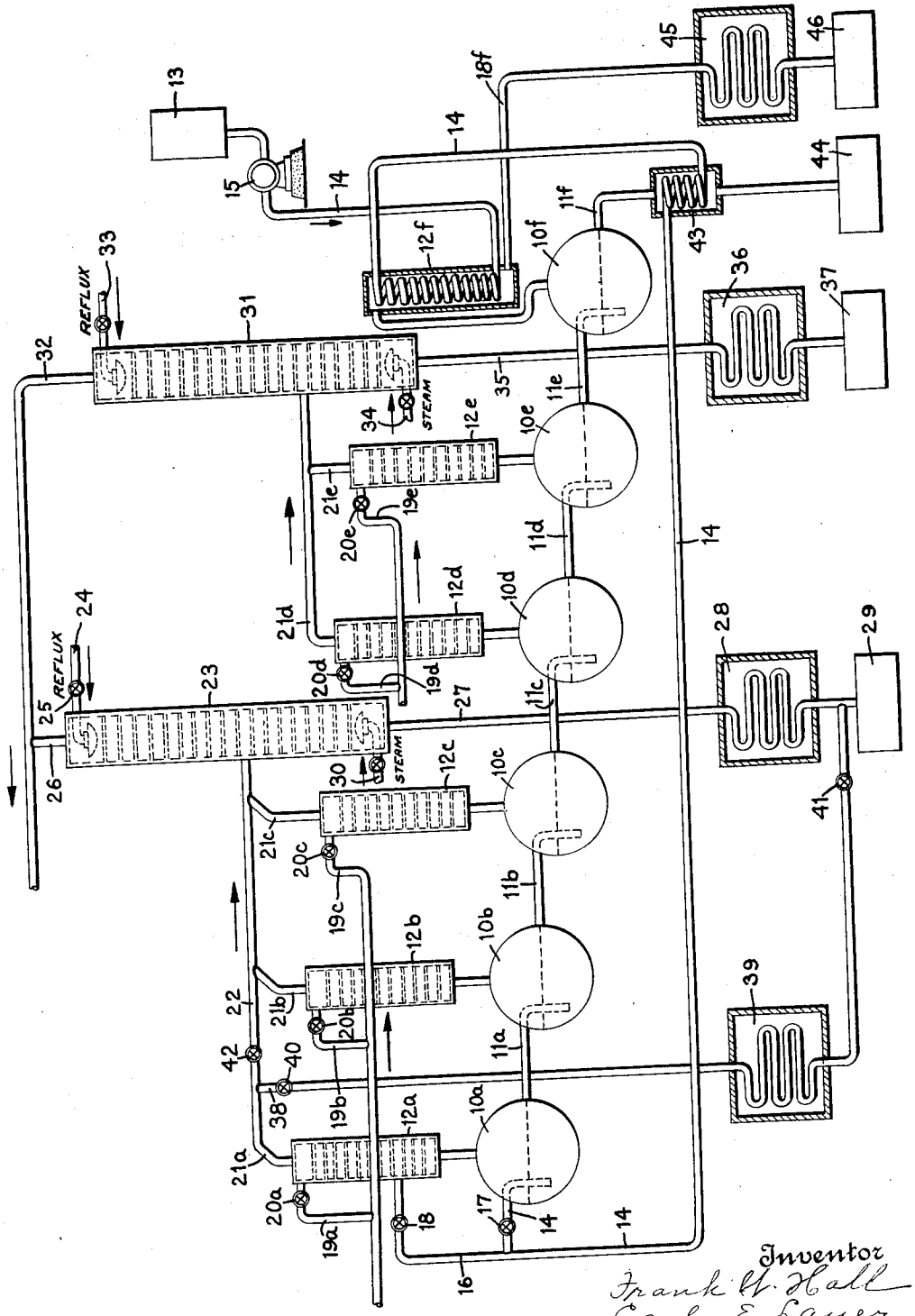
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TREATING HYDROCARBON OIL

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TREATING HYDROCARBON OIL

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This invention relates to a method of treating hydrocarbon oils to effect removal of hydrogen sulphide. The invention contemplates a process in which hydrocarbon oils associated with hydrogen sulphide are subjected to fractionation whereby substantially the entire content of hydrogen sulphide is separated from the hydrocarbons condensable at ordinary temperatures and pressures.

In the distillation of crude petroleum containing free hydrogen sulphide, or sulphur compounds which are decomposed by heat yielding hydrogen sulphide, it is important that the distillates such as kerosene and gasoline be separated from the hydrogen sulphide, the usual method being to contact the condensed distillates with an alkaline solution such for example as caustic soda, which will react with the hydrogen sulphide, eliminating it from the oil. Such processes are costly when applied to oils having a large hydrogen sulphide content and, in addition, are usually only about 90% efficient, thus requiring further expensive desulphurizing treatment for the production of merchantable products. If hydrogen sulphide is not removed from gasoline and kerosene distillates, it is extremely corrosive upon storage tanks and other equipment with which is comes in contact, and its presence may be harmful to the distillates with which it is associated, rendering them more difficult to treat and greatly increasing the expense of the typical treating and purifying processes.

By the practice of the present invention, hydrogen sulphide may be eliminated substantially completely from oil distillates during the process of distillation and at much less expense than by any other method thus far devised.

The invention may be clearly understood when considered in connection with the accompanying drawing which represents, in diagrammatic elevation, apparatus suitable for practicing the invention.

Referring to the drawing, reference numerals 10*a*, 10*b*, 10*c*, etc., represent individual stills in a battery of six stills connected in series by means of the flow lines 11*a*, 11*b*, 11*c*, etc. Stills 10*a* to 10*e* inclusive are fitted with suitable fractionating towers 12*a*, 12*b*, etc., which may be of the type known as bubble towers, or of any other suitable construction. The final still in the series, 10*f*, is fitted with a vapor heat exchanger 12*f*, instead of a fractionating tower.

A source of charging stock for the battery is the tank 13 connected through the charging line 14 and the charging pump 15 to the first still in the battery, number 10*a*. A branch 16 of the charging line 14 enters the fractionating tower 12*a* at an intermediate point, and valves 17 and 18 are provided, as shown, in the lines 14 and 16 respectively. The charging line 14 is connected to the vapor heat exchanger 12*f* and to the residuum heat exchanger 43, as will be explained more fully in a later paragraph.

The fractionating towers 12*a* to 12*c* inclusive are fitted with connections 19*a*, 19*b*, etc. fitted with valves 20*a*, 20*b*, etc., for the introduction of the material to the tower to provide reflux cooling. Vapor lines 21*a*, 21*b* and 21*c* leading from the tops of the corresponding towers are connected to the vapor manifold 22 and enter the fractionating tower 23 at an intermediate point. The fractionating tower 23 may be of any suitable type, as for example a bubble tower similar in general to the towers 12*a*, 12*b*, etc., and is fitted with a suitable connection 24 and valve 25 for the admission of material to supply reflux cooling. A vapor line 26 is provided at the upper end of the tower 23 and a condensate line 27 at the lower end leading to the cooling coil 28 and thence to the storage tank 29. A steam connection 30 is provided in the lower portion of the tower 23.

The vapor lines 21*d* and 21*e*, leading from the tops of the corresponding towers, enter the fractionating tower 31 at an intermediate point. The fractionating tower 31 may be similar in design to the tower 23, being fitted with a similar vapor line 32, reflux connection 33, steam connection 34 and condensate line 35, passing through the cooling coil 36 to the storage tank 37. A line 38 is connected into the vapor manifold 22 at a point between the points of entry of the vapor lines 21*a* and 21*b*, leading to the cooling coil 39 and thence to the storage tank 29. The line 38 is provided with valves 40 and 41, as shown, and the manifold line 22 is provided with valve 42, positioned between the point of entry of the vapor line 21*b* and the line 38.

The still 10*f*, the last of the series, is fitted with a vapor heat exchanger 12*f*, instead of a fractionating tower, as on the other stills of the series. A draw-off or flow line 11*f* connects with the exchanger 43 and passes thence to the storage tank 44. The vapor line 18*f* from the vapor heat exchanger 12*f* passes through the cooling coil 45 to the storage tank 46.

In practicing the invention in connection with the apparatus described, the procedure may be as follows:—

The charging stock, which may consist of a

comparatively high-sulphur crude petroleum of the type generally obtained from the west Texas fields, is pumped from the storage tank 13 by means of the pump 15 through the charging line 14 and into the first still of the series, 10*a*. Under some conditions it may be desirable to close the valve 17 and open the valve 18, whereby the charge passing through the line 16 enters the tower 12*a*, rather than being introduced directly into the still 10*a*. The oil overflows from the still 10*a* through the overflow line 11*a* into the still 10*b*, and so on throughout the series of stills, each individual still being heated by means of furnaces (not shown) to temperatures slightly higher than the preceding still in the series. For example, still number 10*a* may be maintained at a temperature of approximately 410° F., still number 10*c*, at 525° F., while the final still, number 10*f*, may be maintained at 650° F.

Vapors evolved from stills 10*a*, 10*b* and 10*c* pass upward through the corresponding fractionating tower 12*a*, 12*b* and 12*c*, wherein they are subjected to fractionation, the heated vapors being cooled by reflux introduced into the towers through the connections at 19*a*, 19*b* and 19*c*. The reflux material may consist of the crude charge or of the final condensate obtained from these particular towers, or of any other suitable material. The distillation and fractionation is carried on in such manner that the composite vapors from the three towers will have a boiling range within the normal boiling range of commercial gasoline. The vapors from the several towers pass through the vapor lines 21*a*, 21*b* and 21*c*, entering the manifold line 22, through which they pass into the fractionating tower 23 at an intermediate point.

The vapors entering the tower 23 contain all the hydrogen sulphide, which may amount to approximately 0.3% to 0.4% by weight of the gasoline fraction, evolved during the distillation of the oil in the first three stills of the series. The vapors passing upward through the tower are subjected to reflux cooling, a suitable cooling agent being introduced through the line 24 controlled by means of the valve 25. Preferably, the cooling agent may consist of water, although cooling may be applied by other suitable means, as by the circulation of a suitable cooling agent through a closed coil in the top of the tower. In order to aid in fractionation, steam may be introduced into the lower portion of the tower through the line 30. Temperatures of approximately 100°F.–110° F. at the top and 200° F.–210° F. at the bottom may be maintained, and the tower is operated under such conditions that substantially the entire amount of hydrocarbon vapors entering the tower are condensed therein, while the hydrogen sulphide and a small quantity of fixed hydrocarbon gases are distilled out of the top of the tower through the vapor line 26. The condensate from the tower, which has a boiling range of substantially that of commercial gasoline, is withdrawn through the line 27, cooled by passing through the cooling coil 28, and then passes to the storage tank 29. The water from the reflux and the condensed steam may be separated from the condensed gasoline prior to its passage through the cooling coil 28.

With certain classes of charging stock it may be found that hydrogen sulphide is not given off to any great extent from the first still of the battery, which may be due to the fact that charging stock contains no appreciable quantity of free hydrogen sulphide and the temperature of the first still is not sufficiently high to cause decomposition of sulphur compounds with the liberation of hydrogen sulphide. Under such conditions it may be desirable to by-pass the vapors from the first still of the series around the tower 23, which may be accomplished by closing the valve 42 and opening valves 40 and 41, whereby the vapors from the first still of the series, 10*a*, pass through the lines 21*a* and 38 and through the cooling coil 39 to the storage tank 29. Such procedure may prove to be of advantage under the conditions named, in that it will reduce the quantity of steam and reflux cooling, which may be required by the tower 23.

It is desired to point out that the conditions of fractionation maintained in tower 23 are such that the condensate withdrawn from the lower portion of the tower will be substantially free from hydrogen sulphide, while the gases given off from the upper portion of the tower are substantially free from hydrocarbon vapors condensable at ordinary temperatures; thus the gases passing off through the vapor line 26 may consist of about 60% hydrogen sulphide and 40% fixed hydrocarbon gases, and the procedure of rectification or fractionation taking place in the tower does not substantially change the boiling range of the vapors introduced into the tower through the manifold line 22. For example, a sample of the vapors condensed from the manifold line 22 may have an initial boiling point, as indicated by the standard American Society for Testing Materials distillation, of about 115° F. to 120° F., and it will be found that the gasoline fraction, from which the hydrogen sulphide has been removed by fractionation and which is collected in the tank 29, will have a substantially similar initial boiling point of approximately 115° F.–120° F. Thus the process accomplishes the removal of hydrogen sulphide by fractionation without a substantial change in the composition of the hydrocarbon constituents of the distillate.

The stills 10*d* and 10*e* are operated in the same manner as the group of stills 10*a*, 10*b* and 10*c*, except that they are maintained at somewhat higher temperatures, the vapors given off from the fractionating towers being within the normal boiling range of a commercial kerosene distillate, for example between 400° F. and 500° F. The vapors are subjected to fractionation in the towers 12*d* and 12*e*, suitable reflux material, which may be a kerosene distillate of approximately the same composition as the vapors, being supplied to the upper portion of the towers through the connections 19*d* and 19*e*. The vapors from the towers are introduced into the fractionating tower 31 at an intermediate point and therein undergo fractionation, suitable reflux material such as water being supplied through the connection 33, and, if desired, steam being introduced into the connection 34. The hydrogen sulphide contained in the vapors from these stills is produced from the decomposition of sulphur compounds in the stills, all of the original hydrogen sulphide in the crude charge having been apparently removed in the first still of the battery. There being substantially no low-boiling hydrocarbon fraction present, the gases given off from the upper portion of the tower 31 through the line 32 will contain an even greater percentage of hydrogen sulphide than those gases given off from the tower 23. The gases from the two towers 23 and 31 may be combined and disposed of in any suitable way, preferably by being intro-

duced into the furnaces of the stills where they are burned.

The condensate from the tower 31, which constitutes the kerosene fraction of the crude charge, passes through the line 35 and cooling coil 36 to the storage tank 37, and is substantially free from hydrogen sulphide.

The oil from the final kerosene still, 10*e*, overflows to the last still of the series, 10*f*, where a fraction corresponding to a gas oil may be distilled off. This fraction requires no particular fractionation and accordingly the vapors pass through a vapor heat exchanger 12*f*, wherein they give up heat to the crude charge, after which they pass through line 18*f* and the cooling coil 45 to the storage tank 46. If desired, the gas oil fraction may be subjected to fractionation for the removal of hydrogen sulphide, an additional fractionating tower (not shown) being required for this purpose. The residual oil in the still 10*f* overflows through the line 11*f* through the heat exchanger 43 where heat is given up to the crude charge, already previously heated to a certain extent by its passage through the vapor heat exchanger. The residual oil, which may be suitable for a fuel oil or for other purposes, then passes to storage tank 44.

In the practice of the invention in accordance with the foregoing description, distillate oils of the nature of gasoline and kerosene are produced substantially free from hydrogen sulphide, the quantity of hydrogen sulphide removed being approximately 99% of that originally contained in vapors issuing from the fractionating towers. Such removal of hydrogen sulphide greatly decreases the cost of the subsequent chemical treatment given the oil. It is necessary that merchantable grades of gasoline and kerosene be entirely free from sulphur compounds reacting with sodium plumbite solutions, which necessitates a final purifying treatment with sodium plumbite, or the so-called "doctor treatment". Any hydrogen sulphide present will react with and use up the sodium plumbite solution, thus increasing the cost of the treatment. In addition, the corrosion of storage tanks is eliminated and, in fact, corrosion from hydrogen sulphide is substantially limited to those portions of the distilling apparatus which are in contact with both hydrogen sulphide and water or water vapor. Thus, in the apparatus described, the fractionating towers 23 and 31 are practically the only portions of the apparatus which come in contact with both water or water vapor and hydrogen sulphide. It so happens that the corrosion of even this portion of the apparatus is greatly reduced due to the fact that the large quantity of water used as reflux to the towers tends to form an extremely dilute acid solution with the hydrogen sulphide, being so dilute, in fact, as to practically eliminate the corrosion.

Although the invention has been described in connection with a specific application applied to a typical battery of crude stills, it may be carried on in connection with any other type of apparatus wherein oil is distilled and oil vapors associated with hydrogen sulphide are produced.

Obviously many modifications and variations of the invention, as hereinbefore set forth, may be made without departing from the spirit and scope thereof, and therefore only such limitations should be imposed as are indicated in the appended claims.

What we claim is:

1. In the distillation of high sulfur crude petroleum, the process consisting in distilling the crude, fractionating the evolved vapors to separate first a gasoline fraction and then a kerosene fraction, said fractions containing volatile sulfur compounds including hydrogen sulfide, passing the vapors of each of said fractions separately to a rectifying column wherein separation of the volatile sulfur compounds from the respective hydrocarbon fractions occurs without substantial change in the boiling range of the fractions, cooling the upper portion of said column to effect the release of fixed gases containing substantially no hydrocarbons condensable at atmospheric temperature from the top thereof, and heating the lower portion of said tower whereby said fractions substantially free from hydrogen sulfide and the like are withdrawn from the bottom.

2. In the distillation of crude petroleum containing free hydrogen sulfide and volatile sulfur compounds decomposable by heat into hydrogen sulfide and the like, the process consisting in preheating and distilling the crude, fractionating the evolved vapors to separate consecutively from the crude fractions consisting essentially of gasoline and kerosene, passing separately the fractionated vapors of each fraction to a rectifying column, maintaining the upper portion of said column at sufficiently low temperatures to condense substantially all hydrocarbons condensable at atmospheric temperatures, maintaining the lower portion of said column at sufficiently high temperatures that fixed hydrocarbon gases and volatile sulfur compounds are volatilized and separated from the resulting condensate, releasing from the top of the column fixed hydrocarbon gases and volatile sulfur compounds and withdrawing as a liquid from the bottom of the column a rectified hydrocarbon fraction containing substantially no hydrogen sulfide, said rectified hydrocarbon fraction having undergone substantially no change in boiling range during the rectification operation.

3. In the distillation of crude petroleum of high sulfur content, the process consisting in distilling the crude, fractionating the evolved vapors to separate first a gasoline fraction and then a kerosene fraction, said fractions containing volatile sulfur compounds including hydrogen sulfide, passing the vapors of each of said fractions to a rectifying column wherein separation of volatile sulfur compounds occurs without substantial change in the boiling range of the fractions, introducing a reflux medium into the upper portion of said column to effect condensation of the desired hydrocarbons of said fractions, introducing steam into the lower portion of said column to cause separation of the volatile sulfur compounds from the condensate, releasing from the top of the column the volatile sulfur compounds and withdrawing from the bottom of the tower said fractions as condensates substantially free from hydrogen sulfide.

4. The method of refining crude petroleum oils of high sulfur content consisting in charging the crude to a battery of serially connected stills wherein the oil is gradually raised in temperature, distilling the gasoline in the earlier stills and the kerosene in the later stills of the battery, fractionating the vapors evolved from each still to separate vapor fractions consisting essentially of gasoline and kerosene and containing volatile sulfur compounds including hydrogen sulfide, passing the gasoline and kerosene vapor fractions to separate rectifying columns, subjecting the

vapors to rectification in said columns, and separating therein said sulfur compounds from the hydrocarbon fractions, without materially changing the boiling range of said fractions, by regulating the temperature in the tower whereby the vapors of the hydrocarbon fractions substantially free from hydrogen sulfide are condensed and withdrawn from the bottom of the tower while the uncondensable gases containing the sulfur compounds are released from the top of the tower.

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