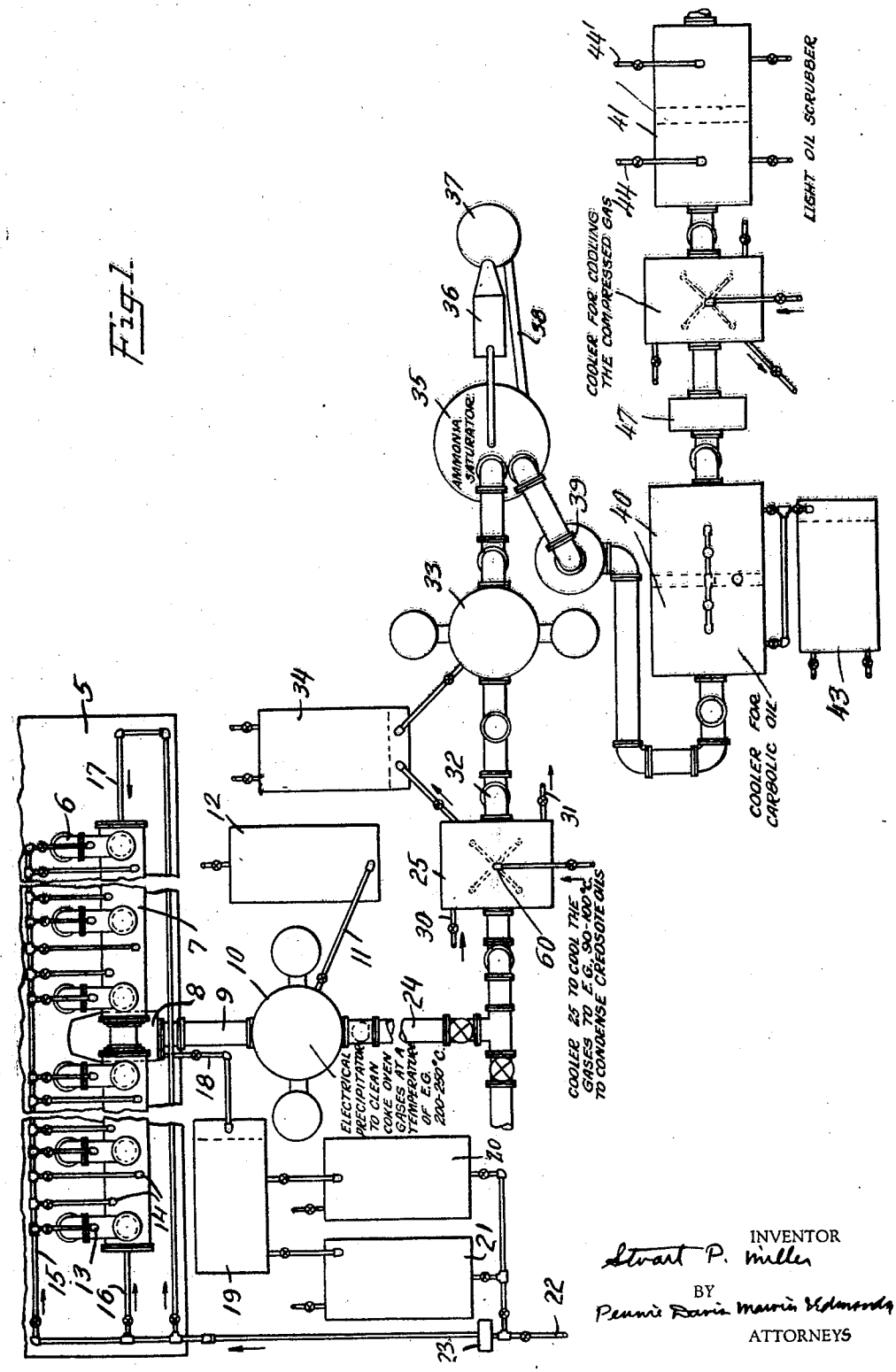
Oct. 6, 1931. S. P. MILLER 1,826,561

RECOVERY OF AMMONIA AND OTHER PRODUCTS FROM COKE OVEN GASES

Filed July 16, 1927 2 Sheets-Sheet 1

Fig. 1.



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Fig. 2.

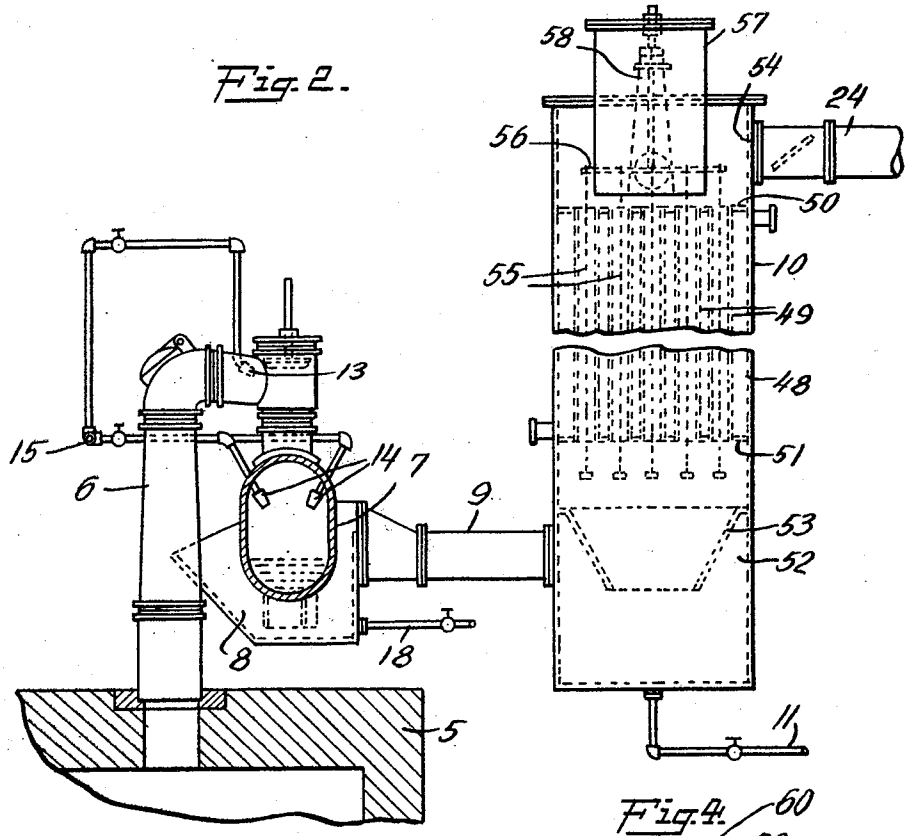


Fig. 3.

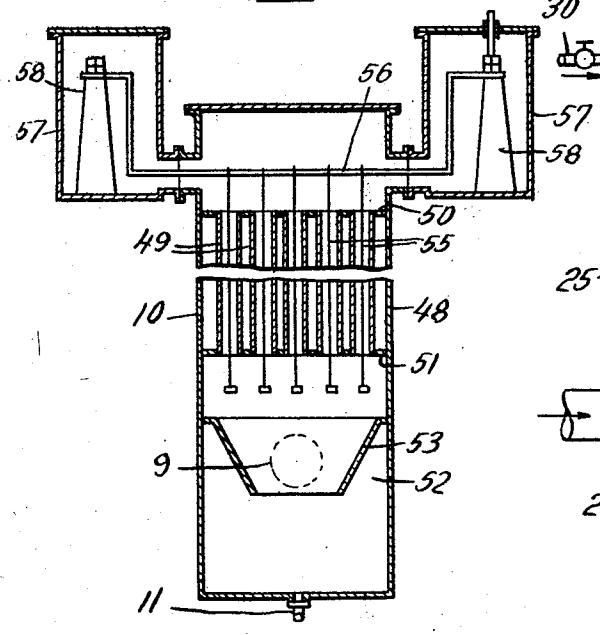
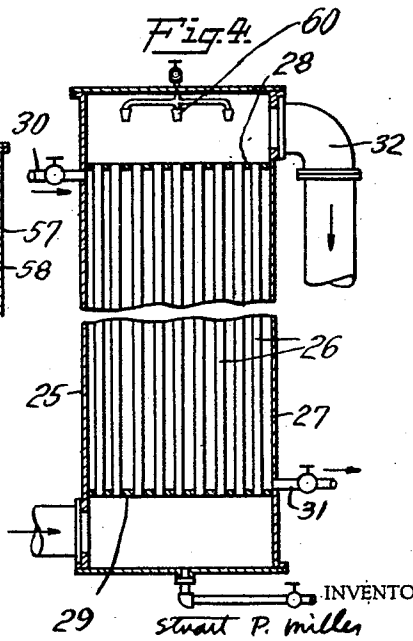


Fig. 4.



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UNITED STATES PATENT OFFICE

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RECOVERY OF AMMONIA AND OTHER PRODUCTS FROM COKE OVEN GASES

Application filed July 16, 1927. Serial No. 206,365.

This invention relates to improvements in the direct recovery of ammonia and of pitch and clean oils from coke oven gases.

In ordinary coke oven operation the coke oven gases are cooled rapidly by the introduction of ammonia liquor, or of ammonia liquor and tar, into the collector main and the gases passing from the collector main are then cooled further in condensers or coolers to relatively low temperatures. This cooling of the coke oven gases results in the separation of coal tar, part of which is usually recovered from the collector main and part from the coolers or condensers; and this tar is ordinarily subjected to distillation in tar stills for the production therefrom of distillate oils and of pitch residues.

In the direct recovery of ammonia it has been proposed to cool the hot coke oven gases to a temperature around 80 to 100° C., then separate tar from the gases by means of an electrical precipitator, and then pass the gases directly to the sulfuric acid saturator to recover the ammonia content of the gases as ammonium sulfate. In such cases also the tar separated from the gases requires distillation to produce oils and pitches therefrom.

The present invention relates to an improved process of recovering ammonia, as well as pitches and oils, from coke oven gases in which the pitches are recovered directly from the gases without necessitating redistillation of tar, and in which clean oils are also directly recovered from the hot coke oven gases without redistillation of tar, and in which the ammonia is also directly recovered from clean coke oven gases.

According to the present invention, I avoid the sudden and rapid cooling of the hot coke oven gases to a low temperature and subject them while they are still at a sufficiently high temperature to retain creosote oils in the vapor state to cleaning with an electrical precipitator to remove from the gases pitch of regulated melting point.

For example, the gases can be cooled to a temperature around 250° C. or around 200° C. and passed through an electrical precipitator at such temperature to remove from the gases all suspended pitch constituents, leaving clean gases still containing creosote oils in the vapor state, including oils of high boiling point, e. g., above 350° C. Instead of treating the gases at 250° C. or 200° C. they may be treated at a lower temperature, e. g. around 160° C. where a softer pitch is desired; and, in certain cases, the gases can be treated at a higher temperature than 250° C. where a heavier pitch is desired and where an increased amount of heavier oils, which may be solid or semi-solid in an isolated state, is desired in the subsequent oil fraction or fractions.

The hot coal distillation gases leave the coke oven at a high temperature, around 600° to 700° C. or higher. The cooling of these gases to a regulated lower temperature can be effected in part by external cooling, but is advantageously effected by the introduction of a regulated and limited amount of ammonia liquor, or of ammonia liquor and tar, into contact with the hot gases, and by insulating the connecting piping if necesary to enable further temperature regulations to be obtained.

The introduction of ammonia liquor may cool some of the gases locally to a low temperature, and may throw out a heavy tar therefrom, but with a limited amount of ammonia liquor introduced into contact with the gases, a part only of the gases will be cooled to a low temperature, and the average temperature of the gases can readily be kept sufficiently high to enable the greater part of the desired creosote oils to be maintained in vapor form, while condensing from vapor to liquid form for the most part only the heavier pitch constituents which are to be separated from the gases at the high temperature of the cleaning operation. A considerable amount of ammonia liquor can be flushed through the bottom of the collector main where it will come in surface contact with the gases but if the ammonia liquor sprayed into the gases is limited the presence of a considerable amount of ammonia liquor flowing through the main will not unduly cool the gases, because of its limited surface contact with part only of the gases, and is advantageous in insuring that any tar thrown

down in the collector main will be flushed out with the ammonia liquor.

By regulating the temperature at which the first cleaning of the gases by the electrical precipitator is carried out, the melting point of the pitch recovered can be regulated and a harder or softer pitch of higher or lower melting point directly produced. This pitch, moreover, when produced from normal coke oven gases, will differ from pitch produced by redistillation of tar in that it will be much lower in free carbon content because it will have been produced without the expensive decomposition of oil constituents and resulting increase in carbon content which takes place when coal tar is distilled in ordinary stills to a pitch residue.

The gases which pass from the high temperature precipitator will have been freed from pitch constituents and will be clean gases containing in vapor state the oils having a dew point lower than the temperature at which they pass through the electrical precipitator. By cooling these gases it is possible to recover directly therefrom clean oils. For example, by cooling the gases to a temperature around 90 to 100° C. it is possible to separate a creosote oil which will be a clean oil, i. e., free or substantially free from pitch constituents. The yield of this oil will, moreover, be greater than the corresponding yield of creosote oil produced by redistillation of a corresponding amount of tar for the reason that such redistillation is accompanied by considerable decomposition of oil with correspondingly lower yields of distillate oil. The directly recovered clean oil will accordingly differ in its composition from oils produced by the usual tar distillation processes in externally heated stills.

The cooling of the gases after the removal of pitch therefrom may be carried out in a single stage, or fractionally in a series of stages, and a single clean oil fraction or a series of fractions recovered. By cooling to around 100° C. or somewhat higher a single oil fraction can be obtained suitable for use for creosoting purposes or for admixture with other tar constituents for creosoting purposes.

The cooling of the gases for the separation of clean oils therefrom is advantageously carried out at a sufficiently high temperature to permit the gases after such cooling and oil separation to be passed directly to the ammonia saturator at a temperature above the dew-point of the gases for water. The gases should not for this purpose be cooled below around 80 to 85° C. and they may be cooled only to around 90 or 100° C. before passing to the saturator. The gases before passing to the saturator will have been freed from all objectionable pitch constituents and also from part of the oil constituents and particularly from the heavier oil constituents, such as creosote oils.

If the gases are cooled only to about 100° C. and the oil separated from them at that temperature and gases then passed to the saturator without material reduction in temperature, the gases will leave the saturator while still at a temperature of 85° or higher and will still contain considerable amounts of oils, including carbolic oils and lighter oils. These gases are advantageously subjected to further fractional cooling for the separation of carbolic oils therefrom and finally are scrubbed for the recovery of lighter oils, such as coke oven light oil. For this purpose two successive scrubbers or coolers may be employed, the first at a temperature which will take out most of the carbolic oils while leaving the coke oven light oil largely in the vapor state and the second at a lower temperature which will take out the coke oven light oil from the gases. The first cooler for taking out the carbolic oils may advantageously be a direct water cooler in which water is sprayed into the gases to cool them to a temperature around 25 to 30° C. This will take out most of the carbolic oils while leaving most of the coke oven light oil in the form of vapor. The gases can then be passed to a scrubber or absorber in which they are scrubbed with an absorbent for the coke oven light oil such as a petroleum oil of the kind commonly used for this purpose and commonly known as "straw oil."

In the carrying out of the process the cooling of the hot clean gases from the temperature at which pitch is separated to the lower temperature of e. g., around 80 to 90° C. is effected either by direct or indirect cooling, i. e., either by the direct introduction of cooling liquid into the gases or by indirect cooling. Scrubbers may be used for effecting the cooling, and also for effecting the removal of as much as possible of the condensed oil vapors from the gases. The complete separation of separated oils is advantageously effected by using an electrical precipitator at the lower temperature, around 80 to 90° C., or somewhat higher, above the dew-point of water. This further treatment of the gases with an electrical precipitator insures removal of all entrained oil from the gases.

The subsequent cooling of the gases after passing them through the saturator can also be followed by a further treatment with an electrical precipitator to insure the removal of all suspended oil and water from the gases leaving the carbolic oil cooler so that these will not be carried over by entrainment into the coke oven light oil scrubber.

In the operation of a by-product coke oven plant for the recovery of pitch, clean oils and direct ammonia in the manner above described, the gases should be passed through the collector main without undergoing too

great a reduction in temperature. If ammonia liquor is used in the collector main it should be regulated in amount to avoid too great cooling and reduction in temperature. If tar and ammonia liquor are used, the cooling of the gases should be similarly regulated, so that the gases will reach the first electrical precipitator, e. g. at a temperature such as those above mentioned, so that pitch will be directly recovered from the precipitator while leaving the desired oils in the form of vapors.

The ordinary coke oven battery has collector mains common to a plurality of ovens, commonly twenty ovens for each collector main, or three collector mains for a battery of sixty ovens. Each collector main has a cross-over main and the three cross-over mains commonly lead to a common condensing system. In such a coke oven installation the high temperature electrical precipitator can advantageously be placed close to or even upon the collector main or at some point in the cross-over main at which the coke oven gases are still at a sufficiently high temperature, and the gases can be kept at the necessary high temperature by limiting the cooling in the collector main. If an entire battery of sixty ovens is to be operated in accordance with the present invention, three high temperature electrical precipitators may be employed, one for each collector main and the clean gases can then be passed to the common condensing system with regulation of temperature therein as above described to leave the gases at a temperature above the dew-point of water as they pass from the condensing system to the saturator.

In the accompanying drawings,

Fig. 1 shows in a more or less diagrammatic manner apparatus suitable for removing pitch, then clean creosote oils, then ammonia and then further clean oils and coke oven light oils from hot coke oven gases according to one of the preferred methods embraced by my invention;

Fig. 2 shows a cross section of the collector main and electrical precipitator of Fig. 1;

Fig. 3 shows a cross section of the electrical precipitator shown in Fig. 2; and

Fig. 4 shows one suitable form of indirect cooler.

In the drawings a coke oven battery is shown conventionally at 5 with uptake pipes 6 leading from the individual ovens to the collector main 7. The gases pass off from the collector main through the center box 8 and the cross-over main 9 through the electrical precipitator 10 where entrained solids and liquids constituting the pitch product are removed from the gases.

The nature of the residue drawn off from the precipitator through the pipe 11 into the receiver 12 will depend to a large extent upon the temperature of the gases passing through the precipitator. This temperature is determined by the control of the operation of the coke oven system, and more particularly by the nature and quantity of the cooling medium sprayed in the goose-necks and collector main and the cooling thereby effected. The goose-necks and collector main are equipped with sprays 13 and 14, which are supplied through the pipe 15 with the cooling liquid, such as a limited amount of ammonia liquor or water. Ammonia liquor, or a mixture of ammonia liquor and tar, is supplied to the ends of the collector main through the pipes 16 and 17 in order to flush the main and remove any deposits of tar, etc. which may tend to collect in the bottom of the main. The hot gases from the ovens on contacting with the ammonia liquor spray and the liquor flowing through the bottom of the collector main are cooled and heavy tar is to some extent thrown out of the gases and removed through the center-box of the collector main through the pipe 18 and run into the decanter 19, together with that portion of the liquor supplied to the collector main which is not volatilized by the hot gases. The use of ammonia liquor in limited amount, or with limited surface contact with the gases, will result in local cooling of some of the gas to a sufficiently low temperature to throw down heavy tar therefrom, but only part of the gases will be so cooled, and only part of the tar will be so separated. The part of the gases not so cooled will result in giving a sufficiently high temperature of the total gas leaving the collector main such that it will carry the greater part of the oils, including heavy and high boiling oils, in vapor form, and suspended particles of pitch recoverable in the electrical precipitator. The pitch so recovered may be of a high melting point, and the gases may be also of a high temperature, even though, due to local overcooling of some of the gases in the collector main, a heavy tar admixed with ammonia liquor is drawn off of the collector main. The flushing of the bottom of the main with a considerable amount of ammonia liquor, or of ammonia liquor and tar, is advantageous in keeping the main free from accumulated tar or pitch by flushing from the main such tar as is thrown down therein, while the limited surface contact of liquor with the gases will cool only the gases coming in contact with it, leaving the gases passing through the upper part of the main uncooled except by the limited spray introduced therein and by radiation from the walls of the main. Local overcooling of some of the gas is unobjectionable where the temperature of the gases as a whole are kept sufficiently high when they enter the elctrical precipitator, and where provision is made for flushing from the collector main such tar as may be thrown down therein.

The liquor supplied to the collector main may be ammonia liquor from the tank 20 either alone or used together with tar from the tank 21, or liquor from an outside source may be supplied through the pipe 22. Pump 23 serves to supply the materials to the sprays and the collector main under the desired pressure.

As the gases leave the collector main they contain heavy tar or pitch and solid impurities entrained therein, which are carried forward by the current of the gases. By proper regulation of the spraying, the temperature of the gases may be controlled and in this way the nature of the residue drawn off from the precipitator 10 may be regulated. According to a preferred method of operation, the temperature of the precipitator is kept between 200 and 250° C., or higher at which temperature a relatively high melting point pitch is thrown down in the precipitator and drawn off into the receiver 12, and a high yield of creosote oil is directly recovered from the gases.

From the precipitator the gases pass through the main 24 to the cooler 25 which may be an indirect cooler such as a heat interchanger or indirect water cooler. An indirect type of cooler is shown in Fig. 4 in which the gases pass up through tubes 26 surrounded by the jacket 27 contained between the heads 28 and 29. Cold water circulated through the jacket enters through the pipe 30 and is led off through pipe 31. The circulation of the water or other cooling medium is regulated so that the gases leaving the cooler by the main 32 are at a temperature of 80 to 100° C. The cooling by water is advantageously supplemented by spraying a limited amount of carbolic oil into the top of the cooler through the spray pipe and nozzles 60. This oil will be vaporized in contact with the gases passing upwardly through the cooler and will assist in condensing heavier oils in the cooler.

According to the preferred method of operation, the gases cooled to about 90° or 100° C. pass from the cooler 25 through the main 32 to the electrical precipitator 33, where entrained condensed clean oil particles are removed from the gases as condensate. This condensate may be drawn off into the storage tank 34 and combined with condensate from the cooler 25, or separate storage tanks may be provided.

The gases leaving the precipitator at a temperature of about 90° to 100° C pass through the saturator 35 where the ammonia is recovered as ammonium sulfate. The saturator may be of the usual type and may include the usual sludge box or drain table 36, centrifuge 37 and drain 38. After leaving the saturator the gases are passed through the acid separator 39.

The gases then pass to further cooling apparatus for recovery of carbolic and coke oven light oils. This apparatus comprises a direct water cooler 40, cooled by direct contact with water spray or films, in which carbolic oil is thrown out, an exhauster 47, a cooler for cooling the compressed gas and a benzol scrubber such as the usual petroleum oil scrubber 41 for recovery of coke oven light oil. The cooler 40 may be followed by a precipitator (not shown) for removing entrained condensate from the gases. Petroleum oil is supplied to the scrubber 41 through the pipes 44 and 44′.

The condenser which precedes the ammonia saturator and which is operated at a sufficiently high temperature to maintain the gases above the dew point of water is advantageously an indirect cooler or condenser where water is used as the cooling medium, since by avoiding direct contact of water with the gases, there is avoided the production of ammonia liquor and the local over-cooling of part of the gases in contact with the water and the throwing down of lighter oils thereby. An indirect cooler, with the cooling medium out of direct contact with the gases but in heat interchanging relation thereto can advantageously be employed.

The condenser for removing the heavy oils may be in part cooled by the introduction therein of the lighter oil, such as the carbolic oil subsequently recovered from the gases, and which, by vaporization, will partially cool the gases. By avoiding the use of water or ammonia liquor in contact with the hot gases before they reach the saturator, the ammonia will be maintained in the gases and recovered in the saturator, except such as may be separated from the gases in the collector main, where ammonia liquor or water is there used for regulating the temperature of the gases.

The condenser which follows the saturator and in which the carbolic oils are recovered may be an indirect cooler or condenser, but is advantageously a direct cooler or condenser provided with a water spray for rapidly cooling the gases to a low temperature. The ammonia will have been eliminated from the gases by the saturator, so that water can be employed in direct contact with the gases, to cool them and to condense the carbolic oil therefrom, without requiring subsequent distillation of the water for the recovery of ammonia.

Figs. 2 and 3 show the precipitator 10 in detail. The electrical precipitators 10 and 33 may advantageously be of the same type. The precipitator 10 consists of a shell 48 enclosing a number of tubes 49 supported in heads 50 and 51 within the shell. The inlet pipe 9 near the bottom of the shell communicates with the chamber 52 which is partially separated from the tube section by the baffle 53. An outlet 54 permits the escape of

gases from the precipitator after the latter have passed through the tubes. The space around the tubes, and the precipitator as a whole, are advantageously provided with insulating material to prevent or minimize loss of heat and lowering of temperature of the gases passing through the precipitator.

A plurality of electrodes 55, preferably in the form of metal rods, extend through the tubes and are supported on the bus-bar 56 near the upper end of the tubes. The bus-bar extends at both ends in casings 57 which enclose insulators 58 upon which the bus-bar is supported. The high tension current line extends into one of the casings 57 and connects with the bus-bar, thus supplying the necessary current from any suitable source of uni-directional current under high tension. The casing of the precipitator is grounded, or otherwise connected to the source of current, to complete the circuit. The casing and tubes form the positive electrode, the electrodes connected to the bus-bar being negative. The form and arrangement of conductors in the circuit can be varied. The arrangement is such as to supply high tension uni-directional current to the electrodes, thereby permitting a continuous silent discharge at high potential between the rod electrodes and the tubes through which the gases pass.

The gases carrying pitch particles in suspended form, together with solid materials such as carbon, etc., in finely divided form, enter the electrical precipitator from the collector main and pass through the tubes in the precipitator, being subjected therein to an electrical discharge which causes them to separate from the gases and condensable vapors. The separated pitch runs down the inner walls of the tubes into the chamber in the bottom of the precipitator and is withdrawn through a pipe 11 and delivered to a suitable storage receptacle 12. The gases carrying condensable clean oil vapors and ammonia escape through the outlet 54 and are delivered through the pipe 24 to the condenser 25.

In my companion application (Ser. No. 206,367) I have set forth a process of recovering directly from coal distillation gases a relatively high melting point pitch product, creosote oil and carbolic oil. In the process described in such companion application, both the creosote oil and the carbolic oil are condensed from the gases before they pass to the saturator, and the gases then pass to the saturator at a low temperature, for example, around 25° to 35° C. Such condensation of carbolic oil at a temperature around 25° to 35° C. is accompanied by condensation of more or less ammonia liquor, which requires subsequent treatment by distillation, etc., to recover the ammonia therefrom. The process of the present application is distinguished from the process of such companion application by the recovery of the ammonia from the gases at a temperature above the dew point of water, such that condensation of ammonia liquor and the necessity of distillation of ammonia liquor are eliminated, except for such ammonia liquor as may be employed for regulation of temperature in the collector main. The present process, in addition to providing for the recovery of pitch, creosote oil and carbolic oil, provides for the direct recovery of ammonia at a temperature above the dew point of water prior to the recovery of carbolic oil, so that the carbolic oil is separated from ammonia-free gases, which gases, after the separation of carbolic oils, can be directly passed to the coke oven light oil scrubber for the recovery of coke oven light oils therefrom.

The carbolic oils recovered in the process of the present invention can be sold or shipped as a commercial product. They can also be advantageously extracted for the recovery of phenols or tar acids therefrom, as described more fully in my prior application, Serial No. 202,736, for example, by subjecting the carbolic oil to intimate contact with a solution of caustic soda, e. g. a 10% solution, separting the resulting carbolate solution from the neutral oil, and decomposing the carbolate solution with carbon dioxide or other acids to set free the tar acids or phenols. The directly recovered carbolic oils obtained by the process of the present invention can advantageously be extracted for the recovery of phenols or tar acids therefrom, since they are free from heavy tar or pitch impurities which interfere with the direct recovery of tar acids from tarry oils.

It will thus be seen that the present invention provides an improved process for the direct recovery of ammonia from coke oven gases and also for the direct production of pitch and of heavy clean oils and light carbolic oil from such gases with avoidance of the need of redistillation of tar to produce either pitch or such clean oils. It will further be seen that the treatment of the gases preceding the direct recovery of ammonia includes cleaning the gases at a high temperature with an electrical precipitator to recover pitch directly as a product of the treatment and a further condensing treatment for the recovery of a heavy clean oil directly from the gases; while the treatment of the gases after the recovery of ammonia includes the direct recovery of carbolic oils and coke oven light oils therefrom.

I claim:

1. The method of recovering ammonia and other products from coke oven gases which comprises subjecting the hot coke oven gases to a cleaning treatment with an electrical precipitator at a sufficiently high temperature

to separate pitch from the gases and leave creosote oils in the form of vapors, cooling the resulting cleaned gases to a temperature above the dew-point of water to separate clean creosote oils therefrom, and then passing the gases while still at a temperature above the dew-point of water to an ammonia saturator.

2. The method of recovering ammonia and other products from coke oven gases which comprises collecting gases from a plurality of ovens of a coke oven battery in a common collector main, subjecting the hot coke oven gases therein to regulated cooling with ammonia liquor, thereby separating a limited amount of heavy tar from the gases, while leaving the gases as a whole at a sufficiently high temperature to keep a large part of the oils in vapor form, passing the gases from the collector main to an electrical precipitator at a temperature sufficiently high to separate pitch from the gases and to leave a large part of the oils in the form of vapors, cooling the resulting gases to a temperature above the dew-point of water to separate creosote oils therefrom and then passing the gases at a temperature above the dew-point of water through an ammonia saturator.

3. The method of recovering ammonia and other products from coke oven gases which comprises subjecting hot coke oven gases to cleaning with an electrical precipitator at a temperature sufficiently high to separate pitch from the gases and to leave a considerable amount of creosote oil in the form of vapors, cooling the gases to separate clean oils therefrom and then passing the resulting gases to an ammonia absorber at a temperature above the dew point of water.

4. The method of recovering ammonia and other products from coke oven gases which comprises subjecting hot coke oven gases to a cleaning with an electrical precipitator at a sufficiently high temperature to separate pitch from the gases but leave a considerable amount of creosote oils in the form of vapors, cooling the gases to a temperature above the dew-point of water which will leave carbolic oils in the form of vapors and separate out clean creosote oils, passing the resulting gases through an ammonia absorber at a temperature above the dew-point of water, then subjecting the gases to cooling for the separation of carbolic oils therefrom and finally subjecting the gases to a scrubbing treatment for the recovery of benzol.

In testimony whereof I affix my signature.

STUART PARMELEE MILLER.