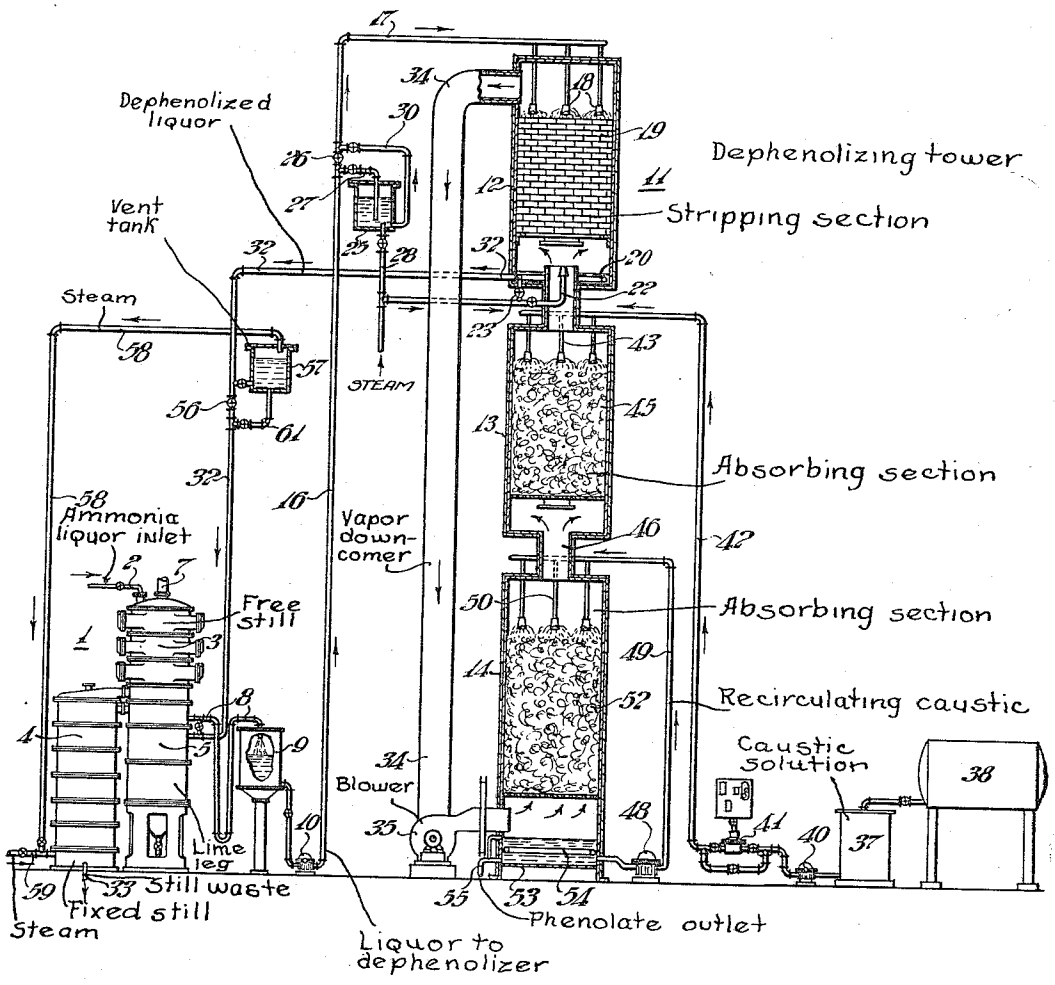
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TREATMENT OF LIQUIDS CONTAINING TAR ACID

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TREATMENT OF LIQUIDS CONTAINING TAR ACID

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My invention relates to the treatment of liquids containing tar acids such as phenol, cresols and analogous compounds, and especially to the treatment of gas liquor and similar condensates from fuel gas, such as coal gas. More specifically my invention relates to the removal and recovery of tar acid from ammoniacal gas liquor and other liquids in which it is present as an impurity.

An object of my present invention is to provide a process for more nearly completely removing tar acids from liquids containing them than has been possible in the past, and suitable apparatus therefor.

A second object of my invention is to provide a process of and apparatus for removing tar acids from gas liquor and other liquids at pressures substantially above atmospheric.

My invention has for further objects such other operative advantages and results as may be found to obtain in the process hereinafter described and claimed.

While the process of my present invention is broadly applicable to the removal of tar acids from any liquids containing them, it is especially adapted to the dephenolization of, or removal of tar acids from, gas liquor which is produced by either direct or indirect cooling of raw coal gas produced in coke ovens, gas retorts, etc. This liquor contains various constituents condensed from the gas, including free and fixed ammonia and certain of the lighter fractions of coal tar, such as phenol, cresols and their homologues, which are known as tar acids.

When this ammoniacal gas liquor is distilled to recover ammonia in the usual manner, the major portion of the tar acids originally present in the liquor is discharged with the ammonia still waste. In the past it has been a common practice to discharge the still waste to streams, or to reservoirs and the like from which at least a portion of it eventually found its way to streams, resulting in the pollution of the water with tar acids. This practice has now been prohibited in many localities, however, because of the disagreeable taste imparted to water containing even minute quantities of tar acids by subsequent chlorination.

Because of the regulations prohibiting the discharge of still waste and other plant effluents contaminated with phenol and its homologues to water courses, disposal of such liquids is now frequently a very serious problem. To overcome this difficulty various methods of dephenolizing the troublesome effluents have been developed.

The dephenolization of gas liquor and ammonia still waste has been the subject of particularly wide interest and considerable research in various quarters, which has resulted in the development of several processes for this specific purpose. The most effective and economical method of removing tar acids from gas liquor heretofore developed appears to be the vapor recirculation process described by Joseph A. Shaw in a copending application Serial No. 20,570, filed November 2, 1927.

My invention is a modification of and an improvement on the above-mentioned Shaw process.

In the Shaw process, gas liquor from which the free ammonia has preferably been removed at least in part, but which still contains tar acids and fixed ammonia, is treated with an inert gas or vapor, such as a mixture of coke oven gas or air and steam, at approximately the boiling point of the liquor and at approximately atmospheric pressure. The vapor is recirculated through a stripping stage in which it removes tar acids from the treated liquor, and through an absorbing stage in which the tar acids are given up to a tar acid absorptive medium such as caustic soda solution.

The dephenolized liquor is then mixed with milk of lime or other suitable alkaline material and distilled for the recovery of the fixed ammonia in the usual manner. The resulting still waste is substantially free from tar acids, but may contain up to 0.1 gram per liter (100 parts per million) or more of these compounds, determined as phenol. Below this point removal at atmospheric pressure becomes more difficult, and requires the use of larger equipment, making the process more expensive.

My improvement on this process consists essentially in conducting the dephenolization at pressures substantially above atmospheric, for example, up to 50 pounds per square inch gauge pressure, or higher. This increased pressure is accompanied by a corresponding increase in the temperatures of the tar-acid-containing liquor and the absorbing solution, so that the whole dephenolizing system is maintained at a higher temperature and pressure than in the Shaw process.

By this means I facilitate the removal of all the tar acids, those having higher boiling points as well as phenol itself, and thereby increase the efficiency of dephenolization.

Furthermore, when dephenolization is practiced at higher pressures the difficulty encountered at atmospheric pressure in removing the

last traces of tar acids (below 100 p. p. m., for example) from the liquor is almost completely eliminated. I have found that by increasing the pressure and temperature at which dephenolization is effected, while leaving the system substantially unchanged in other respects, the tar acid content of the dephenolized liquor is appreciably lowered, and in most instances the removal of tar acids is substantially complete. Another manifestation of the same effect is found in the fact that at higher pressures dephenolization to the usual extent can be accomplished in smaller apparatus.

My process for dephenolizing liquids by vapor recirculation at increased pressures may be applied by removing tar acids from liquids in a single system operated under pressure, or by first removing a portion of the tar acids at approximately atmospheric pressure and following this with a second treatment at increased pressure.

With the objects set forth above and other objects in view, I now describe with reference to the accompanying drawing a preferred method of practicing my invention. In the drawing,

The single figure is a view partly in elevation and partly in vertical section of apparatus suitable for practicing my improved process of removing tar acids from liquids containing them under pressure.

Ammoniacal gas liquor is introduced into an ammonia recovery installation 1 through a pipe 2. This installation 1 is preferably of the usual type consisting of a free ammonia still 3, a fixed still 4 and a lime mixing chamber 5 below the free ammonia still.

The liquor passes downwardly through the free ammonia still 3 and is distilled with steam or other hot vapor to remove free ammonia and other volatile constituents, which leave the still through a vapor pipe 7. From the bottom of this free still the liquor, containing at least a major portion of its original tar acid content, is withdrawn through a sealed discharge 8 to a surge tank 9. From this tank the liquor is delivered by an ammonia liquor pump 10 to the dephenolizing system.

In a preferred type of dephenolizing apparatus, such as that described by F. W. Sperr and J. A. Shaw in a copending application Serial No. 507,618, filed Jan. 9, 1931, (Case No. 154), dephenolization is accomplished in a tower 11. This tower consists of a stripping stage or section 12, and an absorbing stage including a fresh caustic section or shot section 13 and one or more recirculating sections 14. The advantageous results obtained by combining these stages in a single tower are described in the above mentioned application.

As a first illustration of the application of my present invention, operation under pressures somewhat above atmospheric, such as 10 lbs. per sq. in. gauge pressure, will be described. To maintain such pressures, only slight modifications are necessary, since the ammonia liquor at the bottom of the free still is already at a pressure of approximately 3 pounds.

Liquor is delivered by the pump 10 through pipes 16 and 17 to sprays 18 or other suitable distributing devices in the stripping section 12. The liquor is distributed by these sprays over suitable contact material such as wooden hurdles or spiral tile packing 19 with which the interior of this section of the dephenolizer is packed. While passing downwardly through this contact material, liquor is scrubbed with a countercurrent of recirculated gas or vapor which removes substantially all of the tar acids from the liquor. The liquor then collects in a sump or well 20 in the bottom of this section 12 of the dephenolizer.

I have found that several alternative or cooperative methods of maintaining the desired temperature and pressure may be used. A jet of live steam may be introduced into section 12 by a pipe 22, which discharges steam in a direction parallel with the flow of the recirculated vapor. The heat of the steam as well as its ejector effect are thus utilized. Another means of supplying heat is the installation of a closed steam coil 23 in the well 20.

Another method is to heat the liquor to the desired point before its entrance into the stripping section 12. This has the advantage that the circulating gas is contacted with the hottest liquor as it leaves the tower. For this purpose heat is conveniently applied to the liquor in a pressure vessel 25. A valve 26 between pipes 16 and 17 is closed, and liquor from the pipe 16 enters the vessel 25 through a pipe 27. Steam is supplied to the vessel through a pipe 28 to maintain the desired temperature and pressure therein. The liquor passes from the vessel through a pipe 30 into pipe 17, through which it is delivered to the dephenolizer as before.

The dephenolized liquor is withdrawn from the well 20 in section 12 through a pipe 32, and returned to the lime mixing chamber 5, from which it passes to the fixed ammonia still 4 where it is steam distilled for the recovery of ammonia in the usual manner. Still waste substantially completely free from all tar acids is discharged from the still 4 through a pipe 33 for disposal.

Recirculating vapor enriched with phenols removed from the liquor in the stripping section 12 passes through a downcomer 34, which is preferably insulated to prevent condensation, to a vapor pump or blower 35, which returns it to the bottom of the dephenolizing tower. The vapor passes upwardly through the recirculating section 14 in which at least a portion of the tar acids is absorbed, and through the fresh caustic section or shot section 13 in which absorption of the tar acids is completed. The vapor at least substantially free from tar acids re-enters the scrubbing section 12 wherein it removes phenols from a further quantity of liquor.

Fresh caustic solution of the desired strength is made up in a mixing tank or feed tank 37 by dissolving solid caustic or by diluting a concentrated solution supplied from a storage tank 38. This solution is withdrawn from the tank 37 by a pump 40 controlled by an automatic regulating meter 41 and delivered preferably intermittently through the meter 41, a pipe 42 and suitable distributing devices such as sprays 43, to the fresh absorbent section 13 of the dephenolizer 11.

This fresh caustic passes downwardly through steel lathe turnings 45 or other packing material contained in this section in intimate contact with the recirculated vapor, and in so doing absorbs tar acids from the vapor and is thereby partially converted to phenolate and the like. It then passes down through a passage 46 into the recirculating section 14.

Caustic soda solution, or a mixture of caustic and phenolate, is recirculated by a pump 48 through a pipe 49 and sprays 50 over the recirculating section 14. Below the sprays 50 the relatively fresh caustic from the shot section 13

is mixed with the recirculated solution, which is thereby refreshed.

The combined solution passes downwardly through packing material such as steel lathe turnings 52 in this section of the dephenolizer, absorbing tar acids from further quantities of vapor. The partially converted solution collects in a well 53 at the bottom of this section. Surplus caustic-phenolate solution is discharged from this well through a pipe 55 to a phenolate storage tank (not shown).

The recirculatory system is further heated to maintain throughout a temperature high enough to substantially prevent condensation of vapor by means of a steam coil 54, in the solution well 53, or other suitable heating means.

When higher pressures are desired, such as from 40 to 50 pounds per square inch gauge pressure, or higher, the use of the pressure vessel 25 to preheat the liquor is usually necessary. At lower pressures any of the other means of supplying heat to the ammonia liquor mentioned hereinabove may be used alone or in combination to supply enough heat to make the vessel 25 unnecessary.

When operating under these higher pressures, a valve 56 in pipe 32 is closed, and the liquor returning to the still through pipe 32 is passed through a pressure releasing vessel or vent tank 57. Steam is given up by the liquor due to the reduced pressure, and passes from vessel 57 through a vent line 58.

The steam so released may be utilized, for example, to heat the fixed ammonia still 4, replacing part or all of the steam usually supplied for this purpose through pipe 59.

By this expedient the additional expense of heating the liquor to the higher temperature and pressure is balanced by the saving in steam supplied directly to the fixed ammonia still. The liquor passes at normal pressure from the vent tank 57 through a pipe 61, back to pipe 32, and is returned to the lime mixing chamber 5 in the usual manner.

Another modification of this principle is practiced with the use of high pressure steam in the ejector 22. It is possible by the use of steam of sufficiently high pressure to maintain the desired pressure and temperature in the dephenolizer without the use of the preheating tank 25. Furthermore, in some cases it is possible to utilize the ejector effect of this steam to recirculate vapor through the system, thus eliminating the necessity for the blower 35.

The phenolate discharge line 55 is provided with a seal, a pressure releasing tank or valve, or other suitable means of retaining the desired pressure in the dephenolizer 11 while discharging surplus phenolate solution therefrom. Similarly, if the dephenolizer is operated at pressures such that it is not desirable to pass the liquor returning from the dephenolizer to the still through the pressure releasing vessel 57, a seal or other suitable means of retaining the pressure in the dephenolizer is provided in the liquor return line 32.

When dephenolization under pressure, according to my present invention, is practiced as the second stage of a dephenolizing process, the liquor delivered by pump 10 to the stripping section 12 of the pressure dephenolizer may come from the stripping section of a dephenolizer operating at substantially atmospheric pressure instead of coming directly from the free ammonia still as described hereinabove. The dephenolized liquor, however, returns from this second or final stage to the lime mixing chamber of an ammonia still as before.

My invention is not limited to any particular range of pressures, but may be practiced at any pressure substantially above atmospheric. I have found, for example, that the results obtained at 5 to 10 lbs. gauge pressure are appreciably better than those obtained at atmospheric pressure, and that this improvement becomes greater as the pressure is increased. However, when operating at pressures above 50 to 75 lbs., more complicated construction may be necessary to prevent mechanical difficulties. Consequently the preferred pressures in the present process are from 5 to 75 lbs. per sq. in. gauge.

What ever the pressure used, the liquid being treated is kept at a temperature near but usually slightly below its boiling point at that pressure. The recirculated vapor is also kept at a temperature near the boiling point of the liquid, but it may be at somewhat higher temperatures in parts of its cycle. The variation in temperature throughout the cycle is kept very small, however, by insulating the dephenolizer and by other means.

Recirculation of the inert gas or vapor is essential to the economic success of my process, but the efficiency of the stripping stage of my process depends solely on the passage of a suitable gas or vapor through the liquid to be dephenolized at a pressure substantially above atmospheric and at a temperature near the boiling point of the liquid at that pressure.

Any inert gas or vapor may be used, but it is preferable to use an inexpensive, readily available gas, such as air or coke oven gas, which is mixed or preferably saturated with steam or water vapor.

It will be obvious to those skilled in the art that various modifications other than those described hereinabove may be made in the various steps of my process and the various parts of my apparatus without departing from the spirit of my invention, and it is my intention to cover in the claims such modifications as are included within the scope thereof.

I claim as my invention:

1. The process of treating ammoniacal gas liquor containing tar acid, which comprises removing free ammonia from the liquor, transferring tar acid from the liquor to tar acid absorptive means by recirculating gas through the liquor and the said absorptive means at a pressure substantially above atmospheric and at a temperature near the boiling point of the liquor, withdrawing liquor substantially free from tar acid from contact with the recirculating gas, reducing the pressure on the liquor so withdrawn and thereby liberating steam, separating the liberated steam from the liquor, treating the liquor at reduced pressure to liberate fixed ammonia contained therein, and passing the said steam through the treated liquor to remove ammonia therefrom.

2. The process of treating an aqueous liquid containing tar acid which comprises dephenolizing the said liquid in a system maintained at a pressure substantially above atmospheric and at a temperature near the boiling point of the liquid at that pressure, withdrawing dephenolized liquid from the system, reducing the pressure on the withdrawn liquid and thereby liberating steam, separating the liberated steam from the liquid, and passing the said steam through the liquid to remove volatile constituents therefrom.

3. The process of treating ammoniacal gas liquor which comprises distilling the said liquor to remove free ammonia therefrom, transferring tar acid from the liquor to an aqueous alkaline solvent for tar acid by recirculating an inert gas saturated with water vapor through the said liquor and through the said solvent in a system maintained at a pressure between 5 lbs. and 75 lbs. per sq. in. and at a temperature near the boiling point of the liquor at that pressure, withdrawing liquor substantially free from tar acid from the said system, reducing the pressure on the liquor and thereby liberating steam, treating the liquor to liberate fixed ammonia, distilling the liquor to remove ammonia, and discharging still waste substantially free from tar acid.

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