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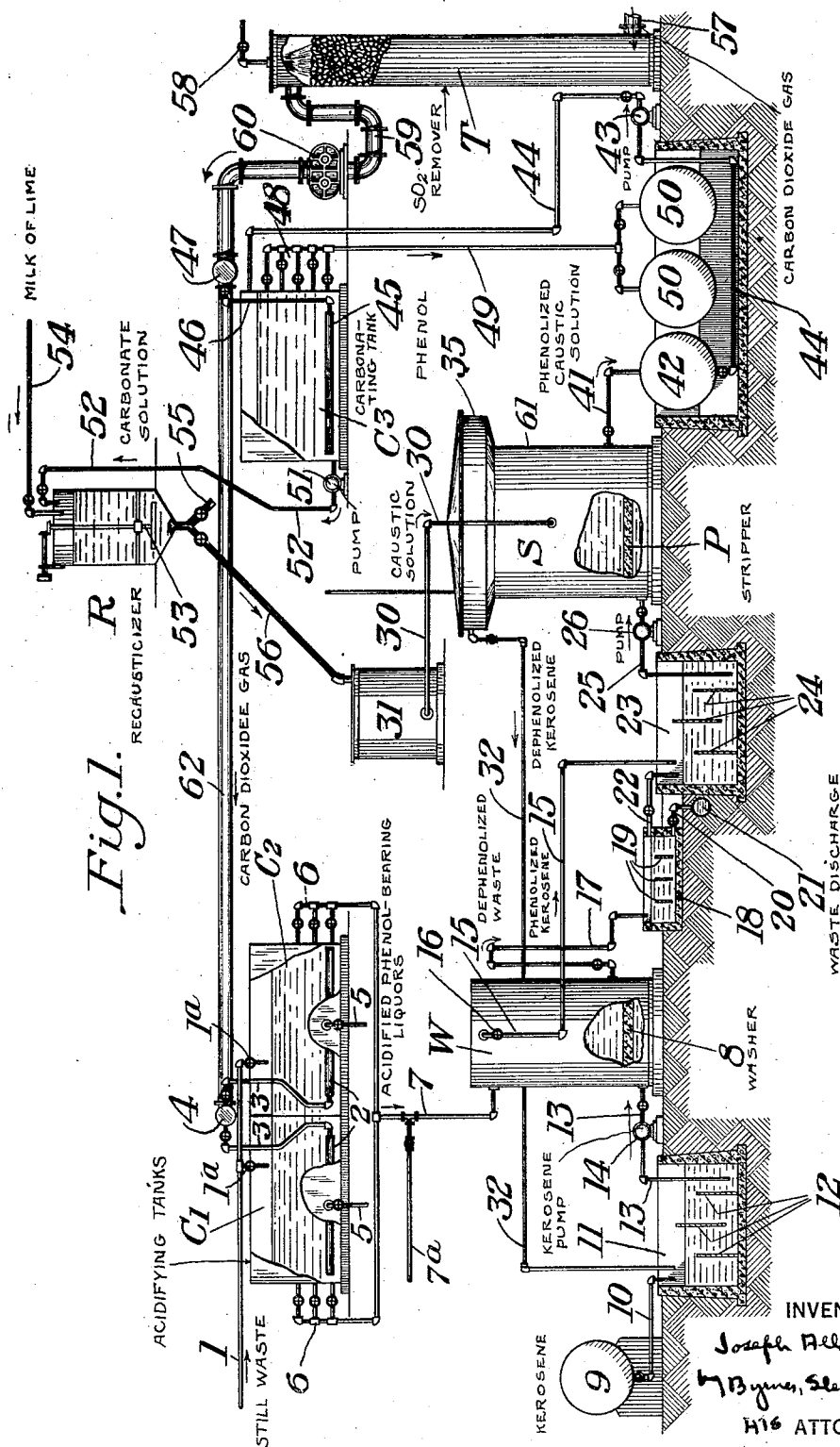
J. A. SHAW

1,832,140

METHOD FOR THE TREATMENT OF PHENOL BEARING LIQUORS

Filed May 27, 1926

3 Sheets-Sheet 1



Nov. 17, 1931.

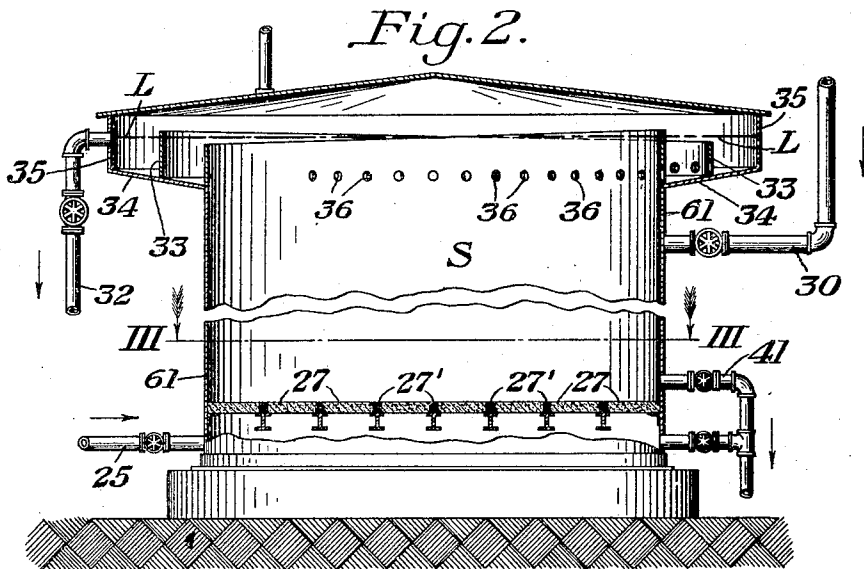
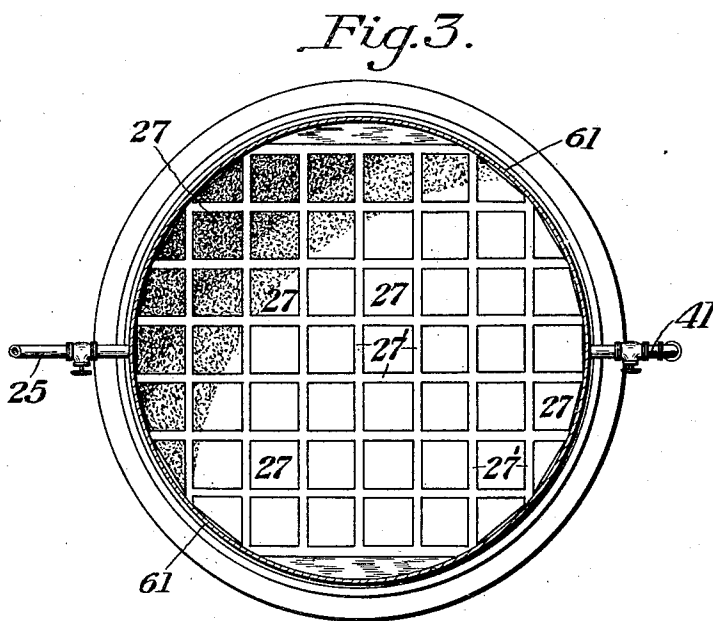
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METHOD FOR THE TREATMENT OF PHENOL BEARING LIQUORS

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3 Sheets-Sheet 2



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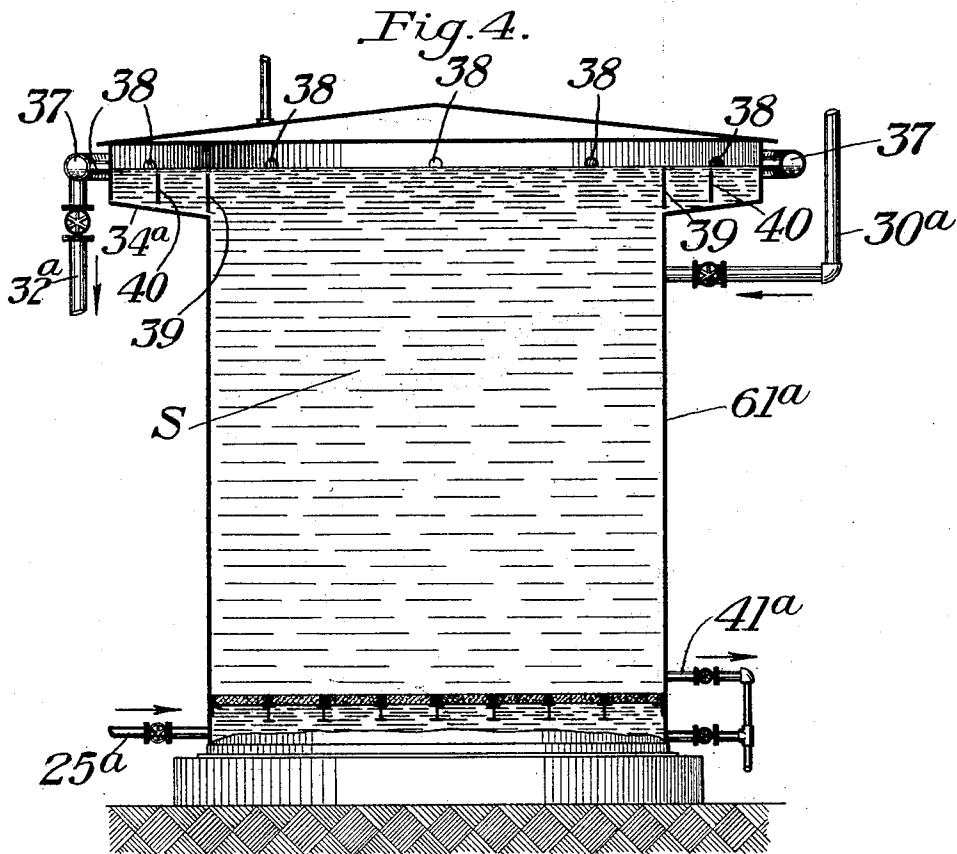
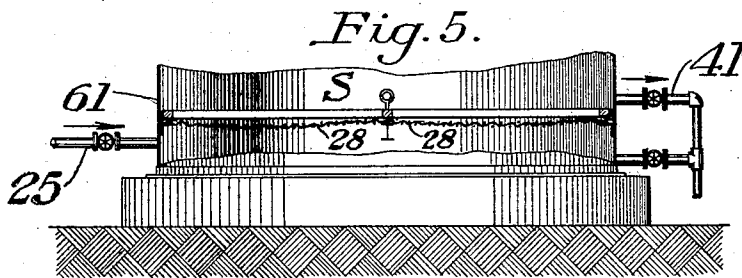
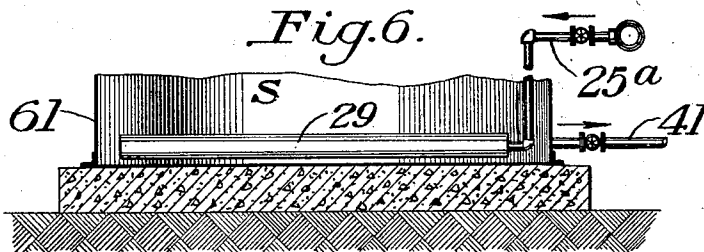
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METHOD FOR THE TREATMENT OF PHENOL BEARING LIQUORS

Filed May 27, 1926

3 Sheets-Sheet 3



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METHOD FOR THE TREATMENT OF PHENOL-BEARING LIQUORS

Application filed May 27, 1926. Serial No. 112,041.

This invention relates to the treatment of phenol-bearing liquors, and is of particular value in the treatment of liquors produced in the recovery of ammonia from coal gas whereby removal of the contained phenol is effected.

Kerosene is a more available and a less expensive solvent than benzol, and operating expenses due to initial cost, losses during use, and the like, are materially reduced as compared to benzol.

It has become important, from the standpoint of public health and convenience, to avoid contamination of rivers, lakes and the like with phenol, since it is almost impossible to remove the phenol by ordinary means if it gets into municipal water supply systems. It is becoming increasingly necessary for gas plants to remove phenol from wastes in which it is contained. The present invention provides for such removal at a minimum of expense, and it is attended with numerous advantages over the present methods employed.

It is common to treat phenol-bearing liquors with benzol, which is immiscible therewith and which extracts the phenol. This extraction is usually practiced on the undistilled ammoniacal liquors. The phenol is then removed from the benzol by treatment with caustic soda, thus forming sodium phenolate, and the phenol is subsequently separated by acidification. While benzol is an excellent solvent for phenol, it also is a solvent for any tar that may be present in the liquor, and after only a moderate period of use it becomes so fouled with such tar that it must be discarded and replaced with fresh benzol.

I employ a phenol absorbing petroleum distillate, such as kerosene, for the phenol extraction. I have found that even though kerosene is not as powerful a solvent for phenol as is benzol, it possesses numerous important advantages over benzol which render it superior for phenol extraction. It is less soluble in water than benzol, and consequently losses due to solution of the extraction agent in either the waste or the caustic solution are decreased. Tar is much less soluble in kerosene than in benzol, and therefore kerosene may be used for longer periods than benzol without undue contamination by dissolved tar. The use of kerosene is attended with much less loss due to evaporation, and the fire hazards are greatly minimized by its use.

I have discovered that the slightly lower solubility of phenol in kerosene as compared to its solubility in benzol, may be offset by introducing the kerosene in an extremely finely divided state. The kerosene is introduced in the finely divided state not only to the liquors to be treated, but also to the caustic solution, where it is stripped of the phenol extracted by it from the liquors. I therefore employ porous means, such as the well known Filtros blocks or plates; alundum plates, fabric diffusers, or the like, through which the kerosene is introduced into the liquor or the caustic solution.

I have further discovered that the tendency of tar to coagulate in the distillation of ammonia from gas liquors results in a reduction of the amount of tar dissolved by the kerosene or other solvent employed if the extraction of phenol is practiced upon the wastes from ammonia stills, as compared to the old practice of treating the ammoniacal liquors before distillation, when the tar is present in a more or less colloidal state. I therefore provide to treat the liquors to coagulate the tar, and thereafter treat the liquors to remove phenol therefrom.

Instead of using sulphuric acid, which is relatively costly, for the liberation of phenol from the sodium phenolate solution, I prefer to treat such solution with carbon dioxide. The carbon dioxide may be conveniently and cheaply found in flue gas and may also be used to acidify the still waste before it is treated with the kerosene. These carbon dioxide treatments are preferably accomplished in tanks provided with porous diffusers which may be similar in character to the diffusers above mentioned.

The use of flue gas is of particular value in a gas plant for a large amount of such gas is available. The presence of nitrogen in the flue gas is unimportant as it is inert and simply passes through the liquids being treated.

The accompanying drawings illustrate more or less diagrammatically a preferred embodiment of the invention with certain modifications of portions of the apparatus.

5 In the drawings—

Figure 1 is a diagrammatic view of an apparatus for the treatment of still waste or other phenol-bearing liquor;

10 Figure 2 is a side elevation, partly broken away, of a portion of the apparatus shown in Figure 1;

Figure 3 is a horizontal section taken on the line III—III of Figure 2;

15 Figure 4 is a view similar to Figure 2 but showing a modified form of apparatus; and

Figures 5 and 6 are views corresponding to the bottom portions of Figures 2 and 4 but showing modified diffusion apparatus.

20 In practicing the invention I prefer to treat the liquors from the ammonia stills. Such liquors, when fresh from the lime leg of the stills, may contain varying percentages of CaCl_2 , $\text{Ca}(\text{CNS})_2$, CaS , CaSO_4 ,
25 CaS_2O_3 , $\text{Ca}_2\text{Fe}(\text{CN})_6$, $\text{Ca}(\text{OH})_2$, CaCO_3 , NH_4OH , slight amounts of tarry materials or tar constituents, any impurities introduced in the liming process, and phenol. The phenol is usually combined with calcium in the form of calcium phenolate, $\text{Ca}(\text{C}_6\text{H}_5\text{O})_2$.

30 The effluent liquors may be treated directly or they may be decanted after settling to effect separation of a large portion of the suspended materials. Whether it is subjected to this decanting treatment or not, the effluent is supplied through a conduit 1 to acidifying tanks C^1 and C^2 arranged for batch treatment. Valves 1^a are provided in the conduit 1 for controlling the flow to the
40 acidifying tanks.

Each of the acidifying tanks is provided with a plurality of porous diffusers 2 which are connected through conduits 3 to a manifold 4 which is connected to a source 57
45 of carbon dioxide gas as hereinafter described. The diffusers 2 are preferably textile fabric tubes through which the carbon dioxide may pass in finely divided form to the liquors in the acidifying tanks. The fabric tubes are vibratile and are therefore effective for discharging the gas into the liquors over a continued period of time without clogging up. These diffusers are more particularly described and claimed in the copending application of Gilbert E. Seil, Serial No. 21,978, filed April 9, 1925. It will be understood, of course, that various other porous
55 diffusers may be used if desired.

The reactions which occur in the acidifying tanks C^1 and C^2 include the following:

- (1) $\text{Ca}(\text{OH})_2 + \text{CO}_2 = \text{CaCO}_3 + \text{H}_2\text{O}$;
- (2) $2 \text{NH}_4\text{OH} + \text{CO}_2 = (\text{NH}_4)_2\text{CO}_3 + \text{H}_2\text{O}$;
- (3) $\text{CaCO}_3 + \text{CO}_2 + \text{H}_2\text{O} = \text{Ca}(\text{HCO}_3)_2$; and
- (4) $\text{Ca}(\text{C}_6\text{H}_5\text{O})_2 + \text{CO}_2 + \text{H}_2\text{O} = \text{CaCO}_3 + 2\text{C}_6\text{H}_5\text{OH}$.

60 After carbonating a batch of the waste

liquors until the above reactions are completed, that is, until the waste is acidified, the CO_2 is shut off and the liquid is allowed to settle. The insoluble materials settle at the bottom of the tanks and may be removed at suitable intervals through drains 5. The supernatant liquor containing the phenol is decanted by suitably manipulating valved manifolds 6 and is allowed to flow through a conduit 7 at a convenient rate. If liquors
70 which are already acid in character are to be dealt with, the acidification may be omitted and the liquors introduced through a conduit 7^a .

The acid liquors which are taken from the tanks C^1 and C^2 or supplied through the conduit 7^a are carried through the conduit 7 to a washer W. The washer comprises a cylindrical shell provided with a porous diffusion means 8 near the bottom thereof. Said
75 diffusion means may comprise a layer of porous ceramic blocks, such as Filtros blocks, a layer of fabric, the above described vibratile fabric tubes, or any other suitable diffusion means. The diffusion means illustrated in the washer W is generally similar to that hereinafter described in connection with the stripping tank.

The purpose of the washer W is to introduce kerosene in finely divided form to the liquors supplied through the conduit 7. Kerosene is withdrawn from a storage tank 9 and flows through a conduit 10 into a sump 11. This sump is provided with a plurality of baffles 12 which are effective for removing
80 any sediment from the kerosene. The kerosene is withdrawn from the sump through a conduit 13 having a pump 14 therein and is introduced to the washer W below the porous diffuser 8. As it passes upwardly through the the diffuser it comes into contact with the phenol-bearing liquors in a very finely divided state. It is found that this is conducive to a very high efficiency of contact between the kerosene and the liquors and, consequently, a high rate of phenol extraction.

I have observed that the amount of phenol extracted by the kerosene is roughly proportional to the amount of phenol originally present in the liquors. The passage of four volumes of kerosene per volume of liquors has been found to remove over 50 per cent of the phenol from liquors containing 2.5 grams of phenol per liter. The passage of sufficient kerosene through the liquors will remove
85 substantially all of the phenol therefrom. In practice the ratio of flow will vary widely with various items of cost, the degree of dephenolization necessary, and the like.

As the introduction of kerosene to the liquors is continued, a substantial portion of the phenol will dissolve in the kerosene, which, being lighter than the liquors, will rise to the top of the washer W. This phenolized kerosene is taken off through a con-
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duit 15 having a valve 16 therein. Preferably this removal is continuous and the dephenolized waste is withdrawn through a sealed drain 17 and emptied into a sump 18. The sump 18 is provided with a plurality of baffles 19 which assist in causing any kerosene that may have been entrained with the dephenolized waste to rise to the top of the liquid in the sump 18. The waste, freed of kerosene, is taken up through a conduit 20 and discharged into a sewer 21, while the supernatant kerosene drains through a conduit 22 into a sump 23. The phenolized kerosene taken from the washer through the conduit 15 is also discharged into this sump.

The sump 23 is provided with baffles 24 which effectively retain any sediment or waste liquors entrained by the enriched kerosene. The kerosene is withdrawn from the sump 23 through a conduit 25 having a pump 26 therein and is discharged in a stripper S. The stripper S comprises an outer shell having a porous false bottom P below which the phenolized kerosene is introduced through the conduit 25. A solution of caustic soda is maintained in the stripper above the false bottom P, and the purpose of the false bottom is to introduce the phenolized kerosene to such caustic solution in a very finely divided state.

The construction of the stripper S is shown in detail in Figures 2 and 3. The false bottom P consists of porous blocks 27 carried by suitable supporting members. For use in the stripper I prefer to use porous blocks of aluminium oxid, such as the well known alundum blocks, as this material is resistant to the action of the caustic solution. In the washer W, however, the well known Filtros blocks are preferred as there is no caustic present in the washer and the Filtros blocks are readily obtained in a highly porous and open grade especially suitable for my purpose.

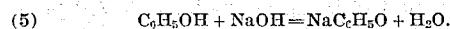
The blocks are cemented together as indicated at 27' so that all the phenolized kerosene introduced below the false bottom must pass through the blocks and be diffused thereby.

Figures 5 and 6 show slightly modified forms of diffusers for use at the bottom of the washer. In Figure 5 there is illustrated a flat vibratile metallic fabric 28 which extends across the bottom of the stripper and is effective for breaking up the phenolized kerosene into a state of fine division. In Figure 6 tubular diffusion means 29 are illustrated. The apparatus shown in Figures 5 and 6 is described and claimed in the copending application of David L. Jacobson, Serial No. 119,176, filed June 28, 1926.

When the finely divided phenol-bearing kerosene passes through the diffusion means, it comes into contact with the caustic solution in the main body of the stripper S. This

caustic solution is supplied through a conduit 30 from a supply tank 31 and it remains above the porous false bottom or other diffusion means employed, due to the positive pressure of the kerosene being forced through the diffuser.

The phenol carried by the kerosene reacts with the caustic according to the following equation:



The sodium phenolate dissolves in the aqueous solution.

Since the kerosene is lighter than the caustic solution, it rises to the top of the stripper, freed from its phenol by contact with the caustic solution, and may be withdrawn for further use.

In order to prevent loss of the aqueous solution by entrainment with the kerosene, I provide means for baffling the kerosene in the course of its flow from the stripper. Referring to Figure 2, it will be seen that the top of the shell 61 is not truly horizontal but is slightly inclined. This means that as the kerosene reaches the top of the shell it flows over at one side only; as the apparatus is shown in the drawings, it will flow over the left hand side.

The kerosene which flows over the top of the shell 61 is caught in an annular passage formed by an upstanding wall 33 and an outwardly extending bottom 34. The top of the wall 33 is also inclined to the horizontal, and in this case the kerosene, as it leaves the annular duct, will flow over the portion of the duct lying at the right hand side of the apparatus, as viewed in Figure 2. This means that the kerosene must flow substantially half way around the stripper before it passes over the wall 33 into an outer annular duct formed by the outwardly extending bottom 34 and an upstanding wall 35. The kerosene is permitted to flow from this outer duct through a conduit 32, and, as shown in Figure 2, this lies at the left hand side of the apparatus as viewed in the drawings, so that in order to reach it the kerosene must again travel half way around the stripper. During this tortuous course whatever caustic solution may be entrained with the kerosene is separated therefrom by gravity and flows back to the stripper through openings 36 in the wall 33 and the shell 61.

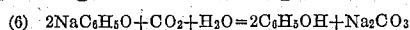
I have indicated by a chain line L the general level of the kerosene at the top of the stripper. It will be seen that the upstanding walls over which the kerosene must flow lie partly above and partly below this line, so that the kerosene is forced to take a path as above described in leaving the stripper. The conduit 32 leads back to the sump 11 from which the kerosene may be again withdrawn and used in the washer on a subsequent batch of phenol-bearing liquor.

Figure 4 illustrates a modified form of stripper in which corresponding parts have been given the same reference character with an "a" suffixed thereto. In this embodiment of the stripper, the shell is flared outwardly near the top and two baffles 39 and 40 are provided. These baffles have their upper edges at substantially the same level, and their lower edges do not meet the outwardly flared shell portion 34^a except for whatever supporting means may be necessary. The kerosene flows over the baffles 39 and 40, and during this time the caustic solution has an opportunity to separate by gravity and flow back to the main body of caustic in the stripper through the spaces below the baffles.

The kerosene leaves the stripper through openings 38 leading to a manifold 37 which is connected to the conduit 32^a.

When the caustic solution in the stripper nears its saturation point for phenol content, it is withdrawn through a conduit 41 to a tank 42 where it is held pending further treatment. Fresh caustic is then admitted to the stripper S from the supply tank 31. When it is desired to recover the phenol from the solution in the tank 42, the solution is pumped by means of a pump 43 in a conduit 44 into a carbonating tank C³. This carbonating tank is provided with a plurality of porous aerators 45 which are connected by conduits 46 to a manifold 47 which is connected to a source of CO₂ as hereinafter described.

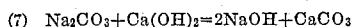
Phenol is liberated in the carbonating tank C³ according to the following reaction:



When this reaction is substantially complete, the liquid in the tank C³ is allowed to settle, whereupon the phenol will float upon the surface in a well defined layer, which may be decanted by means of a manifold 48 and allowed to flow by gravity through a conduit 49 to phenol tanks 50.

The carbonate solution remaining in the tank C³ after the phenol has been decanted is forced by a pump 51 through a conduit 52 into a recausticizer R equipped with an agitator 53.

Milk of lime is introduced to the recausticizer through a conduit 54, and is agitated with the carbonate solution until the following reaction is completed:



The calcium carbonate precipitates and is drawn off as a sludge through a conduit 55. The caustic solution is permitted to flow through a conduit 56 back to the supply tank 31 to renew the caustic solution therein. Additions of fresh caustic may be made to the supply tank 31 as required. The strength of the caustic solution is preferably the highest obtainable in the recausticizer, and may be made even higher by adding caustic soda to the tank 31.

As above stated, I prefer to use CO₂ both for the acidification of the still waste and for the liberation of phenol from the caustic solution. A cheap and convenient source of CO₂ is common flue gas. In Figure 1 I have shown a conduit 57 through which flue gas is supplied from any convenient source. The flue gas passes through the conduit into a tower T which is packed with limestone for the purpose of removing any SO₂ from the gas. A water spray 58 is provided for the promotion of this absorption. The purified flue gas is withdrawn from the top of the tower T through a conduit 59 by means of a pump 60 and is pumped to the manifolds 47 and 48 through a conduit 62.

In the above description I have set out the preferred form of my invention, wherein kerosene is used for absorbing the phenol from the gas liquors, and wherein carbon dioxide is used for acidifying, and caustic soda is used in the stripper. It will be understood that other phenol absorbing petroleum distillates may be used, as, for example, light fuel oil, naphtha or gasoline.

Instead of using caustic soda in the stripper, I may employ other substances, such as potassium hydroxide or calcium hydroxide.

Certain parts of my invention may be advantageously employed where an acidifier other than carbon dioxide is employed. For example, sulphuric acid may be used in connection with certain of the features of my invention. However, flue gas provides one of the most economical sources of acidifier and is, therefore, preferred.

I have illustrated and described a preferred embodiment of my invention and one manner of practicing it, but it will be understood that the invention is not limited to the described embodiment as it may be otherwise embodied or practiced within the scope of the following claims.

I claim:

1. In a method of treating aqueous phenol-bearing liquor, the step consisting in treating the liquor with a phenol-absorbing petroleum distillate.
2. In a method of treating aqueous phenol-bearing liquor, the step consisting in treating the liquor with a phenol-absorbing petroleum distillate in a finely divided state.
3. In the treatment of gas liquor to remove tar acid therefrom, the step which comprises treating the liquor with a petroleum distillate after removal of ammonia from the liquor.
4. In the treatment of gas liquor to remove tar acid therefrom, the step which comprises treating the liquor with a petroleum distillate after removal of ammonia, the distillate being supplied to the liquor in a finely divided state.
5. In a method of removing phenol from gas liquor, the steps consisting in treating the

liquor with a phenol-absorbing petroleum distillate to remove phenol therefrom, and treating the phenol-bearing distillate with caustic soda to form sodium phenolate.

5 6. The process of removing tar acid from aqueous liquor containing it which comprises continuously recirculating a hydrocarbon oil having a substantially different specific gravity therefrom through a cycle comprising an
10 absorption stage in which it is brought into intimate contact with the liquor and a regeneration stage in which tar acid removed from the aqueous liquor in said absorption stage is in turn removed from said hydrocarbon
15 oil.

7. The process of removing tar acid from aqueous liquor containing it which comprises continuously recirculating a hydrocarbon oil having a substantially different specific gravity therefrom through an absorption stage in
20 which it is brought into intimate contact with the liquor and a regeneration stage in which it is brought into intimate contact with an aqueous liquid of strongly absorbent nature
25 with respect to tar acid.

8. The process of removing tar acid from aqueous liquor containing it which comprises continuously recirculating a petroleum distillate oil through a cycle comprising an absorption stage in which it is brought into intimate
30 contact with the liquor, and a regeneration stage in which tar acid removed from the aqueous liquor in said absorption stage is in turn removed from said oil.

9. The process of removing tar acid from an aqueous liquid containing the same, which comprises continuously introducing said liquid and a phenol-absorbing petroleum distillate to contact with each other, and then
40 separating said liquid and said distillate.

10. The method of removing tar acid from an aqueous liquid containing it which comprises establishing a substantially continuous counter-current flow of said liquid and a
45 treating liquid comprising a phenol-absorbing petroleum distillate, and segregating the treated liquid and the treating liquid.

In testimony whereof I have hereunto set my hand.

50 JOSEPH ALLAN SHAW.

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