

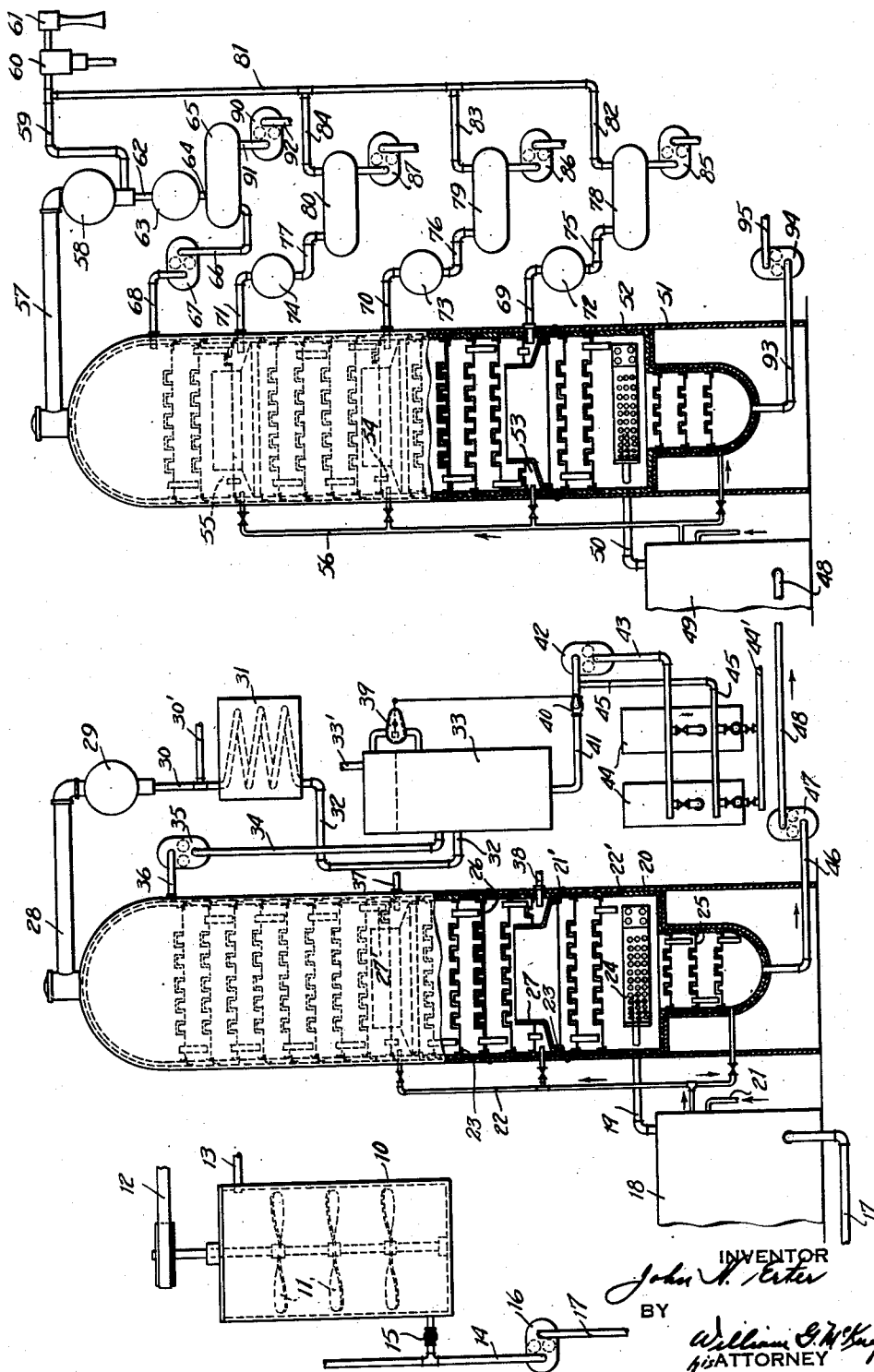
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METHOD OF AND APPARATUS FOR DESULPHURIZING OIL

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METHOD OF AND APPARATUS FOR
DESULPHURIZING OIL

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9 Claims. (Cl. 196—27)

My invention relates to the art of oil fractionation and desulphurization and has special reference to the desulphurization of oils which have a high sulphur content.

Difficulties have been encountered in the removal of sulphur from sulphur bearing oils by pyrolysis due to the corrosive effects of the sulphides on fractionating towers.

It is also known that the vapors from a fractionating tower may be desulphurized by contacting them with a catalytic agent, such as clay or fuller's earth. However, this contacting must take place at high temperature in order to cause desulphurization which means that the vapors must be superheated or the oil withdrawn as a liquid stream must be revaporized and superheated. Such a process has proved to be uneconomical.

It has occurred to me that, if the crude sulphur bearing oil is mixed with a catalytic agent prior to heating and is then flashed into a fractionating tower, the sulphur will be removed from the oil in the form of hydrogen sulphide gas. This hydrogen sulphide at temperatures above approximately 400 degrees F. has a corrosive action on steel and hence to prevent the destruction of the steel shell and any other steel parts of the fractionating tower I line the tower with a non-metallic lining and use bubble trays and stripping section members made of cast iron which is highly resistant to hydrogen sulphide.

I believe that the desulphurization of crude oil is selective as to temperature, that is to say, that different fractions are desulphurized at different temperatures and I believe that as the oil passes through a zone of progressively increasing temperature in the heater along with the catalytic agent the different fractions are desulphurized at the proper temperatures. Furthermore, it appears that the desulphurization temperature of the lighter fractions is higher than that of the heavier fractions and a point is reached where the desulphurization temperature is lower than the boiling point at atmospheric pressure and, inasmuch as desulphurization must take place with the oil in the vapor phase, it becomes necessary to carry on the desulphurization of the heavier fractions under a reduced pressure.

My invention including the method and apparatus for carrying it into effect will be clear and further objects and advantages will be apparent from the following description, taken in connection with the accompanying drawing showing a distillation plant embodying the invention and

which drawing is to be considered a part of this specification.

Referring to the drawing, reference character 10 designates a mixing tank, of which there may be several, provided with a mechanical stirring device 11 driven by belt 12. A supply conduit 13 is connected to tank 10 while a discharge conduit 14 provided with a hand valve 15 connects the tank with a pump 16. Pump 16 is connected by means of a conduit 17 with an oil heater 18 from which oil is discharged through a conduit 19 to within the flash zone of tower 20. A superheater may be incorporated in the setting of heater 18, which is supplied with steam through a conduit 21 and which discharges superheated steam through a conduit 22.

Tower 20 comprises a steel shell 21' which is preferably lined throughout with a non-metallic lining 22' of suitable nature to resist the action of hydrogen sulphide at high temperatures. A ceramic lining may be employed comprising a clay composition. Before the lining is placed in the shell, the latter is provided with suitable cast iron brackets, as is shown at 23, for supporting bubble trays and stripping sections. The lining is then sprayed onto the interior of the shell and forms a coating therein and also coats the brackets. The coating formed on the brackets may be chipped off from that portion of the latter which are to be secured to the bubble trays and stripping sections. Thus the steel shell is completely covered and protected from the corrosive action of the hydrogen sulphide. While it is only necessary to line the tower up to a point above which the temperature is below 400 degrees F., I prefer to completely line the tower in order to be certain that it will not be injured by corrosion.

Conduit 19 discharges into the tower against a perforated baffle 24 made of cast iron. Below baffle 24 are placed suitable bubble trays 25. A branch of steam conduit 22 enters the bottom of the tower below the lowermost bubble tray 25. The portion of the tower above baffle 24 is occupied by bubble trays 26 and stripping sections 27 and 27'.

A conduit 28 communicates with the top of the tower and leads to a condenser 29 which is in turn connected by means of a conduit 30 with cooler 31. A conduit 30' is connected to conduit 30 and serves to introduce water or a neutralizing agent into the latter for purposes hereinafter to be described. Cooler 31 is connected by means of a conduit 32 with an accumulator tank 33. A conduit 34 communicates with tank 33 at a point somewhat above conduit 32 and extends to a

reflux pump 35, the discharge of which is connected by means of a conduit 36 to the upper part of tower 20 above the uppermost bubble tray therein.

5 Conduits 37 and 38 communicate with stripping sections 27 and 27', respectively, for conveying side streams from the tower. Steam may be supplied to stripping sections 27 and 27' through conduit 22.

10 Accumulator tank 33 is provided with a level controller 39 which serves to automatically maintain a constant level somewhat above the lower end of conduit 34 within the tank by actuating a valve 40 in conduit 41 which leads from the bottom of the tank. A vent 33' to the atmosphere is provided at the top of tank 33. Conduit 41 communicates with a pump 42 which discharges through a conduit 43 into one or several run-down tanks 44. A conduit 45 leads from near the bottom of run-down tanks 44 to conduit 41 with which it communicates at a point between valve 40 and pump 42.

A bottoms conduit 46 leads from the bottom of atmospheric tower 20 to a bottoms pump 47 the discharge of which is connected by means of a conduit 48 to a second oil heater 49. A conduit 50 leads from heater 49 to within a vacuum fractionating tower 51. Tower 51 may be similar to atmospheric tower 20 and is provided with a non-metallic lining 52 and with cast iron bubble trays and stripping sections. The vacuum tower here shown is provided with three stripping sections 53, 54 and 55 which may be supplied with superheated steam through a conduit 56 leading from a superheater placed in the setting of oil heater 49.

A conduit 57 communicates with the upper part of vacuum tower 51 and leads to a condenser 58 which is connected by means of conduit 59 with a barometric condenser 60 and a steam jet vacuum pump 61. The lower part of condenser 58 is connected by means of a conduit 62 with a cooler 63, which is connected by means of a conduit 64 with a vacuum run-down tank 65. A conduit 66 leads from tank 65 to a reflux pump 67 which is in turn connected to the upper part of tower 51 by conduit 68. A pump 90 is also connected to vacuum run-down tank 65 by means of a conduit 91 and discharges to storage through a conduit 92.

50 Side streams are withdrawn from stripping sections 53, 54 and 55 through conduits 69, 70 and 71, respectively, to coolers 72, 73 and 74, respectively. These coolers are connected by means of conduits 75, 76 and 77 with vacuum run-down tanks 78, 79 and 80, respectively. A conduit 81 having branch conduits 82, 83 and 84 connects the vacuum run-down tanks with conduit 59. Pumps 85, 86 and 87 serve to pump liquid from vacuum run-down tanks 78, 79 and 80, respectively, to storage. The bottoms are withdrawn from tower 51 through a conduit 93 by a pump 94 and pumped through a conduit 95 to storage or waste.

The operation of the above described apparatus is substantially as follows:

65 Crude sulphur bearing oil is supplied to mixing tank 10 through conduit 13. A suitable catalytic agent, such as clay or fuller's earth or the like is introduced into tank 10 and thoroughly mixed with the crude oil by means of stirrers 11. Hereinafter in this specification the catalytic agent will be referred to as clay as a matter of convenience. The mixture of oil and clay is pumped from tank 10 by means of pump 16 into heater 18 where the oil is gradually heated to around 75 800 degrees F. and the lighter fractions are va-

porized. As the different fractions pass through the zone of progressively increasing temperature in the heater for the desulphurization of that particular fraction, such desulphurization takes place due to the presence of the clay, the resulting liberated sulphur compound being hydrogen sulphide gas and some free sulphur. The vaporized fractions and the hydrogen sulphide pass with the remaining liquid and the clay into tower 20. The vapors pass upwardly through the bubble trays 26, and through different temperature zones within the tower. Different fractions of the desulphurized oil are condensed to liquid form in different zones of the tower as side streams from the stripping sections 27 and 27'.

The tower is operated to discharge gasoline in vapor form from the top thereof through conduit 28, through which conduit also passes the hydrogen sulphide vapor and the steam. The temperature existing within conduit 28 and beyond is well below 400 degrees F. and hence the hydrogen sulphide will not seriously attack the metal of conduit 28. In condenser 29 the gasoline is condensed to liquid form and absorbs a considerable part of the hydrogen sulphide, and the resulting solution passes through conduit 30 to cooler 31. The steam may also be condensed and the resulting water absorbs some of the hydrogen sulphide, although there is ordinarily not enough water for complete absorption. A neutralizing agent, such as lime, may be introduced into conduit 30 through conduit 30' and mixes to some extent with the solution of hydrogen sulphide in gasoline and is carried along therewith through cooler 31 and conduit 32 into accumulator tank 33.

The purpose of this neutralizing agent is to neutralize the hydrogen sulphide so that it may be separated as a harmless chemical from the gasoline fraction. A portion of the solution introduced into accumulator tank 33 is refluxed through conduit 34, reflux pump 35 and conduit 36 to the top of tower 20 and flows downwardly therethrough over the bubble trays therein and is again vaporized by the hot gases passing upwardly through the tower. The remainder of the solution flows from the bottom of tank 33 through conduit 41 to pump 42. Pump 42 serves the double purpose of pumping liquid to one of the run-down tanks 44 and thoroughly mixing the neutralizing agent with the solution of hydrogen sulphide in gasoline so that the hydrogen sulphide will be completely neutralized. The neutralizing agent has a higher specific gravity than the gasoline and thus sinks to the bottom of tank 44 and is recirculated through conduit 45 to pump 42. When one run-down tank 45 is filled, conduits 43 and 44' are connected to the other run-down tank 44 and the contents of the first tank 44 is allowed to stratify. The heavier neutralized or absorbed hydrogen sulphide will collect in the bottom of the tank from where it may be drawn off through conduit 44', leaving gasoline in tank 44.

Kerosene is removed as a side stream through conduit 37 and may be conducted directly to storage while light gas oil drawn off as a side stream through conduit 38 may be conducted to storage.

The heavier fractions of the original charge, which are not vaporized in heater 18, pass along with the clay downwardly over bubble trays 25 in the lower part of tower 20 and form the bottoms which are withdrawn through conduit 46 and forced by means of pump 47 through conduit 48 to the second heater 49. In heater 49 the oil and clay pass through a second zone of increasing

temperature. The pressure in heater 49 is less than atmospheric due to the fact that a partial vacuum is maintained in vacuum tower 51 and hence a portion of the oil is vaporized and desulphurized while passing through this zone. The vaporization takes place in heater 49 at a lower temperature than would have been possible in the first heater due to the lower pressure. From the heater the oil, hydrogen sulphide and clay pass through conduit 50 into vacuum tower 51. The oil vapor passes upwardly through a zone of decreasing temperature in tower 51 where the heavier fractions are condensed and separated.

The vacuum tower is operated to discharge heavy gas oil in the form of a vapor from the top thereof and this gas oil passes along with the hydrogen sulphide resulting from the desulphurization process through conduit 57 to condenser 58. The superheated steam introduced into tower 51 may also pass through conduit 57 to condenser 58. In the condenser only the gas oil is condensed while the steam and the hydrogen sulphide vapor pass through conduit 59 to barometric condenser 60 and steam jet vacuum pump 61. The action of vacuum pump 61 is to maintain a vacuum in tower 51 while barometric condenser 60 condenses the steam and also absorbs the hydrogen sulphide vapors.

The liquid gas oil passes from the bottom of condenser 58 through conduit 62 to cooler 63 and thence through conduit 64 to vacuum run-down tank 65. A portion of the liquid gas oil is refluxed from tank 65 through conduit 66, through reflux pump 67 and conduit 68 to the upper part of tower 51 to serve as reflux liquid for forming liquid seals on the bubble trays. The remaining gas oil is pumped from tank 65 by pump 90 to storage.

Side streams of light wax distillate, heavy wax distillate and lubricating oil are removed from stripping sections 55, 54 and 53, respectively, and are conveyed through the respective coolers to vacuum run-down tanks 80, 79 and 78, respectively, from which they are pumped to storage. The bottoms from tower 51 include the clay originally introduced in tank 10 and are removed by pump 94. The clay may be reclaimed from the bottoms and used again, but this is not ordinarily profitable and the bottoms are usually run to coke or used as fuel.

Inasmuch as the boiling point of light gas oil is approximately 570 degrees F. under atmospheric conditions, and the desulphurization temperature is approximately 700 degrees, the gas oil will be in the vapor phase at 700 degrees and hence may be desulphurized under atmospheric pressure. The boiling point and desulphurization temperature of the heavy gas oils are about the same and hence in order to get complete desulphurization it is necessary that, as to the heavier constituents, the process be performed under a partial vacuum in order that the heavy gas oils will be in the vapor phase. The boiling point of the heavy wax distillate is below the desulphurization temperature at atmospheric pressure and hence it is absolutely necessary, in order to have them in the vapor phase, to carry out the desulphurization step under vacuum. Hence, the dividing line between the fractions which may be desulphurized at atmospheric pressure and those that require vacuum appears to fall between the light and heavy gas oils but my invention is not limited to such a line of demarcation, as this may vary with different kinds of crude oil used.

It will be seen that in the desulphurizing and

fractionating process the oil passes first through a zone of increasing temperature in the first heater and then through a zone of decreasing temperature in the atmospheric tower while under a relatively high pressure to desulphurize and fractionate the lighter fractions. The heavier fractions which remain unvaporized are passed through a zone of increasing pressure in the second heater and then through a zone of decreasing temperature in the vacuum tower while under a relatively low pressure to desulphurize and fractionate these heavier fractions.

While I have advanced the theory that the desulphurization takes place progressively as to temperature for different fractions, it is to be understood that the correctness of the theory does not affect the validity of this patent.

The scope and breadth of my invention is to be limited only by the appended claims viewed in the light of the prior art.

What I claim is:

1. The method of fractionating sulphur bearing oil which comprises mixing a catalytic agent with the oil, passing the mixture of oil and catalytic agent through a zone of progressively increasing temperature to effect vaporization of a portion of the oil and to cause its desulphurization and the formation of a gaseous sulphur compound, passing the oil, catalytic agent and sulphur compound into an atmospheric fractionating tower having a non-metallic lining, withdrawing liquid oil and catalytic agent from the lower part of said tower, separating fractions of the oil introduced in vapor form in said tower, withdrawing the gaseous sulphur compound from the upper part of the tower, passing the mixture of oil and catalytic agent withdrawn from said atmospheric tower through a second zone of progressively increasing temperature under a relatively lower pressure than the pressure of first-mentioned zone to effect vaporization of the oil and to cause its desulphurization and the formation of a gaseous sulphur compound, passing the oil and sulphur compound into a vacuum fractionating tower having a non-metallic lining, maintaining a partial vacuum in said tower, separating fractions of the oil in the tower and withdrawing the gaseous sulphur compound from said tower.

2. The method of fractionating sulphur bearing oil which comprises mixing a catalytic agent with the oil, passing the mixture of oil and catalytic agent through a zone of progressively increasing temperature to effect vaporization of a portion of the oil and to cause its desulphurization and the formation of a gaseous sulphur compound, passing the oil, catalytic agent and sulphur compound into an atmospheric fractionating tower having a non-metallic lining, withdrawing liquid oil and catalytic agent from the lower part of said tower, separating fractions of the oil introduced in vapor form in said tower, withdrawing the gaseous sulphur compound from the upper part of the tower, passing the mixture of oil and catalytic agent withdrawn from said atmospheric tower through a second zone of progressively increasing temperature under a relatively lower pressure than the pressure of the first-mentioned zone to effect vaporization of the oil and to cause its desulphurization and the formation of a gaseous sulphur compound, passing the oil and sulphur compound into a vacuum fractionating tower having a non-metallic lining, maintaining a partial vacuum in said tower, separating fractions of the oil in the tower, withdraw-

ing a light fraction of oil in vapor form and the gaseous sulphur compound from said tower and separating the sulphur compound from said light fraction.

5 3. Apparatus for the refining of sulphur bearing oil comprising, in combination, a tank, means to supply oil to said tank, mixing means in said tank for mixing the oil with a catalytic agent, a heater, means to conduct oil and catalytic agent from said tank to said heater, means to heat the oil and catalytic agent in said heater to partially vaporize the oil in the presence of the catalytic agent and to thereby form a gaseous sulphur compound, an atmospheric fractionating tower having a ceramic lining, means to convey the oil, catalytic agent and sulphur compound from said heater to said tower, means to remove liquid oil and catalytic agent from the lower part of said tower, means to condense fractions of the vaporized oil in said tower, means to convey a vaporous fraction of oil and the sulphur compound from said tower, means to separate the sulphur compound from said oil fraction, means to convey the liquid oil and catalytic agent removed from the lower part of said atmospheric tower to a second heater, means to heat the oil and catalytic agent in said second heater to vaporize the oil in the presence of the catalytic agent and to thereby form a gaseous sulphur compound, a vacuum fractionating tower having a ceramic lining, means to maintain a partial vacuum in said tower, means to convey the vaporized oil, catalytic agent and sulphur compound to said vacuum tower, means to separate fractions of oil having different boiling points in said tower, means to convey a vaporous fraction of oil and the sulphur compound from said tower and means to separate the sulphur compound from said oil fraction.

40 4. Apparatus for the refining of sulphur bearing oil comprising, in combination, a tank, means to supply oil to said tank, mixing means in said tank for mixing the oil with a catalytic agent, a heater, means to conduct oil and catalytic agent from said tank to said heater, means to heat the oil and catalytic agent in said heater to partially vaporize the oil in the presence of the catalytic agent and thereby form a gaseous sulphur compound, an atmospheric fractionating tower having a ceramic lining, means to convey the oil, catalytic agent and sulphur compound from said heater to said tower, means to remove liquid oil and catalytic agent from the lower part of said tower, means to condense fractions of the vaporized oil in said tower, means to convey a vaporous fraction of oil and the sulphur compound from said tower, means to separate the sulphur compound from said oil fraction, means to convey the liquid oil and catalytic agent removed from the lower part of said atmospheric tower to a second heater, means to heat the oil and catalytic agent in said second heater to vaporize the oil in the presence of the catalytic agent and to thereby form a gaseous sulphur compound, a vacuum fractionating tower having a ceramic lining, means to maintain a partial vacuum in said tower, means to convey the vaporized oil, catalytic agent and sulphur compound to said vacuum tower, means to introduce steam into said tower, means to separate fractions of oil having different boiling points in said tower, means to convey a vaporous fraction of oil, steam and the sulphur compound from said tower, and means to separate the sulphur compound from the oil

fraction, said last mentioned means comprising a barometric condenser.

5 5. Apparatus for the refining of sulphur bearing oil comprising, in combination, a tank, means to supply oil to said tank, mixing means in said tank for mixing the oil with a catalytic agent, a heater, means to conduct oil and catalytic agent from said tank to said heater, means to heat the oil and catalytic agent in said heater to partially vaporize the oil in the presence of the catalytic agent and thereby form a gaseous sulphur compound, an atmospheric fractionating tower having a ceramic lining, means to convey the oil, catalytic agent and sulphur compound from said heater to said tower, means to remove the liquid oil and catalytic agent from the lower part of said tower, means to condense fractions of the vaporized oil in said tower, means to convey a vaporous fraction of oil and the sulphur compound from said tower, means to separate the sulphur compound from said oil fraction, means to convey the liquid oil and catalytic agent removed from the lower part of said atmospheric tower to a second heater, means to heat the oil and catalytic agent in said second heater to vaporize the oil in the presence of the catalytic agent and to thereby form a gaseous sulphur compound, a vacuum fractionating tower having a ceramic lining, means to maintain a partial vacuum in said tower, means to convey the vaporized oil, catalytic agent and sulphur compound to said vacuum tower, means to introduce steam into said tower, means to separate fractions of oil having different boiling points in said tower, means to convey a vaporous fraction of oil, steam and the sulphur compound from said tower, and means to separate the sulphur compound and the steam from the oil fraction, said last mentioned means comprising a barometric condenser.

40 6. Apparatus for the refining of sulphur bearing oil comprising, in combination, a tank, means to supply oil to said tank, mixing means in said tank for mixing the oil with a catalytic agent, a heater, means to conduct oil and catalytic agent from said tank to said heater, means to heat the oil and catalytic agent in said heater to partially vaporize the oil in the presence of the catalytic agent and thereby form a gaseous sulphur compound, an atmospheric fractionating tower having a ceramic lining, means to convey the oil, catalytic agent and sulphur compound from said heater to said tower, means to remove the liquid oil and catalytic agent from the lower part of said tower, means to condense fractions of the vaporized oil in said tower, means to convey a vaporous fraction of oil and the sulphur compound from said tower, means to separate the sulphur compound from said oil fraction, means to convey the liquid oil and catalytic agent removed from the lower part of said atmospheric tower to a second heater, means to heat the oil and catalytic agent in said second heater to vaporize the oil in the presence of the catalytic agent and to thereby form a gaseous sulphur compound, a vacuum fractionating tower having a ceramic lining, means to maintain a partial vacuum in said tower, means to convey the vaporized oil, catalytic agent and sulphur compound to said vacuum tower, means to introduce steam into said tower, means to separate fractions of oil having different boiling points in said tower, means to convey a vaporous fraction of oil, steam and the sulphur compound from said tower, means to liquefy the vaporous oil fraction and means to separate the sulphur com-

pound from the oil fraction, said last mentioned means comprising a barometric condenser.

7. Apparatus for the refining of sulphur bearing oil comprising, in combination, a tank, means to
 5 supply oil to said tank, mixing means in said tank for mixing the oil with a catalytic agent, a heater, means to conduct oil and catalytic agent from said tank to said heater, means to heat the oil and catalytic agent in said heater to partially vaporize
 10 the oil in the presence of the catalytic agent and thereby form a gaseous sulphur compound, an atmospheric fractionating tower having a ceramic lining, means to convey the oil, catalytic agent and sulphur compound from said heater to said
 15 tower, means to remove the liquid oil and catalytic agent from the lower part of said tower, means to condense fractions of the vaporized oil in said tower, means to convey a vaporous fraction of oil and the sulphur compound from said
 20 tower, means to separate the sulphur compound from said oil fraction, means to convey the liquid oil and catalytic agent removed from the lower part of said atmospheric tower to a second heater, means to heat the oil and catalytic agent in said
 25 second heater to vaporize the oil in the presence of the catalytic agent and to thereby form a gaseous sulphur compound, a vacuum fractionating tower having a ceramic lining, means to maintain a partial vacuum in said tower, means to
 30 convey the vaporized oil, catalytic agent and sulphur compound to said vacuum tower, means to introduce steam into said tower, means to separate fractions of oil having different boiling points in said tower, means to convey a vaporous fraction of oil, steam and the sulphur compound from
 35 said tower, means to liquefy the vaporous oil fraction and means to separate the sulphur com-

pound and the steam from the oil fraction, said last mentioned means comprising a barometric condenser.

8. Apparatus for the refining of oil comprising, in combination, a tank, mixing means within said
 5 tank, a heater, a conduit connecting said tank with said heater, a fractionating tower, a conduit connecting said heater with said tower, a non-metallic lining in said tower, a condenser, a conduit connecting the upper part of said tower with
 10 said condenser, a second tank, a conduit connecting said condenser with said second tank, a conduit communicating with said last mentioned conduit, a run-down tank, a conduit connecting said
 15 second tank with said run-down tank, a pump interposed in said last mentioned conduit and a conduit connecting the lower part of said run-down tank with said last mentioned conduit at a point between said second tank and said pump.

9. The method of fractionating sulphur bearing oil which comprises mixing a catalytic agent with
 20 the sulphur bearing oil, passing the mixture of oil and catalytic agent through a zone of progressively increasing temperature to vaporize and desulphurize a portion of the oil in said zone,
 25 passing all of the mixture so heated into a zone of progressively decreasing temperature to separate fractions of the desulphurized oil, passing the portion of the oil not vaporized and the catalytic agent through a zone of progressively increasing
 30 temperature at a relatively lower pressure than the pressure of the first zone to vaporize and desulphurize a portion of the oil and passing all of the last heated mixture into a zone of progressively decreasing temperature to separate frac-
 35 tions thereof.

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