

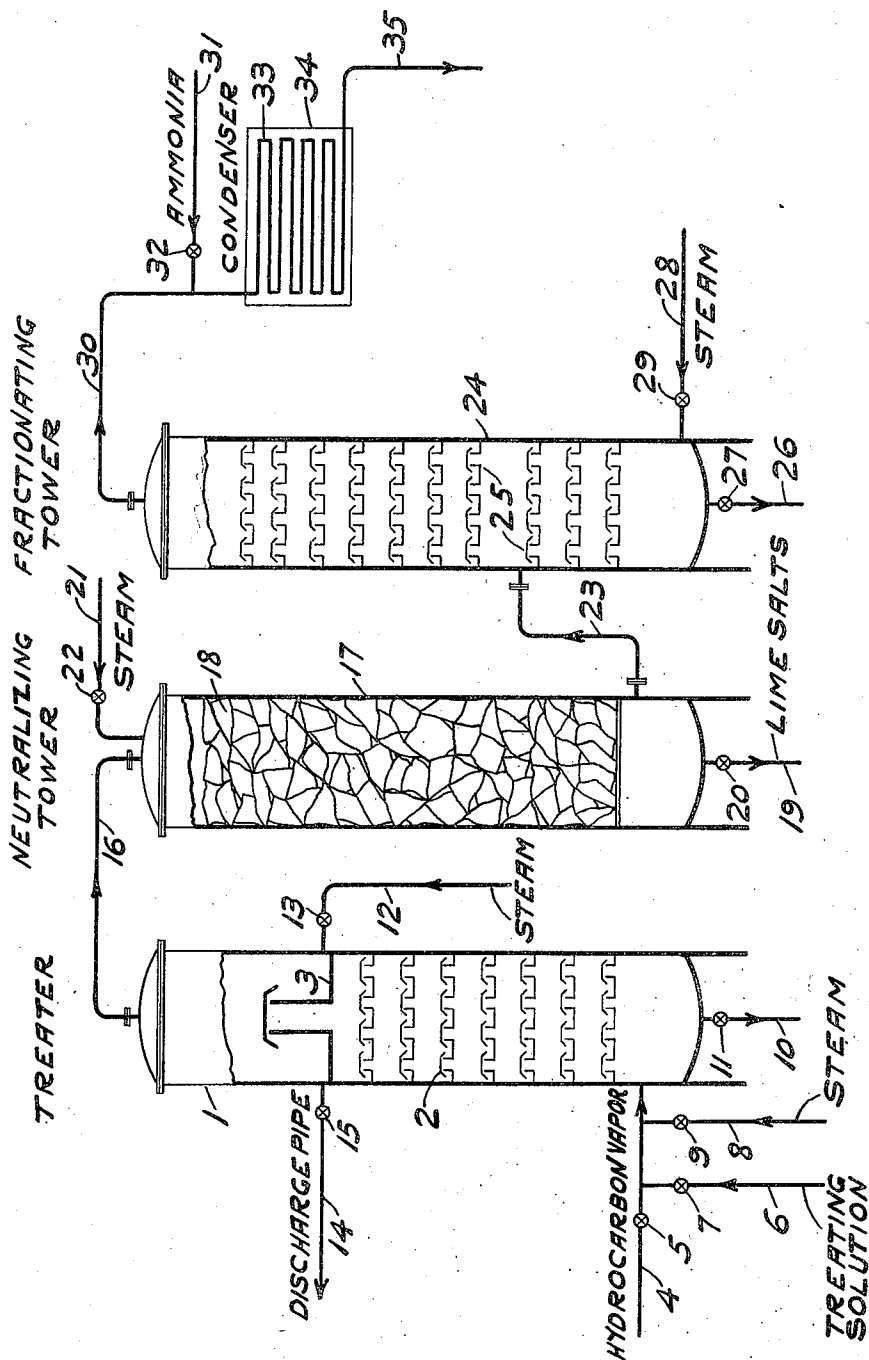
Jan. 11, 1938.

W. A. CRAIG

2,104,791

PROCESS OF TREATING HYDROCARBON OILS

Original Filed Jan. 21, 1936



INVENTOR

WALLACE A. CRAIG.

BY

Marvin L. Chappell
ATTORNEY

UNITED STATES PATENT OFFICE

2,104,791

PROCESS OF TREATING HYDROCARBON OILS

Wallace A. Craig, Los Angeles, Calif., assignor to
Vapor Treating Processes, Inc., Los Angeles,
Calif., a corporation of California

Original application January 21, 1936, Serial No.
60,039. Divided and this application Janu-
ary 12, 1937, Serial No. 120,205

4 Claims. (Cl. 196—36)

This invention pertains to an improved system or method of treating, purifying and refining hydrocarbon oils with maintained aqueous solutions of metallic salts. More specifically, this invention pertains to improving the treating characteristics of metallic salt solutions in order to maintain definite concentrations thereof at the best or more desired treating temperatures, when used to purify and refine mineral hydrocarbon oils in vapor phase, such as gasoline or naphtha, or other petroleum oil products derived by distillation or cracking of mineral oils.

This application is a division of my application Serial No. 60,039, filed January 21, 1936, for Process of treating hydrocarbon oils.

Treatment of hydrocarbon oils in vapor phase with maintained aqueous solutions of metallic salts is generally known in the refining art, in which the degree of refinement by the treatment is determined, in part, by the concentration of the metallic salt maintained in the liquid phase, and the desired concentration of the treating solution has been generally controlled primarily by controlling the temperature of the system and the partial pressure of the water in the vapor phase.

My invention is an improvement in the method described in U. S. Patent #1,790,622, granted to Arthur Lachman, dated January 27, 1931, for Method of refining mineral oils, and U. S. Patent #1,809,170, granted to Arthur Lachman, dated June 9, 1931, for Process of refining hydrocarbons, which disclose methods of refining hydrocarbon oils in vapor phase with water solutions of the metallic salts of zinc, copper, cadmium, mercury, iron, chromium, manganese, aluminum, nickel or cobalt, which may be the chloride, bromide, iodide, sulphate, nitrate, and also any of the water soluble salts of the above named metals of organic acids, such as the sulphonic acid of benzol, toluol, xylol, or the sulpho acids derived from the treatment of petroleum oils with sulphuric acid. U. S. Patent #1,809,170 was reissued March 3, 1936, as Re. #19,879, in which the said enumerated metal salts have been designated "heavy metals".

The method described in the aforesaid patents for refining oil comprises, passing the oil, such as gasoline stock, in vapor phase through and in contact with a hot water solution of any of the aforesaid metallic salts, in which a tower filled with contact material and a substantially concentrated water solution of the metallic salt is employed.

While it is possible to maintain any desired concentration of the metallic salt in the liquid phase by the proper choice of temperature and partial pressure of water vapor, the operating conditions during the treatment of a light petroleum distillate, such as naphtha stocks, are re-

stricted by the characteristics of the latter. In order to maintain the distillate or naphtha stock in vapor phase during treatment, certain conditions of temperature and vapor pressure must be observed. It is necessary, therefore, to choose operating conditions that will maintain the concentration of the salt solution at the desired strength and at the same time maintain the distillate or naphtha stock under treatment in vapor phase.

The treatment of hydrocarbons containing unsaturated hydrocarbons with metallic salt solutions at elevated temperatures causes the polymerization of a certain percentage of the more unstable unsaturated hydrocarbons. A portion of these polymers have sufficiently high boiling points that, under normal operating conditions, they condense within the treating vessel and may be removed. The lower boiling polymers pass through the system with the gasoline and are separated from the desired material by fractionation. The amount of polymers which remain in vapor phase depends upon the operating conditions of temperature and pressure which are maintained within the treater.

There are times when it is beneficial to maintain the salt solution at a relatively low concentration. If it becomes desirable to lower the concentration within the treating vessel, it may be accomplished by lowering the temperature or increasing the partial pressure of the water in the vapor phase, or both. However, such changes also affect the liquid-vapor equilibrium of the hydrocarbon oil, as shown in the following Table No. 1, which illustrates the treatment of a cracked gasoline stock under varying conditions.

Table No. 1

	Column			
	1	2	3	4
Metallic salt used for treating	ZnCl ₂	ZnCl ₂	ZnCl ₂	ZnCl ₂
Treating temperature—°F.	370	350	370	350
Treating pressure lb./sq. in. gage.	25	25	25	25
Mol. per cent of water in vapor phase	37.1	37.1	50.0	50.0
Zinc chloride concentration—wt. %	83.5	80.5	81.0	78.0
Average boiling point at 1 atmos. pressure of hydrocarbons in vapor phase—°F.	335	310	350	330

Under the chosen conditions of temperature and water vapor pressure, as shown in column 1 of Table No. 1, a zinc chloride concentration of 83.5% is obtained, and the hydrocarbon oil in vapor phase has an average boiling point of approximately 335° F. Column No. 2 shows that a reduction in temperature reduces the zinc

chloride concentration, and reduces the average boiling point of the hydrocarbon vapors. Column No. 3 shows the effect of increasing the partial pressure of the water in vapor phase, while column 4 shows the combined effect of temperature reduction and increased water vapor pressure. These examples show that temperature reduction and increase of partial pressure of water vapor decrease the metal salt concentration; that a decrease in temperature decreases the average boiling point of the hydrocarbon vapors, but that an increase of water vapor pressure increases the average boiling point of the hydrocarbons under treatment.

In the commercial operation of units used for treating vaporized light petroleum hydrocarbons, such as naphtha stocks, with aqueous zinc chloride or other like metal salt solutions, I have also determined that a drop in temperature occurs as the material passes through the system, and that in order to prevent partial condensation of the higher boiling hydrocarbons, it is necessary to readjust the temperature-vapor pressure relationship at various points in the system, so that all of the desired higher boiling hydrocarbon portion will be maintained in vapor phase throughout the treating system until condensation is desired. Under normal conditions of operation, I have determined that the temperature drop between the treating vessel and the point at which final condensation is effected is more or less fixed for given apparatus; that, if the most efficient treating temperature is known, the final vapor temperature can be determined and the correct vapor pressure calculated to maintain substantially all of the desired hydrocarbons in the vapor stream without condensation thereof during the treating and fractionation operation. At times the temperature of the vapors may be so low that the vapor pressure of the oil must be reduced an excessive amount to accomplish the desired results. Steam is usually employed to obtain the reduction of the vapor pressure of the oil, but excessive additions of steam may reduce the treating efficiency. In many instances this difficulty may be corrected by operating the treating vessel at a higher temperature and treating with a more concentrated solution of metallic salt. However, there are hydrocarbon oils which are susceptible to overtreatment, and it becomes necessary to maintain the concentration of the salt in the treating solution at a sub-normal value.

Now I have discovered that, in the refining of vaporized hydrocarbons such as naphtha or gasoline stocks with aqueous zinc chloride and other like metal salt treating solutions, the aforesaid difficulties may be overcome by dissolving in the treating solution certain compounds which will decrease the vapor pressure of the treating solution at a given temperature, or modify the temperature-vapor pressure-concentration relationship. Such compounds may be inert or non-reactive soluble metallic salts, such as calcium chloride or sodium chloride.

The following Table No. 2 shows the effect of varying amounts of calcium chloride upon a solution of zinc chloride. These data show how the treating temperature can be increased and the water vapor pressure decreased without affecting the concentration of zinc chloride in the liquid phase or the average boiling point of the hydrocarbon oils in the vapor phase.

Table No. 2

	Column			
	1	2	3	4
Ratio zinc chloride/calcium chloride.....	ZnCl ₂ only	20/1	10/1	10/1
Treating temperature—°F.....	350	360	380	395
Treating pressure lb./sq. in. gage.....	25	25	25	35
Mol. per cent water in vapor phase.....	44.0	34.4	18.7	21.8
Zinc chloride concentration—wt. %.....	80	79.6	80.6	80.1
Average boiling point at 1 atmos. pressure of hydrocarbons in vapor phase—°F.....	320	320	320	320

An object of the invention is to refine hydrocarbons in vapor phase at a given temperature, with a water solution of a metallic salt, at a desired vapor pressure.

Another object of the invention is to refine hydrocarbons in vapor phase at a given temperature, with a water solution of a metallic salt treating agent, maintained at a desired vapor pressure by the addition of an inert compound which is soluble in the treating solution.

Another object of the invention is to refine hydrocarbon oil vapor by contact with a reactive salt solution containing a relatively non-reactive salt or compound dissolved therein, in quantities sufficient to modify the temperature-vapor pressure-concentration relationship of the solution to the desired degree.

Various other objects and advantages of the present invention will be apparent from the description of the preferred form or example of the method embodying the invention. For this purpose reference is made to the accompanying drawing, in which there is illustrated a form of apparatus in which the invention may be performed. The drawing represents a diagrammatical view of apparatus, in which the parts are in sectional elevation.

In the drawing, 1 represents generally a treat-er for contacting hydrocarbon oil vapor with refining agent, the lower section of which is filled with bubble cap trays 2, and provided with a compartment trap 3 stationed above the last tray or row of bubble caps. Pipe 4, controlled by valve 5, connects treater 1 near the bottom to a source of hydrocarbon vapor to be treated, such as a fractionating column, still, or other form of vaporizer. Pipe 6, controlled by valve 7, connects hydrocarbon vapor pipe 4 to a source of the treating solution. Pipe 8, controlled by valve 9, connects pipe 4 to a source of steam. Pipe 10, controlled by valve 11, connects treater 1 at the bottom to a storage for waste supply not shown. Pipe 12, controlled by valve 13, connects the compartment trap section of treater 1 to a source of steam. A discharge pipe 14, controlled by valve 15, connects the compartment trap section of treater 1 to a storage for spent treating solution not shown.

Pipe 16 connects treater 1 at the top to the top of neutralizing tower 17. Neutralizing tower 17 is filled with lime stone lumps 18. Pipe 19, controlled by valve 20, connects neutralizing tower 17 at the bottom to a storage for lime salt solution not shown. Steam pipe 21, controlled by valve 22, connects neutralizing tower 17 at the top to a steam supply.

Pipe 23 connects neutralizing tower 17 near the bottom to the lower section of fractionating tower 24. Fractionating tower 24 is provided with bubble cap trays 25. Pipe 26, controlled by valve 27, connects fractionating tower 24 at the bottom

to a storage for the higher boiling oil and polymers separated by the fractionation operation. Steam pipe 28, controlled by valve 29, connects fractionating tower 24 near the bottom to a source of steam supply.

Pipe 30 connects fractionating tower 24 at the top to condenser coil 33. Condenser coil 33 is stationed in condenser box 34. Pipe 31, controlled by valve 32, connects pipe 30 to a source of ammonia supply not shown. Pipe 35 connects condenser coil 33 to a storage for treated hydrocarbon oil stock not shown.

The preferred operation, as carried out in the apparatus just described, is as follows:

Treater 1 is first filled up to the level of the discharge pipe 14 with the treating solution to be employed, heated to a desired temperature, preferably ranging from about 360 to 390° F., by a heater not shown, which discharges the heated solution through pipe 6, controlled by valve 7, pipe 4, and into said treater 1 near the bottom.

The treating solution is preferably a water solution of zinc chloride and calcium chloride, in which the ratio of the zinc chloride to the calcium chloride ranges from about 10 to 20 parts by weight zinc chloride to one part by weight calcium chloride, with a solution containing 79.6 to 80.1 per cent by weight zinc chloride, as illustrated in Table 2 heretofore described. While the preferred salts employed to make the treating solution are zinc chloride and calcium chloride, it is to be understood that any of the other salts or mixtures thereof and compounds heretofore enumerated may be used in like manner at various ratios and concentrations to suit the oil to be treated and the product desired.

Hydrocarbon oil vapor, such as gasoline or naphtha stock, coming from any of the known refinery vaporizers, or vaporizer and fractionating system, at or above the vapor temperature of the stock to be treated, passes through pipe 4, controlled by valve 5, and into the lower section of treater 1. At the same time a regulated quantity of steam, which may be superheated to any required temperature so as to maintain the oil vapor at any required treating temperature, is continuously passed into the oil vapor passing through pipe 4, the steam coming through pipe 8, controlled by valve 9.

The treating solution may also be continuously or intermittently introduced into pipe 4 through pipe 6, controlled by valve 7, in quantities sufficient to maintain the treating solution in treater 1 at the required strength and purity to continuously effect uniform treatment of the oil vapors.

The hydrocarbon vapors, commingled with steam, pass from pipe 4 into treater 1, and are therein intimately contacted with treating solution and treated to the required degree as they pass up through the bubble cap tray system 2. The spent or partially spent treating solution is continuously or intermittently discharged from treater 1 through pipe 14, controlled by valve 15, to a storage tank not shown, and may be thereafter recovered for reuse by known methods. Steam may also be introduced into the upper section of treater 1 through pipe 12, controlled by valve 13, to maintain the oil in vapor phase.

From treater 1 the treated oil vapors and gaseous products of reaction pass through pipe 16 and then through neutralizing tower 17, wherein a portion of the acid constituents produced during the treating operation, such as

hydrochloric acid when a metal chloride is used as one of the treating agents, are partially neutralized and removed from the gaseous products as calcium salts, through pipe 19, controlled by valve 20. A regulated quantity of steam is preferably continuously introduced into tower 17 through pipe 21, controlled by valve 22, in order to facilitate the action between the acid constituents and the lime stone, and to maintain the oil in vapor phase.

From neutralizing tower 17 the treated oil vapors pass through pipe 23 and into fractionating tower 24, and are therein fractionated, and the higher boiling oils, together with the polymerized products, separated from the lower boiling treated oil vapor. The higher boiling oils and polymerized products are withdrawn from tower 24 through pipe 26, controlled by valve 27, to a storage not shown. Steam is introduced into the lower section of tower 24 through pipe 28, controlled by valve 29, to strip the condensed bottoms of any lower boiling hydrocarbons they may contain. The fractionated oil vapors, separated from the higher boiling constituents, pass from tower 24 into pipe 30, and are therein treated with ammonia gas to neutralize any acid constituents which may have escaped neutralization during the passage of the oil vapors through neutralizing tower 17. From pipe 30, the completely neutralized, treated, fractionated oil vapor, such as gasoline stock, passes through condenser coil 33 and is therein condensed to a liquid, and passes therefrom to a storage not shown through pipe 35.

The following data illustrate the benefits which are derived by adding a material which modifies the temperature-vapor pressure-concentration relationship of a treating solution. Using a solution of zinc chloride as a treating medium, the following conditions exist within a treating unit:

	Lower section of tower 1	Upper section of tower 1	Bottom of tower 17
Temperature—°F.....	370	350	300
Pressure—lb./sq. in. gage.....	25	23	18
Mol. per cent of water in vapor phase.....	61.5	67.9	69.3
Zinc chloride concentration—wt. per cent.....	80	-----	-----
Average boiling point at 1 atmos. pressure of hydrocarbons in vapor phase—°F.....	360	355	325

Under these conditions, partial condensation of hydrocarbon vapors will occur within the treating unit, indicated by the progressive drop in the average boiling point of the hydrocarbons in vapor phase.

Using a solution of zinc chloride and calcium chloride, in which the zinc chloride/calcium chloride ratio is 10/1, the following conditions were obtained:

	Lower section of tower 1	Upper section of tower 1	Bottom of tower 17
Temperature—°F.....	380	360	310
Pressure—lb./sq. in. gage.....	25	23	18
Mol. per cent of water in vapor phase.....	18.7	32.2	61.0
Zinc chloride concentration—wt. per cent.....	80.6	-----	-----
Average boiling point at 1 atmos. pressure of hydrocarbons in vapor phase—°F.....	320	320	320

The addition of calcium chloride to the treating solution makes it possible to increase the treating temperature and reduce the steam requirements without affecting the concentration of the zinc chloride. Higher temperature throughout the treating unit is thereby obtained and less steam is required to maintain the desired average boiling point for the hydrocarbons in the vapor phase.

While the process herein described is well adapted for carrying out the objects of the present invention, it is to be understood that various modifications and changes may be made without departing from the spirit of the invention, such, for example, as the use of other forms of contact towers or mechanical mixers, and the invention includes all such modifications and changes as appear within the scope of the appended claims.

I claim:

1. In the process of refining hydrocarbon oil vapor by contact with aqueous maintained solution of a "heavy metal" salt selected from the group consisting of the chloride, bromide, sulphate, and nitrate of zinc, copper, cadmium, iron, chromium, manganese, aluminum, nickel and cobalt, at refining temperature, the improvement which comprises, modifying the temperature-vapor pressure-concentration relationship of said "heavy metal" salt solution sufficiently to

refine the oil vapor, at required temperature and pressure, by adding thereto sodium chloride.

2. In the process of refining hydrocarbon oil vapor by contact with aqueous maintained solution of zinc chloride, at refining temperature, the improvement which comprises, modifying the temperature-vapor pressure-concentration relationship of said zinc chloride solution sufficiently to refine the oil vapor, at required temperature and pressure, by adding thereto sodium chloride.

3. In the process of refining hydrocarbon oil vapor by contact with aqueous maintained solution of aluminum chloride, at refining temperature, the improvement which comprises, modifying the temperature-vapor pressure-concentration relationship of said aluminum chloride solution sufficiently to refine the oil vapor, at required temperature and pressure, by adding thereto sodium chloride.

4. In the process of refining hydrocarbon oil vapor by contact with aqueous maintained solution of copper chloride, at refining temperature, the improvement which comprises, modifying the temperature-vapor pressure-concentration relationship of said copper chloride solution sufficiently to refine the oil vapor, at required temperature and pressure, by adding thereto sodium chloride.

WALLACE A. CRAIG.