Aug. 6, 1935. J. BECKER 2,010,003

COKE OVEN GAS BY-PRODUCT RECOVERY

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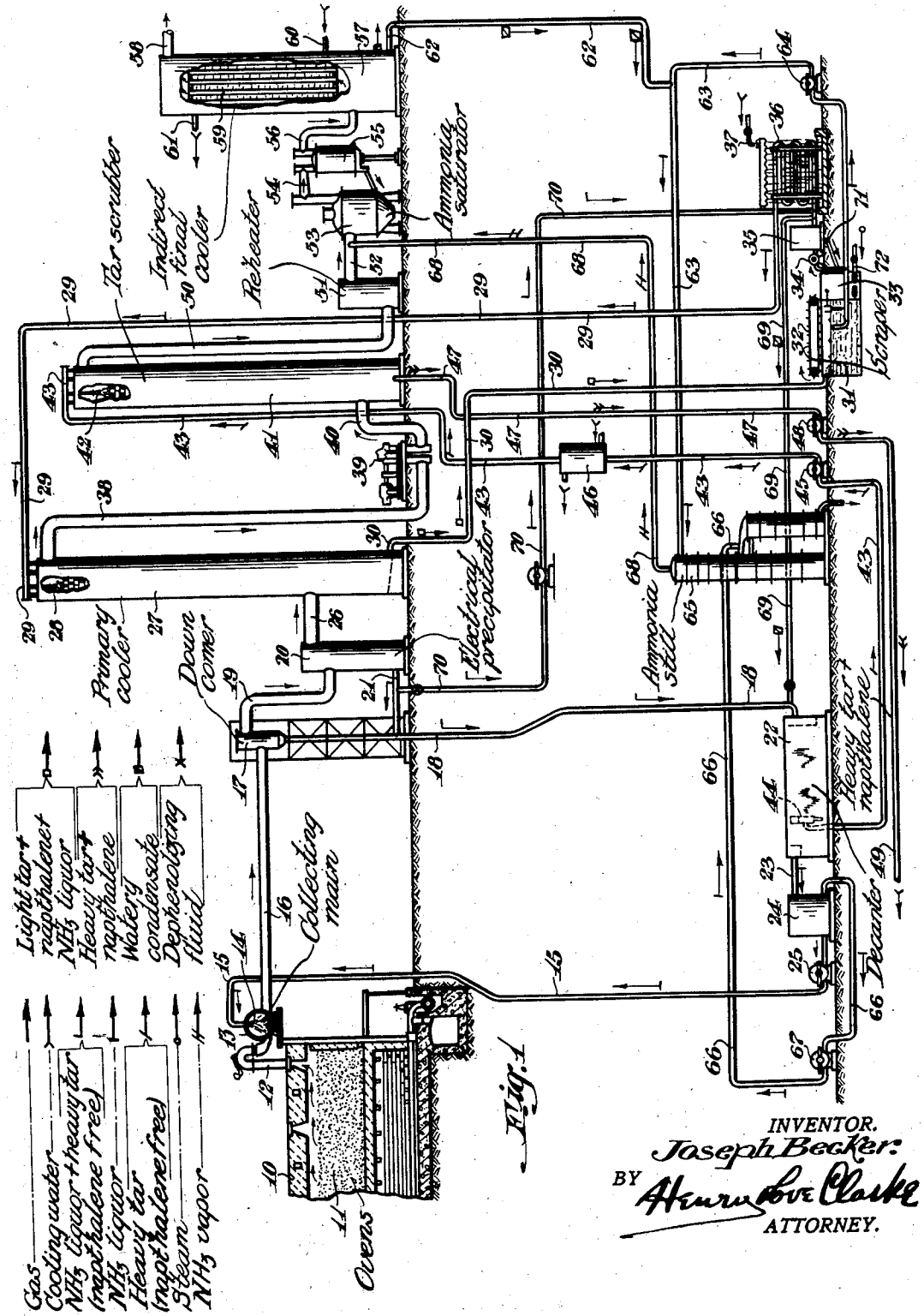


Fig. 1

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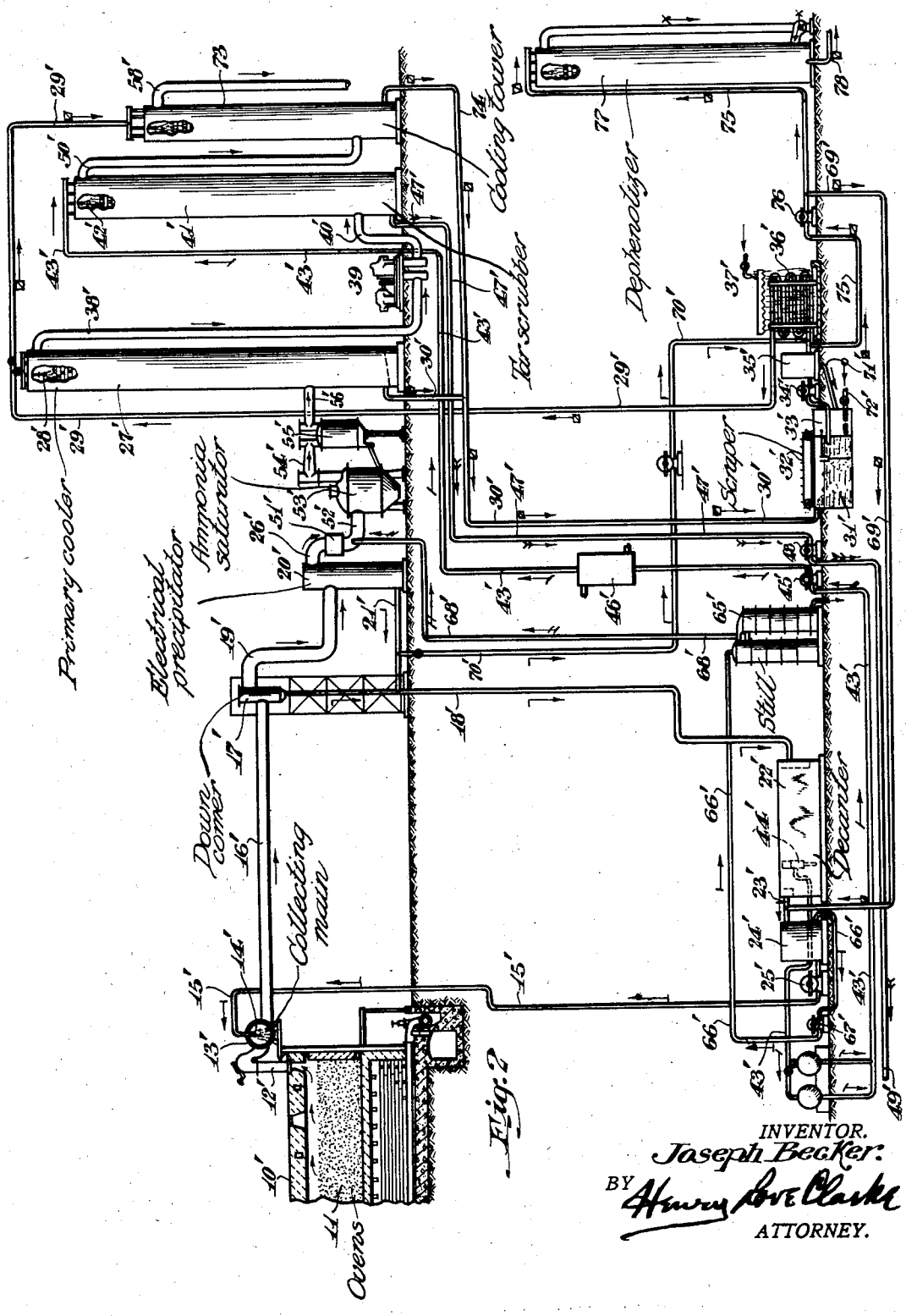


Fig. 2

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COKE-OVEN GAS BY-PRODUCT RECOVERY

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3 Claims. (Cl. 23—196)

This invention relates to the recovery of by-products from ammonia-charged gas such as coke oven gas, and has for an object a simplification and increased efficiency in such recovery, and more particularly an effective removal of the tar and ammonia and naphthalene and then effecting delivery of the cooled gas, for the benzol scrubbers or other disposition, without subjecting such gas to a final cooling treatment that involves either naphthalene stoppages or final coolers or the installation of extensive apparatus for the employment or purification of final cooler waters or that involves the pollution of the atmosphere or the loss of phenols or cyanogen or like constituents of the gas; and the invention has for further objects such other improvements or advantages as may be found to obtain in the employment of the method or apparatus hereinafter described or claimed.

The invention comprises the combining and balancing with each other of certain steps and apparatus in a system for accomplishing such objects as above mentioned; for instance, as follows. The very hot gas issuing from the retorts is immediately sprayed and washed with ammonia liquor, to take out the fixed ammonia compounds such as ammonium chloride, and also, with some temperature reduction, dropping out the heaviest tars, and the used wash-liquor and condensates and such tars are drained off and collected and separated for recirculation or other use, while the still hot gas is conveyed to a tar precipitator, which it passes through at a high temperature such as about or somewhat above the dew point of the water vapor with which the gas has been saturated by the free and combined water constituents of the coal carbonized in the retorts. Such temperature may be about 180° to 200° F., depending on the moisture content of the coal carbonized, and yet at a temperature enough reduced so that most of the tar content, especially the heavier tar, is precipitated. At such temperatures most of the naphthalene content of the gas is still in vapor form and passes through the tar precipitator and is not removed with or by the tar; and so the tar drained from the precipitator is substantially naphthalene-free and is collected along with the also substantially naphthalene-free heavy tar drained from the above-mentioned initial washing treatment of the gas. After the tar precipitator the gas is cooled and washed with watery ammonia liquor condensate, and in such primary washing and cooling, down to, for instance, about 75° to 100° F., most of the water vapor and remaining tar oils and much of the naphthalene are condensed and washed out of the gas, and are drained off and collected and separated for further disposition and for recirculation of the recovered watery ammonia liquor condensate along with the also separated wash liquor. From such cooling and washing treatment, the cooled gas is passed into a tar scrubber and scrubbed with the substantially naphthalene-free tar collected as above-mentioned, this tar having been somewhat cooled but not enough to prevent it from flowing freely in the scrubbing operation. Such substantially naphthalene-free tar has a high capacity for taking up naphthalene and consequently scrubs most of the residual naphthalene out of the gas, so that the gas leaving the tar-scrubber has had its naphthalene content reduced far more than it would have been reduced by mere cooling and condensation, and in fact so that any residual naphthalene content is so little that the gas may be still further cooled, down to the desired final cooling extent, without occasioning any substantial deposition of naphthalene in the final cooling system. With the gas in such condition, the final cooling, for its delivery to the benzol scrubbers or other disposition, can be effected without risk of clogging the final cooling apparatus with naphthalene deposits and without the employment of large volumes of wash water that require to be purified before it can be discharged or reused. The final cooling can be and preferably is effected in an indirect cooler, without any risk of internally clogging with naphthalene the tubes that are externally cooled by a clean flow of water. Or relatively small direct cooler apparatus may be employed without risk of clogging the hurdles with naphthalene deposits, and with the cooling effected by a flow of watery condensate recirculated from and to the watery condensates derived and collected from the previous steps in the gas treatment, and any phenols or cyanogen or like constituents washed out of the gas in such direct final cooling or temperature conditioning are saved and recovered incidentally in the dephenolizing treatment through which the accumulating surplus of watery constituents from the entire gas-treatment system is passed. The ammonia is removed from the gas by ammonia saturator apparatus intervening the tar scrubber and the final indirect cooler, or intervening the tar precipitator and the primary washer and cooler, the latter being the preferred position in the system when the final cooling or temperature regulation is to be effected by relatively small di-

rect cooler apparatus as above mentioned. In either instance the ammonia saturator is preceded by a heating unit proportioned to bring or maintain the gas to the proper temperature for passing through the ammonia saturator. An ammonia still is provided for the distillation of surplus ammonia liquor accumulating in the system and the ammonia vapor from such still is led into the gas entering the ammonia saturator.

In the accompanying drawings, showing, for purposes of exemplification, preferred embodiments of the invention, without limiting it to such illustrative instances:

Figure 1 is a somewhat conventional and diagrammatic illustration of an embodiment of the invention in one arrangement of apparatus for practicing it; and

Fig. 2 is a similar illustration of an embodiment of the invention in another arrangement of apparatus for practicing it.

In the embodiment illustrated in Fig. 1: 10 indicates a battery of coke ovens, from each of which the gas distilled out of the coal charge 11 in the coking chamber passes off through the ascension pipe 12 into the collecting main 13, and is there immediately sprayed with ammonia liquor, by spray device 14 fed from the pipe line 15. This spraying removes from the gas fixed ammonia compounds such as ammonium chloride and at the same time reduces the very high temperature of the gas, so that some of the heaviest tar also condenses and drops out into the bottom of the collecting main and is carried out with the flushing liquor, and along with the gas, through the suction-main 16. The suction-main discharges into the downcomer 17, from which the said tar and flushing liquor drain off through the drain line 18, while the gas passes off through the secondary suction-main 19 into the electrical tar-precipitator 20, through which it passes while still hot enough to maintain a temperature about at or somewhat above the dew-point of its water vapor, with which it is saturated from the free and combined water constituents distilled out of the coal. Preferably this temperature at which the gas flows off from the collecting main and through the suction-mains and electrical tar-precipitator is around 180° to 200° F., but may be somewhat less, depending on the moisture of the coal distilled and the proportion of watery condensate dropped out in the collecting main and suction-main; but the temperature is still high enough so that substantially all the naphthalene content of the original distillate gas is carried along in vapor form with the gas and is not condensed or taken up by the tar to substantial extent in either the collecting main or suction main or electrical tar-precipitator; and in consequence both the tar from the downcomer 17 and the tar from the electrical tar-precipitator 20, which also drains off (through connection 21) into the drain line 18, are substantially naphthalene-free. All of this hot and substantially naphthalene-free tar, together with the flushing liquor from the downcomer, discharges into the decanter-tank 22 and is there separated, the tar settling and the clear fixed ammonia-liquor decanted off through pipe 23 into collecting tank 24, from which it is drawn off through pump 25 and recirculated through the aforesaid pipe line 15 leading back to the ammonia-liquor sprays in the collecting main 13. The still hot tar-free gas passes off from the tar-precipitator through the connection 26 into the primary cooler and washer 27, through which it passes in countercurrent and direct contact with watery ammonia liquor condensate that is discharged by the sprays 28 that are distributed in the top of the cooling tower and fed by the wash-liquor line 29. In this cooling and washing operation the gas is cooled down to around 75° to 100° F. and much watery condensate drops out and there is also condensation and washing out of some of the naphthalene and some ammonia and other constituents such as phenols and cyanogen or hydrocyanic acid, and also light tar or tar oils that were still in the hot gas leaving the electrical tar-precipitator. All such wash liquor and watery and other condensates are drained off from the primary cooler and washer 27 through the drain line 30 that discharges into the secondary decanter-tank 31 in which the tar or tar oils and watery condensate and naphthalene separate and from which the naphthalene is discharged by the naphthalene scraper 32, into the naphthalene-sump 33, into which the tar or tar oils also discharge. The watery condensate or watery ammonia liquor condensate decanted off from the decanter-tank 31 is forced by the pump 34 through the filter 35, to remove residual naphthalene, and thence through the cooling coils 36, which are cooled by water spray 37, and is recirculated back to wash-liquor line 29 to the sprays at the top of the aforesaid primary cooling-tower 27. The cooled and washed gas from said primary cooler and washer 27 is drawn off through gas line 38 and exhauster 39 and forced through connection 40 into tar-scrubber 41, through which such cooled and cleaned gas passes upward in counter-current and direct contact with the substantially naphthalene-free tar that is delivered into the top of said tar-scrubber through the tar sprays 42 that are fed by the tar line 43 that leads back to the aforesaid decanter-tank 22, from which the said substantially naphthalene-free tar is drawn off through regulating device 44 and is thence forced through tar line 43 by pump 45. Said tar line 43 passes through a cooler or temperature regulator 46 that somewhat reduces the temperature of the hot tar but still leaves it hot enough to flow freely and to be sprayed freely into the aforesaid tar-scrubber 41. Such substantially naphthalene-free tar has a high carrying capacity for naphthalene and removes from the gas much more of its naphthalene content than would be removed by mere condensation upon mere lowering of the gas temperature to the extent to which the gas is ordinarily cooled in the final coolers of a coke-oven gas by-product recovery system; and consequently the gas issues from the tar scrubber substantially free of naphthalene or of any sufficient content thereof to occasion the clogging of final coolers with naphthalene deposits. The tar drained from the tar scrubber and charged with absorbed naphthalene passes off through the tar-drain line 47 and pump 48 to the tar-storage line 49. The naphthalene-free gas issuing from the tar scrubber 41 passes through the gas line 50 to a reheater 51 that properly conditions its temperature and delivers it through connection 52 into the ammonia saturator 53 in which it is freed of ammonia, the ammonia being recovered as ammonium sulphate in the usual manner. From the ammonia saturator the gas, now substantially ammonia-free as well as substantially naphthalene-free, passes through connection 54 to the usual acid separator 55, which removes any acid traces carried off by the gas from the saturator; and from the acid

separator the clean gas passes through the connection 56 to the indirect final cooler 57, in which the gas is cooled to its proper temperature for either delivery to the benzol scrubbers or delivery into a distribution system. The gas leaves the indirect final cooler through the gas main 58, after having passed through the tubes 59 in the final cooler that are kept cool by the cooling water that surrounds them and is fed into the cooling tower at 60 and discharged at 61. This indirect final cooler requires to be only large enough to effect reduction of the gas temperature down to normal from the not very elevated temperature at which the gas has issued from the acid separator and ammonia saturator apparatus, which may be a temperature below or even much below 140° F. There is no direct contact between the gas passing through the tubes 59 and the cooling water surrounding them in this indirect final cooler, and so a continuous flow of clean water can be maintained, or much of the same water may be cooled and recirculated to and through the cooling chamber. The watery condensates dropping out of the cooled gas into the bottom of the final cooler 57 are drained off through the drain line 62 and led into the ammonia-liquor line 63 through which the surplus watery ammonia liquor condensate decanted from the decanter-tank 31 is pumped, by a pump 64, to the ammonia still 65. Such surplus ammonia liquor and drainage that are carried to the still include the surplus of the drainage from primary cooler 27 that is not recirculated to said primary cooler through wash-liquor line 29. Any accumulating surplus of fixed ammonia liquor in the tank 24, over and above that required to be recirculated to spray the gas collecting main 13, is drawn off through pipe line 66 and pump 67 and delivered into the fixed leg of the ammonia still, for dissociation of the fixed ammonia compounds and recovery of the ammonia. The ammonia vapor recovered from the ammonia still 65 is led through ammonia vapor line 68 back into the gas stream that is passing into the ammonia saturator through the connection 52 from the reheater 51. Part of the watery condensate ammonia liquor that has been decanted from the decanter-tank 31 and passed through the naphthalene filter 35 may be led over, through the valve-controlled connection-line 69, to the primary decanter-tank 22, to further help maintain the balance of watery condensate that is being recirculated to spray the hot gas in the gas collecting main 13, such spray liquor requiring to be maintained at a low enough concentration of ammonium chloride to still take up such fixed ammonium compounds from the gas in the said collecting main. A part of the tar drainage from the tar-precipitator 20 may be led through the valved auxiliary drain line 70 into the condensate that is passing into the cooling coils 36 and being cooled and recirculated to the primary cooler and washer 27. The naphthalene from the naphthalene filter 35 is drained through connection 71 into the same naphthalene-sump 33 that receives the naphthalene and tar from the aforesaid decanter-tank 31; and this collecting sump is heated by steam connections 72, so that the collecting tar and naphthalene may be kept fluid and separated and drawn off from said sump to storage. The complete system is so balanced that there are substantially no wash liquors or waste liquors to be purified or disposed of except the limited waste from the relatively minor operation of the fixed leg of the ammonia still. The final cooler operation is simplified to the point where only a final cooler of relatively small dimensions is required, and there is no risk of naphthalene stoppages in it and there is no volume of final cooler water to be purified or disposed of by special supplementary apparatus; and there is also no waste of by-products such as phenols that ordinarily have to be discharged from the large volume of cooling water employed in direct contact with the gas in direct final coolers.

In the embodiment illustrated in Fig. 2, the apparatus corresponding with that in Fig. 1 is indicated by like reference numerals with the prime mark. There are, however, certain differences of arrangement and of apparatus units. The ammonia saturator 53' and acid separator 55' precede the primary cooler and washer 27'; and the superheater or re-heater preceding the ammonia saturator 53' is reduced to a mere temperature regulator 51', in conduit 52' in view of the fact that such apparatus unit immediately follows the electrical tar-precipitator 20' from which the gas issues at an already high temperature and requires but little temperature elevation to insure its passing through the ammonia saturator hot enough to still carry through the saturator-bath constituents whose deposition would be detrimental to the quality of the ammonium sulphate recovered from the saturator. The gas issuing from the tar scrubber 41' is already ammonia-free and tar-free as well as naphthalene-free, and has been washed and cooled in the primary cooler 27' and not much reheated in tar scrubber 41', and so requires but little final cooling and in fact rather merely a temperature regulating to the normal temperature level at which such gas may best be delivered to the benzol washers or to other disposition or distribution. Therefore the final cooling is effected in a temperature regulator cooling tower 73 of relatively small size and having the character of a contact cooler through which the gas passes in counter-current and direct contact with watery condensate that is sprayed into the top of said cooling tower 73 from an extension of the same wash-water line 29' that feeds the primary cooler and washer 27'. In view of the fact that the ammonia is removed from the hot gas before such gas enters the primary cooler and washer 27', the condensate and wash liquor discharged from said primary washer 27' is largely watery condensate with but little ammonia content; and so also the drainage from the cooler 73 is watery condensate and is led through drain 74 to joint the drain 30' from the primary cooler 27'. As none of the watery condensate collected in the decanter-tank 31' requires to have its surplus accumulation delivered to an ammonia still for recovery of ammonia, the ammonia still 65' is constituted of only a fixed leg for treatment of the surplus concentrated fixed ammonia liquor withdrawn from the primary ammonia-liquor collecting-tank 24'. The surplus of the accumulating watery condensate decanted from the decanter-tank 31' is led off through the discharge line 75 and pump 76 to the top of the dephenolizing tower 77, from which there is a complete recovery of all the residual phenols and only a phenol-free aqueous waste passes off from the bottom of said dephenolizing tower through the waste drain 78. All of this system is so balanced that there is substantially complete recovery of all by-product values and so that there is practically no problem

of purification or disposal of large volumes of wash liquor or waste liquor, and so that the step of final cooling or temperature conditioning of the gas for delivery to the benzol scrubbers or to other disposition or distribution is reduced to an extreme of simplicity and reduced apparatus equipment.

The invention has been hereinbefore described as embodied and practiced in certain exemplifying instances, but is not limited thereto or to less than all the possible embodiments that may be within the scope of the claims hereinafter made.

I claim:

1. A coke-oven gas by-product recovery method comprising: spraying the gas with ammonia-liquor immediately as it is collected from the distilling chambers, to wash out hot condensates therefrom; conveying the still hot gas directly to a hot tar-precipitation treatment and intermediately draining off ammonia liquor and other hot condensates yielded during such collecting and conveying; subjecting the hot gas to a tar-precipitation treatment while still at a temperature of about or above the water-vapor dew-point and thereby recovering a substantially naphthalene-free tar; collecting and separating the said naphthalene-free tar and ammonia liquor and other hot condensates from the aforesaid several operations; subjecting the hot gas from the tar-precipitation treatment to a primary cooling and washing treatment by direct contact with ammonia-liquor, thereby removing naphthalene and the residual tar oils; draining off the wash-liquor from such primary cooling and washing treatment and subjecting it to separation of naphthalene and tar oils and watery condensate ammonia-liquor; subjecting the gas from the primary cooling and washing treatment to a scrubbing treatment with the napthalene-free tar, thereby removing most of the residual naphthalene from the gas and further cooling it; draining off the tar from such scrubbing treatment and delivering it to further treatment or storage; passing the cooled and substantially naphthalene-freed gas through an ammonia recovery treatment, and thence through a final indirect cooling treatment without contact with the cooling fluid, and then passing it to further disposition; draining the watery condensates from the final gas cooling and passing them to further disposition; and returning the aforesaid separated ammonia liquors to the spraying of the initial gas collecting and to the primary cooling and washing treatment of the gas.

2. A coke-oven gas by-product recovery method comprising: spraying the gas with ammonia-liquor immediately as it is collected from the distilling chambers, to wash out hot condensates therefrom; conveying the still hot gas directly to a hot tar-precipitation treatment and intermediately draining off ammonia liquor and other hot condensates yielded during such collecting and conveying; subjecting the hot gas to a tar-precipitation treatment while still at a temperature of about or above the water-vapor dew-point and thereby recovering a substantially naphthalene-free tar; collecting and separating the said naphthalene-free tar and ammonia liquor and other hot condensates from the aforesaid several operations, and returning such ammonia liquor to the spraying of the initial gas collecting; subjecting the hot gas from the tar-precipitation treatment to a cooling and washing treatment by direct contact with watery condensate, thereby removing naphthalene and the residual tar oils; draining off the wash-liquor from such cooling and washing treatment and subjecting it to separation of naphthalene and tar oils and watery condensate, and cooling and returning such condensate to the cooling and washing treatment of the gas; subjecting the gas from the primary cooling and washing treatment to a scrubbing treatment with the naphthalene-free tar, thereby removing most of the residual naphthalene from the gas and further cooling it; draining off the tar from such scrubbing treatment and delivering it to further treatment or storage; subjecting the gas to ammonia recovery treatment intermediate some of its foregoing treatments; and passing the cooled and substantially naphthalene-freed and ammonia-freed gas to further disposition.

3. A coke-oven gas by-product recovery method comprising: spraying the gas with ammonia-liquor immediately as it is collected from the distilling chambers, to wash out hot condensates therefrom; conveying the still hot gas directly to a hot tar-precipitation treatment and intermediately draining off ammonia liquor and other hot condensates yielded during such collecting and conveying; subjecting the hot gas to a tar-precipitation treatment while still above a temperature at which substantial amounts of naphthalene would enter the tar and thereby recovering a substantially naphthalene-free tar; collecting and separating the said naphthalene-free tar and ammonia liquor and other hot condensates from the aforesaid several operations, and returning such ammonia liquor to the spraying of the initial gas collecting; subjecting the hot gas from the tar-precipitation treatment to an ammonium sulphate recovery treatment, and then to a cooling and washing treatment by direct contact with condensate water, thereby removing naphthalene and the residual tar oils; draining off the cooling water and watery condensates from such cooling and washing treatment and subjecting it to separation of naphthalene and tar oils and condensate water, and cooling and returning such condensate water to the cooling and washing treatment of the gas; subjecting the gas from the cooling and washing treatment to a scrubbing treatment with the substantially naphthalene-free tar, thereby removing substantially all of the residual naphthalene from the gas; draining off the tar from such scrubbing treatment and delivering it to further treatment or storage; and passing the cooled and substantially naphthalene-freed and ammonia-freed gas to further disposition.

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