

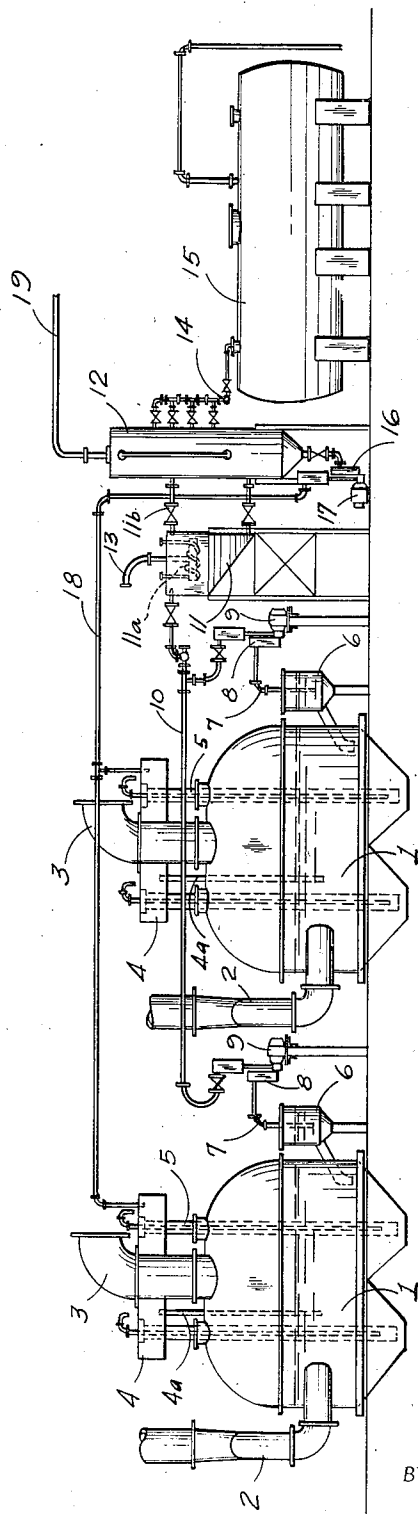
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METHOD FOR RECOVERING PYRIDINE

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BY

INVENTORS
MAX D. WALD
& FRANK A. KARNATZ.
Richey Watts
ATTORNEYS.

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METHOD FOR RECOVERING PYRIDINE

Max D. Wald, University Heights, Ohio, and Frank A. Karnatz, Indianapolis, Ind., assignors, by direct and mesne assignments, to Republic Steel Corporation, Cleveland, Ohio, a corporation of New Jersey

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This invention relates to a new and improved method for recovering pyridine economically and efficiently from coke oven gases.

Altho it has long been known that pyridine is present in gases which are formed when coal is being coked, the only method proposed, so far as we are aware, for recovery of pyridine from such gases is the so-called "batch" process, and it has been used little, if at all, in the commercial production of pyridine.

This "batch" process consisted briefly of passing coke oven gases thru a saturator containing dilute sulphuric acid until the solution was substantially saturated with pyridine, that is, until the pyridine content was approximately 5%. Then the saturator was cut out of the line and emptied and the liquid was treated with ammonia to "spring" or release the pyridine which then rose to the surface and could be separated from the other liquid and thereby recovered.

There were certain outstanding objections and disadvantages inherent in this "batch" process. A considerable amount of equipment was required which not only would occupy space that might be at a premium at the coke plant but which would be expensive to install and to maintain. For example, storage tanks for the saturator solution and for the pyridine-free solution are necessary. The saturator in operation must be taken out of service so that the acid bath can be removed, and a spare saturator must always be available and ready for operation.

Another disadvantage was that the recovery of pyridine was inefficient or quite expensive. Since the sulphuric acid solution would rather quickly lose its power to absorb pyridine, the solution had to be withdrawn from the saturators at comparatively short intervals to avoid the loss of pyridine in the gases leaving the saturators and in the ammonium sulphate removed. The pyridine in the saturator bath goes to contaminate the ammonium sulphate and is lost. If, in order to avoid the loss of pyridine either in the gases leaving the saturator or in the precipitated ammonium sulphate, the saturator solution were withdrawn from the saturator at more frequent intervals, considerable labor would be required, inasmuch as the saturator or saturators would have to be emptied every day, and it would be necessary to have a clean saturator available for operation daily.

Thus the "batch" process was inherently objectionable in that it was expensive in its apparatus requirements and inefficient and unduly expensive in operation. The present method

avoids the objections and disadvantages of the "batch" process and has been found, in commercial operation, to be highly efficient and yet inexpensive.

The present invention may be briefly described as follows:

Coke oven gases, which have been freed from tar and other substances in the ordinary well-known manner but which contain ammonia and pyridine, are passed through a solution of dilute sulphuric acid wherein the ammonia and pyridine contents of the gases are absorbed. The solution containing ammonium sulphate and pyridine and its compounds is, preferably continuously, removed from the saturator and treated with ammonia gas derived from the distillation of the ammonia liquor obtained in the coking process. This treatment liberates the pyridine, the latter being separated and recovered while the solution from which the pyridine has been removed is returned to the saturator. The free acid content of the solution in the saturator is maintained substantially constant, as is conveniently done by adding fresh sulphuric acid continuously or periodically to the solution in the saturator to compensate for the acid which has been neutralized by ammonia in the formation of ammonium sulphate. The precipitated ammonium sulphate may be removed from the saturator periodically. The pyridine content of the saturator solution is maintained below about 3% and preferably below about 2%, as may be done by withdrawing the solution from the saturator at a suitable rate.

The present method differs from the "batch" process in such important particulars as the maintenance of a substantially constant free sulphuric acid content in the solution in the saturator; the prevention of the pyridine content from exceeding the point where losses of pyridine begin to occur either in the outgoing gases or in contamination of the precipitated ammonium sulphate; the practicing of the process continuously which is reflected directly in a reduction in the apparatus required because only one saturator is required per operating unit for long time operation with an additional saturator as a stand-by; and the reduced amount of labor required as contrasted with that required by the "batch" process.

The present invention will be fully understood by those skilled in the art by the following rather detailed description of the manner in which it has been practiced heretofore on a commercial scale.

As is shown by the drawing accompanying and forming a part of this application, the apparatus comprises a saturator 1 into which coke oven gases may enter thru main 2 and from which gases may escape into main 3. A second saturator is provided as a stand-by and is constructed like saturator 1 and is equipped with gas mains 2 and 3 and other connections and apparatus like the one about to be described.

Each saturator 1 is provided with drain tables 4 onto which the precipitated ammonium sulphate deposited in the hopper bottom part of the saturator may be discharged for separation from the saturator solution. The precipitated ammonium sulphate with some solution may be conveniently removed onto the drain tables by use of an ejector 5 which consists of two concentric tubes extending from above the drain table outside of the saturator to a point within the precipitate in the saturator, the inner tube being attached to a source of compressed air (not shown) and the upper end of the outer tube being connected to discharge onto the drain tables. The liquid which drains off from the precipitate returns to the saturator thru pipe line 4a and the ammonium sulphate is dried by means of centrifugal dryers and is then ready for sale.

Each saturator 1 is connected from a point well below the surface of the liquid contained therein to a reservoir 6 known as a lye pot. The construction and arrangement of this so-called lye pot and the pipes leading to and from it are such that certain operations are inherent in its use. This apparatus operates to show the level of liquid in the saturator because of the open connection between the pot and the saturator. This apparatus also inherently operates to reduce the amount of ammonium sulfate in the liquid passing into pipe 7 as compared with the amount in the liquid in the saturator. The sulfate so removed consists of sulfate in suspension as well as sulfate in solution in the liquid in the saturator.

When the present process is operating, sulfate in suspension is settling toward the bottom of the saturator under the force of gravity. Since the inlet pipe to the lye pot extends upwardly from a substantially horizontal open end such settling sulfate will tend to continue on past the open end of the inlet pipe and will not tend to flow up thru that pipe with outgoing liquid. A similar action takes place in the lye pot itself. As a result the amount of sulfate in suspension in the liquid entering pipe 7 is less than in the liquid in the saturator and the decrease is inherent in the normal operation of the apparatus including the pot 6, its intake pipe, and pipe 7.

The normal inherent operation of the lye pot and its intake pipe is to tend to cool the liquid passing therethru. This cooling action is the result of the exposure of these parts to the atmosphere as appears in the drawing and the lack of application of external heat to these parts. In view of the exposure of the lye pot to the air and the slow movement of liquid through it substantial cooling action is inherent and inevitable. Thus saturator liquid heated by the entering gases tends to cool in passing thru these parts. Since the solubility of ammonium sulfate decreases with temperature decreases, sulfate which was in solution tends to precipitate out in solid form as the temperature of the liquid

decreases and such sulfate is collected in solid form in the lye pot 6. A pipe 7, which has an inlet end below the surface of solution in the reservoir, leads to a centrifugal pump 8 which is driven by motor 9 which withdraws the saturator solution from the reservoir and pumps it into the pipe line 10 which empties into a treating or neutralizing tank 11. The tank 11 is preferably provided with a sloping bottom and an outlet near the lower end thereof which opens into a separating tank 12. A line 13 which is connected to a source of ammonia vapor enters the top of tank 11 and discharges ammonia into the lower portions of the pyridine-containing saturator solution therein. The tank 11 is provided with a cooling coil 11a and an outlet 11b in the upper portion thereof thru which the neutral solution may pass into the tank 12. The pyridine, which has been released from the saturator solution and which floats on the solution in tank 12, may be withdrawn therefrom thru line 14 to a tank 15 from which it may be removed for subsequent use or treatment. The pyridine-free solution in the lower part of tank 12 is withdrawn from the bottom thereof and may be pumped by centrifugal pump 16 actuated by motor 17 thru line 18 to the drain tables 4 of the saturator and returned thru pipes 4a into the saturators.

Such gases as enter tank 11 with the ammonia vapor and are not absorbed by the liquid, for example, carbon dioxide and hydrogen sulphide, pass into tank 12 and escape therefrom through vent 19.

Fresh sulphuric acid may be added to the solution in the saturators periodically or continuously by being delivered onto the drain tables or pumped into the saturator thru a line (not shown). When the present method is to be initiated, one or more saturators are supplied with a suitable quantity of water containing between about 6% and about 8% of sulphuric acid. In the apparatus shown on the accompanying drawing each saturator contains about 4,000 gallons of such a solution. Commercial, 77%, 60° Bé. sulphuric acid may be used.

Coke oven gases from which ingredients named above have been removed but containing ammonia and pyridine bases, are then passed thru mains 2 continuously into the solutions in the saturators. The ammonia and pyridine contents of the gases are absorbed by the solution substantially completely while the gases are passing therethru and, as time goes on, ammonia sulphate precipitates out of the solution and collects in the bottom parts of the saturators, and the pyridine content in the solution increases. It is preferable not to begin withdrawal of the solution from the saturators until the pyridine content is sufficiently high to make the recovery thereof economical. After a few hours, for example 4 hours, the pyridine concentration in the saturator solution will be sufficiently high for this purpose when the entering gases contain about .15 lb. of pyridine per ton of coal, for at that time the concentration should be about 1% and thereafter the removal of the solution may be continuous. When the pyridine concentration approximates 5%, much of the pyridine content in the gases entering the solution will not be absorbed but will pass out with the outgoing gases and with the ammonium sulphate. For the most efficient recovery of pyridine it is, therefore, preferable to maintain the pyridine con-

centration under about 1%, altho it may rise to as high as 2% without serious losses, and to maintain the acid concentration between about 6% and about 8%.

When the pyridine in the saturator solution has risen to the concentration desired, the solution is withdrawn, preferably continuously, and the withdrawn solution is treated as it is withdrawn, with ammonia gas in tank 11 and the pyridine content is recovered in tank 12. The solution which has been freed from pyridine is also preferably continuously returned to the saturators. It has been found that when 10,000-12,000 cubic feet of coke oven gas is being treated per minute, and the gas contains about .15 lb. of pyridine bases, the solution may be continuously withdrawn from the saturator at the rate of about three to four gallons per minute, and that the recovery under these conditions is above about 90% of the total pyridine content of the gases. When the loss amounts to as much as 10%, about two-thirds of the loss is by way of contamination of the sulphate and one-third is by way of the gas leaving the saturators.

When about 3800 tons of coal containing about .15 lb. of pyridine are coked per day, about 40 to 48 tons of 60° Bé., commercial sulphuric acid are added per day to the solution in the saturators to maintain the acid concentration at between about 6% and 7% strength.

The liquid withdrawn from the upper portion of tank 12 consists of pyridine, picoline, and higher homologues, together with some solution of sulphate of ammonia. This liquid may be further treated to recover and refine these ingredients.

Having thus described the present invention so that those skilled in the art may be able to understand and practice the same, what we desire to secure by Letters Patent is defined in what is claimed.

What is claimed is:

1. The method of recovering pyridine which includes the steps of continuously passing coke oven gas containing pyridine through a solution of dilute sulfuric acid in a chamber, maintaining the free acid concentration of said liquid substantially constant, maintaining the pyridine concentration of said liquid below about 3%, continuously flowing liquid containing pyridine from a point below the surface of liquid in said cham-

ber upwardly into and below the surface of the liquid in a second chamber, continuously withdrawing liquid from the second said chamber from a point above the bottom thereof, continuously treating the thus withdrawn liquid with ammonia gas to release the pyridine contained therein, continuously separating the thus liberated pyridine from the liquid by gravity, and continuously returning the liquid from which the pyridine has been so removed to the liquid in the first said chamber.

2. The method of recovering pyridine which includes the steps of continuously passing coke oven gas containing pyridine through a solution containing between about 6% and about 8% of sulfuric acid in a chamber, maintaining the free acid concentration of said liquid substantially constant, maintaining the pyridine concentration of said liquid below about 2%, continuously flowing liquid containing pyridine from a point below the surface of liquid in said chamber upwardly into and below the surface of the liquid in a second chamber, continuously withdrawing liquid from the second said chamber from a point above the bottom thereof, continuously treating the thus withdrawn liquid with ammonia gas to release the pyridine contained therein, continuously separating the thus liberated pyridine from the liquid by gravity, and continuously returning the liquid from which the pyridine has been so removed to the liquid in the first said chamber.

3. The method of recovering pyridine which includes the steps of continuously passing coke oven gas containing pyridine through a solution of dilute sulfuric acid in a chamber, maintaining the free acid concentration of said liquid substantially constant, maintaining the pyridine concentration of said liquid below about 3%, continuously flowing liquid containing pyridine from a point below the surface of liquid in said chamber upwardly into and below the surface of the liquid in a second chamber, continuously withdrawing liquid from the second said chamber from a point above the bottom thereof, continuously treating the thus withdrawn liquid with ammonia gas, continuously recovering pyridine liberated thereby from said liquid, and continuously returning the liquid to the first said chamber.

MAX D. WALD.
FRANK A. KARNATZ.