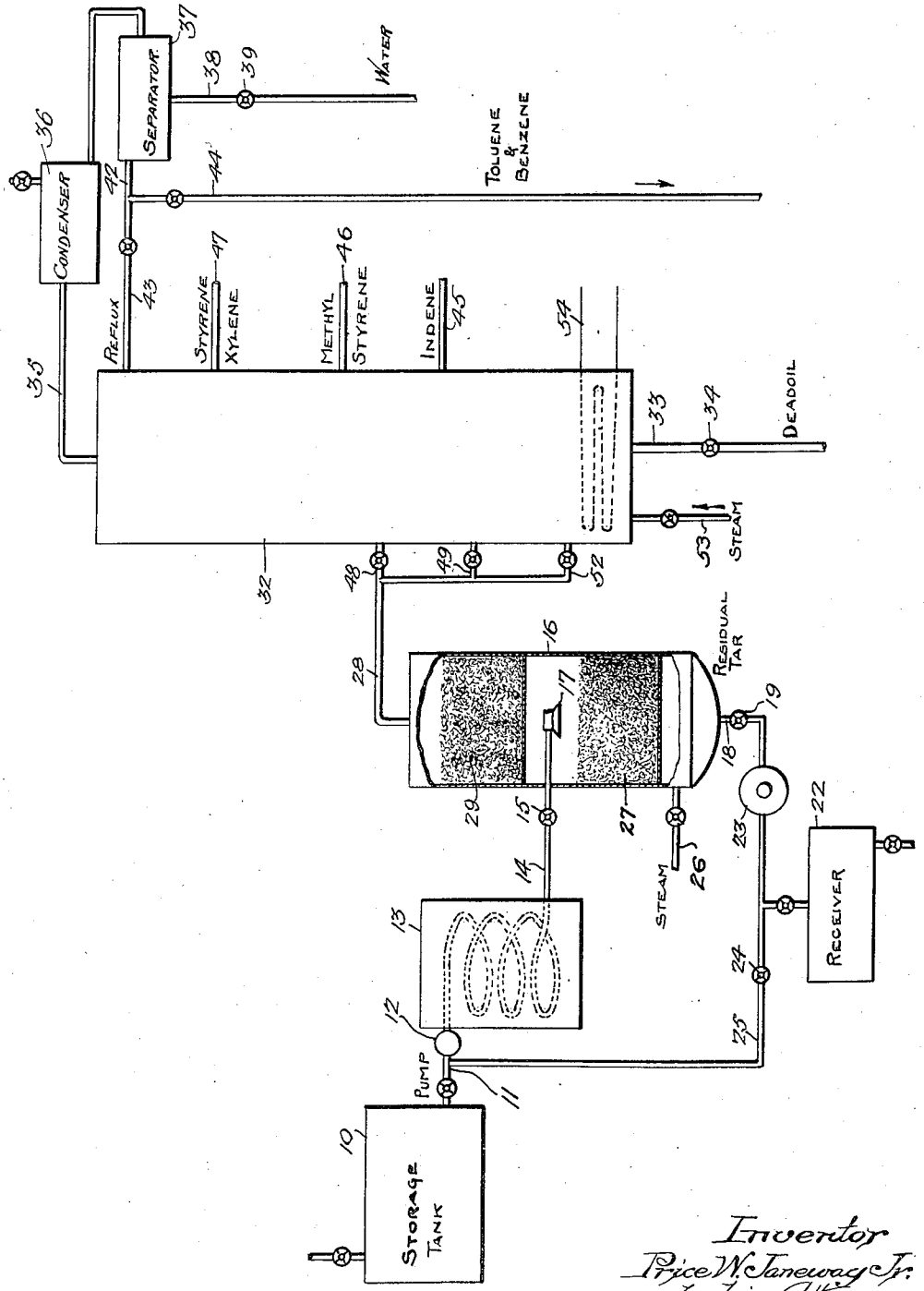
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CHEMICAL PROCESS

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CHEMICAL PROCESS

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4 Claims. (Cl. 196—76)

This invention pertains to the recovery of valuable hydrocarbons from tar formed during the production of combustible gas by processes involving the pyrolytic decomposition of hydrocarbon oil with or without the aid of catalysts.

Various processes are known for the manufacture of combustible gas such as carburetted water gas and oil gas wherein a petroleum oil such as crude oil or a fraction or fractions thereof, for example, gas oil, residuum oil, etc., is pyrolytically decomposed.

In such processes the gas leaving the gas-making apparatus is usually brought into contact with water such as in the wash box, and as a result the tar which separates from the gas is usually recovered in the form of an emulsion with water. The tar emulsion in extreme cases, may contain as high as 95% water or even higher. In some cases, the tar emulsion may be in the form of a pasty solid of very high viscosity. As a rule, the tar emulsion will contain at least 50% water and in this respect differs from tars obtained in processes for the production of coal gas or coke oven gas or in many oil cracking processes for the production of motor fuel, for in the latter processes the tar as recovered is not in an emulsion form. Therefore, the term "tar emulsion" or "petroleum tar emulsion" as used hereinafter and in the claims refers to emulsions of tar and water produced in the manner described, namely during the manufacture of combustible gas by processes involving the pyrolytic decomposition of petroleum oil.

The recovered mixture of tar and water from gas-making operations involving the decomposition of petroleum oil is usually first collected in a settling tank for the separation of as much water as possible by layer formation and decantation.

In accordance with prior art practice the relatively stable tar emulsion which remains after separation of the water layer has usually been treated according to some method of dehydration, such as centrifuging or distillation.

Centrifugal methods of treating tar emulsions, however, separate only the tar and the water of the emulsion and do not separate lighter tar constituents from the heavier. Furthermore, the presence of free carbon in the emulsion may give rise to operating difficulties.

The separation of the tar emulsion by ordinary distillation methods results in fractions which comprise (1) water, (2) a distillate from the tar comprising light oil and dead oil, and (3) residual tar.

For purposes of convenience in description, that portion of the distillate boiling up to approximately 200° C. (392° F.) at atmospheric pressure, will be designated "light oil" and that portion of the distillate boiling above approximately 200° C. at atmospheric pressure will be designated "dead oil." These may be separated from each other by distillation.

The light oil fraction contains, among other things, valuable saturated and unsaturated aromatic hydrocarbons such as benzene, toluene, xylene, styrene, methyl styrene, indene, etc.

The dead oil fraction contains naphthalene, methyl and other substituted naphthalenes, and may contain anthracene, methyl anthracene, as well as numerous other hydrocarbons for the most part as yet unidentified.

The residual tar contains free carbon, pitch and other bitumens and usually contains constituents which are polymerizable.

The residual tar has a number of uses. For example, it may be used as a road tar or as a heavy liquid fuel. For both purposes, the viscosity of the residual tar is of importance, among other things, because of its effect upon the ease of handling.

Due to the fact that the tar is subjected to elevated temperatures for considerable lengths of time such as of the order of 10 to 16 hours in ordinary distillation procedures of the prior art for breaking emulsions and for the separation of light oil and dead oil as distillate, substantial polymerization is caused to take place. Such polymerization tends to reduce the quantity of distillate on the one hand and to increase the viscosity of the residual tar on the other, both of which are undesirable.

In copending application Serial Number 342,735, filed June 27, 1940, by Edwin L. Hall and Howard R. Batchelder, there is described and claimed a process for breaking tar emulsions with the recovery of light oil and substantial quantities of dead oil containing considerable quantities of constituents in readily heat polymerizable state. In said process a tar emulsion is rapidly heated to an appropriate temperature capable of volatilizing considerable dead oil along with more volatile constituents and is then discharged into a separation zone which may be maintained at any desired suitable pressure, such as atmospheric or subatmospheric. In the separation zone the vaporized material is separated from the unvaporized material and taken off overhead. As a result a relatively large percentage of extremely heat sensitive unsaturated resin-forming material

boiling within the dead oil range is recovered from the tar which is not the case in prior art practice for in the latter practice, these materials are polymerized and left behind in the residual tar.

At the time of their separation in the separation zone the extremely heat sensitive unsaturated resin-forming constituents boiling within the dead oil range are for the most part in monomeric form and if it is desired to recover these constituents as such, they are cooled before any substantial polymerization thereof is capable of taking place.

On the other hand, when it is desired to produce heat polymer from these constituents after their separation from the residual tar such cooling is not essential.

This invention comprises an improvement over the process of said copending application and in one aspect is based upon a differential in heat sensitivity between the unsaturated constituents boiling within the dead oil range, the composition of which has not as yet been established, and the unsaturated constituents boiling within the light oil range, the latter including materials such as styrene and methyl styrene as well as others as yet not identified.

It has been discovered that this differential in heat sensitivity is sufficient to permit the heat polymerization of the heat sensitive unsaturated constituents boiling within the dead oil range in the presence of the heat sensitive unsaturated constituents boiling with the light oil range without causing a substantial heat polymerization of the latter heat sensitive unsaturated materials.

The foregoing discovery makes it possible to separate by distillation the light oil without material polymerization of its heat sensitive unsaturates while subjecting the heat sensitive unsaturates in the dead oil to heat polymerization to form high quality resins.

In accordance with this invention the vaporized constituents separated from the unvaporized constituents in the process of said copending application are directly subjected to fractional distillation in a manner such that the residuum of said fractional distillation is collected separately from the residual tar. Preferably this fractional distillation is so conducted that the dead oil fraction including any heat polymer formed therein comprises the residuum and the light oil including the heat sensitive unsaturates contained therein are taken off overhead.

However, since the heat polymer formed from the heat sensitive dead oil constituents is the least volatile of all the materials in process during this fractional distillation, any other desired cut points between the residuum and overhead may be made.

The process lends itself suitably to the simultaneous separation of the overhead into various fractions by the employment of an efficient fractionating column from which side streams may be taken off.

For example, and assuming that the dead oil for the most part is concentrated in the residuum, such side streams might comprise an indene fraction, a methyl styrene fraction and a styrene fraction. Water, benzene and toluene may be taken off overhead.

After condensation the water layer may be separated from the benzene-toluene layer by any suitable means, such as by decantation.

The presence of the water, which of course originated in the emulsion during the fractionation and any stripping steam which might be added, assists these separations by reduction in the partial pressures of the various hydrocarbon materials undergoing distillation.

The fractionation may be conducted in a manner to polymerize a large part or substantially all of the heat polymerizable unsaturated hydrocarbons boiling in the dead oil boiling range.

On the other hand the fractionation may be conducted in a manner to minimize the polymerization of such unsaturates and to recover a large and even a preponderant part thereof in monomeric form for any desired utilization as for example for the production of catalytic polymer.

In any case, due to the collection of the residue of the fractionation separate and apart from the collection of the tar residue, any heat polymer formed during the fractionation of the vaporized constituents of the emulsion after separation from the unvaporized constituents thereof may be recovered separate from the tar residue and not lost therein.

Further features of the invention will become apparent to persons skilled in the art as the specification proceeds and upon reference to the drawings in which:

Figure 1 is a diagrammatical illustration of one form of the invention.

Referring now more particularly to Figure 1, 10 is a storage tank for tar emulsion which flows through line 11 and pump 12 into pipe still 13 in which the emulsion is heated to a desired temperature, such as between 100° to 350° C., and at any desired pressure such as between atmospheric and 150 pounds per square inch.

The heated material flows from still 13 through line 14 and valve 15 into separating chamber 16 through nozzle 17.

Upon its release into separating chamber 16 the heated material is rapidly separated into vaporized and unvaporized portions.

The interior of chamber 16 is constructed so as to permit the rapid separation of vaporized from unvaporized material. For example, chamber 16 may be relatively empty in the separation zone.

Unvaporized tar constituents descend through chamber 16 and are withdrawn through outlet 18 controlled by valve 19 and are collected in the receiver 22, or a part thereof may be recycled with the assistance of pump 23 through valve 24 and line 25 which connects with line 11. Recycling a part of the residual tar may be resorted to to increase the rate of flow through pipe still 13, one purpose of which may be to reduce any tendency for accumulations to adhere to the inner side walls thereof. Due to the increased rate of flow through pipe still 13, the total time of heating of the dead oil constituents need not be increased even if the recycled tar contains dead oil constituents, and the same may apply to the residual tar because of its more rapid transit.

It is preferred not to extend the total time during which the dead oil constituents are held in process at considerably elevated temperatures during the separation of these constituents from the residual tar beyond two hours and more preferably not beyond one hour because of the extremely heat sensitive unsaturated material therein which it is desired to take off overhead which would not be accomplished if such constituents were polymerized to a relatively non-volatile form or decomposed as a result of the treatment.

Short separating times such as below thirty minutes are particularly desirable.

If desired, the descending unvaporized tar particles may be contacted in chamber 16 with a heated gaseous medium such as steam to effect a further separation of volatile material therefrom.

For this purpose steam may be injected into chamber 16 at any suitable point, such for example as illustrated at 26.

If desired, phase contacting means 27 may be arranged in chamber 16 to assist in the contact of descending tar particles with ascending heated gaseous medium, the latter being sufficient to volatilize the more volatile constituents of the tar not only by virtue of added heat but also by virtue of reduction in partial pressure.

Vaporized tar constituents and steam pass up through chamber 16 and are withdrawn through line 28.

To remove any unvaporized particles and any foam from the ascending vapors, phase separating means may be arranged in the upper portion of chamber 16. The ascending vapor comes into contact with the contacting means 29 causing unvaporized particles and foam to coalesce into liquid droplets of sufficient size to drop down through the ascending vapors and into the lower portion of chamber 16 from which they may be removed along with the residual tar.

Phase separating means 27 and phase contacting means 29 may be of any suitable design, construction, and arrangement and may include any of the various means employed for contacting phases and for removing entrained particles from contacting vapor and liquid phases.

The contacting means 27 and 29 are preferably so chosen as to effect a relatively small hold-up, if any.

Hydrocarbon and water vapors flow through line 28 into tower 32 in which a separation between light oil and dead oil constituents is made.

It may be preferred to hold the materials in process in tower 32 for a sufficient length of time to polymerize at least the preponderant portion of the heat polymerizable constituents boiling within the dead oil range.

As pointed out previously, due to the wide time differential for heat polymerizing dead oil and light oil constituents, substantially all of the heat polymerizable dead oil constituents may be polymerized in tower 32 if desired without causing from a practical standpoint an appreciable heat polymerization of heat polymerizable light oil constituents.

The dead oil heat polymers are soluble in the unpolymerized portion of the dead oil and may be drawn off in solution therein through line 33 controlled by valve 34.

The sharpness of separation between unpolymerized dead oil and the light oil will of course depend upon the efficiency of tower 32. The polymerized portion of the dead oil is sufficiently nonvolatile as to present no particular problem in the separation of light oil therefrom.

On the other hand the fractionation may be performed so as to minimize the polymerization of heat sensitive unsaturated hydrocarbons in the dead oil boiling range and to remove a large proportion thereof in monomeric form for any desired utilization. To this end the fractionation may be conducted rapidly to provide dead oil and light oil fractions and the subjection of the material to heat while in process minimized.

Vapors leaving tower 32 through line 35 are condensed in condenser 36 and the condensate flows into separator 37 in which hydrocarbon distillate and water separate in layers, the water being drawn off through line 38 controlled by valve 39 and the hydrocarbon distillate being drawn off through line 42. That portion of the hydrocarbon condensate which is not returned to the tower through line 43 as reflux is withdrawn off through line 44 as a product fraction.

As previously intimated the composition of the product fraction may comprise any part or all of the light oil and may even contain some dead oil, depending upon the construction and operation and efficiency of tower 32.

For example, if the efficiency of tower 32 is hardly more than a few theoretically perfect plates, hardly more than a rough separation between light oil and dead oil will be made. On the other hand, if tower 32 is relatively efficient a sharp separation between light oil and dead oil may be made. In this connection it is to be understood that although for convenience in description a cut point of 200° C. has been mentioned, it is to be understood that any other suitable cut point between light oil and dead oil may be employed. As an example of another suitable cut point 210° C. might be mentioned.

It is of course to be understood that tower 32 may be designed and constructed to make separations between the light oil constituents by making provisions for side streams and the same may in fact also apply to the dead oil.

As illustrated, tower 32 is constructed for taking off at 45 an indene fraction; at 46 a methyl styrene fraction; and at 47 a styrene-xylene fraction. In this event the overhead hydrocarbon fraction will comprise a fraction of benzene and toluene.

It will of course be understood that any other number of side streams might be taken off either greater or less in number than those illustrated.

The vapors flowing through line 28 will enter the tower 32 at an appropriate point depending upon its design and operation and for purposes of illustration, there has been shown a plurality of alternative inlets 48, 49 and 52.

Steam or any other gaseous medium in addition to that provided by the water in the emulsion and that injected at 26 if any, may be injected into tower 32 at any suitable point as desired, for example, as illustrated at 53.

Any other auxiliary device to assist in making the desired separations may be employed.

For example, heating coil 54 may be provided in the bottom of tower 32 to assist in the polymerization of the heat polymerizing constituents of the dead oil, if desired. In such case, if desired, the preponderant portion of the dead oil may be taken off as a side stream or overhead leaving as residue a highly concentrated solution of polymer in the higher boiling non-heat-sensitive constituents of the dead oil. The heat polymer may be thus concentrated to resin having any desired melting point.

It will be understood of course that heating coil 54 is also adapted to act as a reboiler.

Other variations are possible.

For example, still 13, separator 16 and tower 32 may be employed merely for the separation of the bulk of the water and benzene which are taken overhead from the remaining constituents which may flow off in the liquid phase into a still for the separation of the remaining light oil.

Such a still may, if desired, be a duplicate of pipe still 13, and may have associated with it

duplicates of the other apparatus of Figure 1 such as separating chamber 16 and tower 32, or this still may be of any other desired description.

It is preferred to maintain a uniform feed of emulsion to the still 13 and to that end it may be preferred to provide the emulsion storage tank 10 with agitation means, such as for example a stirrer.

Any desired means of heating still 13 may be employed such as firing by solid or fluid fuel, though heating by superheated steam may be preferred from the standpoint of securing more uniform heating.

Therefore, changes, omissions, additions, substitutions and/or modifications might be made within the scope of the claims without departing from the spirit of the invention which is limited only as required by the prior art.

I claim:

1. A process for the dehydration of a petroleum tar emulsion with the simultaneous separation of the constituents of the tar into tar residue and lower boiling constituents with increased separation from said tar residue of heat sensitive unsaturated hydrocarbon material boiling above 200° C. and with the separation of said lower boiling constituents into light oil and dead oil fractions with the heat polymerization of heat sensitive unsaturated hydrocarbon material boiling above 200° C. separated from said tar residue, which comprises flowing a stream of petroleum tar emulsion through a heating zone and heating said stream therein, passing the resulting stream of heated material into a separating zone for the separation of vaporized hydrocarbon constituents including light oil and dead oil constituents and of water vapor from unvaporized constituents including tar residue, after separation removing said unvaporized constituents from said separating zone for collection, after separation removing said vaporized hydrocarbon constituents from said separating zone, passing said removed vaporized hydrocarbon constituents into a fractionating zone arranged to collect a residue separate from the collection of said unvaporized constituents, subjecting said vaporized hydrocarbon constituents to fractionation in said fractionating zone and collecting a dead oil fraction as residue therefrom, supplying sufficient heat during said fractionation to cause the heat polymerization of at least a part of the heat sensitive unsaturated hydrocarbon material boiling above 200° C., and recovering the resultant heat polymer in solution in said last named dead oil fraction.

2. A process for the dehydration of a petroleum tar emulsion with the simultaneous separation of the constituents of the tar into tar residue and lower boiling constituents with increased separation from said tar residue of heat sensitive unsaturated hydrocarbon material boiling about 200° C. and with the separation of said lower boiling constituents into light oil and dead oil fractions with the heat polymerization of heat sensitive unsaturated hydrocarbon material boiling above 200° C. separated from said tar residue, which comprises flowing a stream of petroleum tar emulsion through a heating zone and heating said stream therein, passing the resulting stream of heated material into a separating zone for the separation of vaporized hydrocarbon constituents including light oil and dead oil constituents and of water vapor from unvaporized constituents including tar residue, after separation removing said unvaporized constituents from said separating zone through phase contacting means in countercurrent contact with stripping steam and collecting the resulting stripped unvaporized constituents, after separation removing said vaporized hydrocarbon constituents from said separating zone through phase separating means for the removal of entrained particles of unvaporized constituents, passing said removed vaporized hydrocarbon constituents into a fractionating zone arranged to collect a residue separate from the collection of said unvaporized constituents, subjecting said vaporized hydrocarbon constituents to fractionation in said fractionating zone and collecting a dead oil fraction as residue therefrom, and supplying sufficient heat during said fractionation to cause the heat polymerization of at least a part of the heat sensitive unsaturated hydrocarbon material in said dead oil fraction.

3. A process for the dehydration of a petroleum tar emulsion with the simultaneous separation of the constituents of the tar into tar residue and lower boiling constituents and with separation from said tar residue of heat sensitive unsaturated hydrocarbon material boiling above 200° C. and with the separation of said lower boiling constituents into light oil and dead oil fractions with the heat polymerization of heat sensitive unsaturated hydrocarbon material boiling above 200° C. separated from said tar residue, which comprises flowing a stream of petroleum tar emulsion through a heating zone and heating said stream therein, passing the resulting stream of heated material into a separating zone for the separation of water vapor and of vaporized hydrocarbon constituents including light oil constituents and dead oil constituents containing heat sensitive unsaturated hydrocarbon material boiling above 200° C. from unvaporized constituents including tar residue, after separation removing said unvaporized constituents from said separating zone for collection, after separation removing said vaporized hydrocarbon constituents from said separating zone, passing said removed vaporized hydrocarbon constituents while still in vapor phase into a fractionating zone arranged to collect a condensate residue separate from the collection of said unvaporized constituents, subjecting said vaporized hydrocarbon constituents to fractionation in said fractionating zone and collecting dead oil constituents as residue therefrom, supplying sufficient heat during said fractionation to cause the heat polymerization of at least a part of the heat sensitive unsaturated hydrocarbon material boiling above 200° C., and recovering the resulting heat polymer as at least a part of said last named residue.

4. A process for the dehydration of a petroleum tar emulsion with the simultaneous separation of the constituents of the tar into tar residue and lower boiling constituents and with separation from said tar residue of heat sensitive unsaturated hydrocarbon material boiling above 200° C. and with the separation of said lower boiling constituents into light oil and dead oil fractions with the heat polymerization of heat sensitive unsaturated hydrocarbon material boiling above 200° C. separated from said tar residue, which comprises flowing a stream of petroleum tar emulsion through a heating zone and heating said stream therein, passing the resulting stream of heated material into a separating zone for the separation of water vapor and of vaporized hydrocarbon constituents including light oil constituents and dead oil constituents containing heat sensitive unsaturated hydrocarbon material boiling above 200° C. from unvaporibed constituents including

tar residue, after separation removing said unvaporized constituents from said separating zone for collection, after separation removing said vaporized hydrocarbon constituents from said separating zone, passing said removed vaporized hydrocarbon constituents into a fractionating zone arranged to collect a condensate residue separate from the collection of said unvaporized constituents, subjecting said vaporized hydrocarbon constituents to fractionation in said fractionating zone and collecting a hydrocarbon fraction boiling above 200° C. as residue therefrom, supplying sufficient heat during said fractionation to cause the heat polymerization of the preponderant part of said heat sensitive unsaturated hydrocarbon material boiling above 200° C., and recovering the resultant heat polymer in said last named hydrocarbon fraction.

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