqueous acid liquor to convert said tar bases to their corresponding salts and treating said mixture to recover said tar bases and said pyridine bases in a single stream.

2. Process as claimed in claim 1, wherein the mineral acid is sulfuric acid.

3. In a coke oven by-product recovery process, wherein hot coke oven gases are treated to remove tar containing tar bases and tar acids therefrom, and wherein said gases are subsequently treated with a mineral acid to remove ammonia and pyridine bases therefrom with the production of an aqueous acid liquor containing salts of pyridine bases, an ammonia salt and the free acid, the steps of distilling said tar to produce a stream containing tar acids, tar bases, and neutral oils, contacting said stream with a weak caustic solution to separate said tar acids from said tar bases and neutral oils, mixing said tar bases and neutral oils with said aqueous acid liquor to convert said tar bases to their corresponding salts dissolved in said aqueous acid liquor, separating the dissolved salts of said tar bases and of said pyridine bases from said neutral oils and treating said acid liquor to recover the pyridine and tar bases contained therein.

4. Process as claimed in claim 3, wherein said mineral acid is sulfuric acid.

5. Process as claimed in claim 3 wherein said acid liquor containing said dissolved salts is contacted with ammonia to spring the pyridine and tar bases contained therein, and the pyridine and tar bases are then removed from the aqueous liquor.

6. In a coke oven by-product recovery process, wherein hot coke oven gases are treated to remove tar containing tar bases therefrom, and wherein said gases are subsequently treated with a mineral acid to remove ammonia and pyridine bases therefrom with the production of an aqueous acid liquor containing salts of pyridine bases, an ammonia salt and the free acid, the steps of mixing the tar bases removed with the tar with said aqueous liquor to convert said tar bases to their corresponding salts dissolved in said aqueous liquor, contacting said aqueous liquor containing said dissolved pyridine and tar base salts with ammonia to spring the pyridine and tar bases contained therein, and removing the pyridine and tar bases from the liquor.

7. In a coke oven by-product recovery process, wherein hot coke gases are treated to remove tar containing tar bases therefrom, and wherein the gases are also treated with an aqueous acid liquor to convert said tar bases to their corresponding salts and treating said mixture to recover said tar bases and pyridine bases in a single stream.

8. In a coke oven by-product recovery process wherein hot coke oven gases are treated with an aqueous liquor to remove ammonia and tar containing tar bases therefrom, wherein said gases are subsequently further treated with an aqueous acid liquor to remove ammonia and pyridine bases therefrom with the production of an aqueous acid liquor containing salts of pyridine bases, an ammonia salt and free acid, and wherein said aqueous liquor used to remove ammonia and tar from said gases is distilled to recover ammonia therefrom as a vapor stream, the steps of mixing the tar bases removed from the tar with said aqueous acid liquor containing salts of pyridine bases, an ammonia salt and free acid to convert said tar bases to their corresponding salts dissolved in said acid liquor, contacting said aqueous acid liquor containing dissolved pyridine and tar base salts with ammonia to spring the pyridine and tar bases contained therein, decanting the spring pyridine and tar bases from their aqueous liquor, and stripping dissolved pyridine and tar bases from the liquor remaining after said decantation.

9. A process as claimed in claim 8, wherein the ammonia vapor used in said stripping step is subsequently used to spring the tar and pyridine bases.

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