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PROCESS OF PURIFYING AND REFINING HYDROCARBON OILS WITH ALUMINUM SALTS

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This invention relates to an improved process of purifying and refining hydrocarbon oils obtained by distillation or cracking of mineral oils such as lubricating oil stocks, lamp oil distillates, gasoline or naphtha distillates derived from shale oil, and more specifically refers to the treatment of gasoline or naphtha stock produced by cracking crude petroleum oils or distillates derived from relatively high sulphur bearing mineral oils, in which hydrogen sulphide, mercaptans and other sulphur bearing compounds, as well as varying percentages of oxygenated hydrocarbons and unstable hydrocarbons (such as diolefins and acetylenes) may be present or formed during said distillation or cracking operation.

This application is a division of my application Serial Number 381,065, filed July 26, 1929, for Process of purifying and refining hydrocarbon oils.

Reference is made to United States Patent Number 1,508,170, granted June 9, 1921 to Arthur Lachman, Serial Number 361,513, filed May 8, 1929, for Process of refining hydrocarbon oils, which discloses a vapor phase method or process for purifying and refining mineral oil products with a water solution of certain metallic salts, or mixtures of the same, such as zinc, copper, cadmium, mercury, iron, chromium, manganese, aluminum, nickel or cobalt water soluble salts which may be the chloride, bromide, iodide, sulphate, sulphite, nitrate and also any of the water soluble salts of the above named metals of organic acids, such as the sulphonic acids of benzol, toluol and xyol, or the sulphonic acids derived from the treatment of petroleum oil with sulphuric acid.

For the purposes of simplifying the description of my invention, reference will be made mainly to gasoline stock. Crude gasoline stocks obtained by distillation or cracking petroleum oils consist of a mixture of saturated and unsaturated hydrocarbons, together with sulphur compounds, nitrogen bases and other substances of an undefined nature. These latter substances are readily oxidizable at ordinary temperature and are usually responsible for the change of color which takes place when refined gasoline is stored. These oxidizable substances are removed with difficulty when gasoline stocks are treated by the methods known in the art.

By well-known methods, crude gasoline stocks obtained by distillation of crude petroleum oil, or by cracking a higher boiling petroleum oil, are customarily treated with approximately from 1 per cent to as high as 8 per cent or higher by weight, sulphuric acid, the quantity of sulphuric acid depending upon the nature of the gasoline stock to be treated and the degree of refinement desired. This acid treatment, usually consists in commingling the gasoline stock with the required amount of sulphuric acid necessary to obtain the desired extraction, either by the well-known batch or continuous treatment, after which the products of the acid reaction are permitted to settle and are then withdrawn from the treating line stock. The acid treated gasoline stock is then neutralized by washing with a water solution of an alkali and finally with water. This treatment removes most of the impurities, but subsequent treatments are usually necessary to deodorize and remove or convert corrosive sulphur compounds into noncorrosive bodies.

For this purpose, a water solution of sodium plumbite or sodium hypochlorite is usually employed to render the gasoline stock “sweet” to the “doctor test”. In these treatments, particularly where hypochlorite of soda is employed, chlorinated hydrocarbons may be formed to a small extent, which may be converted into corrosive compounds during a subsequent distillation.

The general objections to a treatment of this character are as follows: (1) Gasoline purified by this method frequently becomes discolored when stored for a period of time; (2) considerable quantities of sulphuric acid are required, which are difficult to recover; (3) as high as 10 per cent of the valuable unstable hydrocarbons contained in the gasoline stock may be lost; and (4) the treatment must frequently be followed by a sweetening process, such as that heretofore described.

Now, I have discovered that the sulphuric acid normally used to treat crude gasoline stocks may be reduced to a great extent, and in many cases may be entirely eliminated by the employment of a water solution of certain metallic salts, or mixtures of the same, which may be zinc, copper, cadmium, mercury, iron, chromium, manganese, aluminum, nickel or cobalt water soluble salts such as the chloride, bromide, iodide, sulphate, sulphite, nitrate, nitrite, and also any of the water soluble salts of the above named metals of organic acids, such as the sulphonic acids of benzol, toluol and xyol, or the sulphonic acids derived from the treatment of petroleum oils with sulphuric acid.

The process, described briefly, consists in passing the hydrocarbon oil product, such as gasoline stock, in a liquid phase, commingled with a sub-
substantially concentrated water solution of any of the above named salts or mixtures thereof, through a heating coil under a pressure sufficient to prevent any substantial vaporization therein, at temperatures of approximately 300 to 600 degrees F., and then immediately releasing the pressure and separating by distillation the purified hydrocarbon oil product from the water solution of the metallic salt or salts, the extracted impurities and products of polymerization or condensation; or, as shown in Figure II, the gasoline stock and water solution of metallic salt or salts may be first separated out, heated and then commingled under a pressure.

The hydrocarbon oil stock to be treated by my invention may or may not have had a preliminary treatment with sulphuric acid, or other agents to partly purify the same, or may be first partly purified by my invention and the purification completed by methods known in the art, such as treatment with caustic alkali, sulphuric acid, etc. In the case of gasoline stocks produced by cracking high sulphur bearing crude petroleum oil or residuums, it may be advantageous to treat such gasoline stocks with sulphuric acid or sulphuric anhydride at low temperatures, ranging from approximately 0 to 30 degrees F., before the treatment with a concentrated water solution of any of the aforesaid water soluble metallic salts at the elevated temperatures and pressures heretofore stated, and this treatment may also be followed by treatment with an alkaline water solution of sodium, potassium, or calcium hydroxide, or the carbonates of sodium or potassium.

Although a solution of less concentration may be employed, which may range from 50 or less to approximately 25 per cent, the strength of the water solution of the metallic salt or mixtures of salts employed is preferably a substantially concentrated solution, and the temperature employed for the treatment is preferably approximately 300 to 600 degrees F., followed by a distillation and fractionation operation to separate the products of reaction and higher boiling polymerized products from the purified gasoline or naphtha stocks.

One of the principal objects of this invention is to accomplish a purification of gasoline or naphtha stocks produced by thermoechemical decomposition of high boiling petroleum oils, by treating the same, under a pressure sufficient to prevent any substantial vaporization thereof, and at a temperature of approximately 300 to 600 degrees F., followed by a distillation and fractionation operation to separate the products of reaction and higher boiling polymerized products from the purified gasoline or naphtha stocks.

Another object of the invention is to provide a continuous, rapid and economical process for purifying gasoline stocks produced by the thermoechemical decomposition of higher boiling petroleum oils, by treating the same, under superatmospheric pressure sufficient to maintain a liquid phase, with a substantially concentrated water solution of a metallic salt, at temperatures of approximately 300 to 600 degrees F., to polymerize substantially all the unstable hydrocarbons contained therein, and at the same time remove oxygenated hydrocarbons and render the gasoline "sweet" to the "doctor test".

Another object of the invention is to provide a continuous, economical method for improving the color and removing gums and gum forming material from gasoline or naphtha stock, so that the same may be kept in storage for relatively long periods of time without changing color or quality by the formation of polymerized bodies.

Various other objects and advantages of the present invention will be apparent from the description of the preferred form or example of the process embodying the invention. For this purpose, reference is made to the accompanying drawings, in which there are illustrated two forms of apparatus in which the invention may be performed.

Figure I represents one form of an apparatus for holding any one of the metallic salt or salts, in which the petroleum oil product to be treated is first commingled with the water solution of a metallic salt and thereafter heated to a reaction temperature, by causing the same to pass through a heating coil under pressure.

Figure II represents another form of apparatus in which the petroleum oil product and the water solution of a metallic salt are separately heated to a reaction temperature, and are thereafter commingled by means of a jet mixer.

In Figure I, 3 represents generally a tank for holding a gasoline or other petroleum oil stock to be processed. Pipe 1, controlled by valve 2, connects the gasoline stock tank 3 near the top to a source of supply not shown. Pipe 4, controlled by valve 5, connects gasoline stock tank 3 to the inlet side of pump 6. Pipe 7, controlled by valve 41, connects pipe 4 to a fractionating tower not shown. Pipe 7 connects pump 6 to jet mixer 8.

13 represents generally a tank for holding a substantially concentrated water solution of a metallic salt, such as zinc chloride, zinc bromide, zinc iodide, etc., or any of the other metallic salts herebefore enumerated. Pipe 14, controlled by valve 15, connects tank 13 near the top to a source of supply not shown. Pipe 11, controlled by valve 12, connects tank 13 near the bottom to the inlet side of pump 10. Pipe 12 connects the discharge side of pump 10 to jet mixer 8.

Pipe 16 connects jet mixer 8 to heater coil 38. Heater coil 38 is stationed in the furnace 17. Furnace 17 is provided with a burner 18 which leads to a supply of fuel not shown. Pipe 33, controlled by pressure relief valve 19, connects heater coil 38 to inlet of jet mixer 8. Distillation tower 20 is provided with bubble trays 21. Pipe 22, controlled by valve 23, connects distillation tower 20 near the bottom to a source of water supply not shown. Pipe 25, controlled by valve 24, connects distillation tower 20 at the bottom to tank 26. Pipe 26, controlled by valve 27, connects tank 26 to a storage not shown. Pipe 29 connects distillation tower 20 at the top to condenser coil 31. Condenser coil 31 is stationed in condenser box 30, which is provided with a water inlet pipe 32 and a water outlet pipe 31. Pipe 32 leads to a source of water supply not shown, and pipe 37 leads to a waste receiver not shown.

Pipe 33 connects condenser coil 31 to treated gasoline tank 34. Pipe 36, controlled by valve 35, connects the treated gasoline tank near the bottom to a pipe of the same caliber as the above mentioned to a point in the gasoline pipe of the same caliber as the above mentioned to a point in the gasoline pipe.
fractionating tower not shown. Pipe 7 connects pump 6 to heater coil 38. Heater coil 38 is stationed in a furnace 41. Furnace 17 is provided with a burner 18 which leads to a fuel supply not shown.

10. A tank generally for holding a concentrated water solution of a metallic salt, such as zinc chloride, zinc bromide, zinc iodide, etc., or any of the other metallic salts heretofore enumerated. Pipe 14, controlled by valve 15, connects tank 13 near the top to a source of supply not shown. Pipe 11, controlled by valve 12, connects tank 13 near the bottom to the inlet side of pump 10. Pipe 9 connects the discharge side of pump 10 to heater coil 44. Heater coil 44 is stationed in furnace 42. Furnace 42 is provided with a burner 43 which leads to a fuel supply not shown.

Pipe 45 connects heater coil 44 to jet mixer 8. Pipe 39 connects heater coil 38 to jet mixer 8. Pipe 16 connects jet mixer 8 to reaction chamber 45.

Pipe 47, controlled by pressure release valve 19, connects reaction chamber 45 to distillation tower 20. Distillation tower 20 is provided with a bubble tray 21. Pipe 22, controlled by valve 23, connects distillation tower 20 to a source of water supply not shown. Pipe 25, controlled by valve 24, connects the bottom of distillation tower 20 to tank 26. Pipe 28, controlled by valve 27, connects tank 25 to a storage not shown.

Pipe 29 connects distillation tower 20 at the top to condenser box 31. Condenser box 31 is situated in condenser box 30, which is provided with a water inlet pipe 32 and a water outlet pipe 37. Pipe 32 leads to a source of water supply not shown, and pipe 37 leads to a waste receiver not shown. Pipe 33 connects condenser box 30 to treated gasoline tank 34. Pipe 36, controlled by valve 35, connects treated gasoline tank 34 near the bottom to a storage not shown. The process as carried out in the apparatus described in Figure 1 is as follows:

Tank 3 is filled with the petroleum oil product to be treated by operation of valve 2. Petroleum oil distillate, such as gasoline stock, contained in tank 3, is permitted to flow through pipe 4 and into the inlet side of pump 6, the rate of flow being governed by operation of valve 5. Pump 6 continuously pumps the gasoline stock, under a pressure of approximately 100 to 1,000 pounds gauge, into jet mixer 8, wherein the gasoline stock is continuously commingled with the necessary quantity of a substantially concentrated water solution of metallic salts such as aluminum chloride from the supply tank 13.

The water solution of metallic salt contained in supply tank 13 is permitted to flow through pipe 11 and into the inlet side of pump 16, which discharges the same under a pressure ranging from approximately 100 to 1,000 pounds gauge through pipe 9 and into said jet mixer 8, the rate of flow being governed by operation of valve 12.

The quantity of water solution of metallic salt may range from as low as 1 per cent to as high as 10 per cent or higher, by volume, depending upon the make of the apparatus. For example, if a crude gasoline stock contains a high percentage of impurities to be extracted, as high as 10 per cent by volume or more of a concentrated water solution of any of the aforesaid metallic salts or mixtures of the same may be employed. The pressure is maintained on the system by means of pumps 6 and 16 so regulated that the commingled mixture of the water solution of metallic salt or salts and gasoline stock under treatment, passing through coil 38, will be maintained in a substantially liquid phase, such pressure depending upon the boiling point of the gasoline stock and the temperature thereof.

From jet mixer 8, the gasoline stock, commingled with the water solution of the metallic salt or salts, passes through heater coil 38, pipe 39 and pressure release valve 19, where the pressure is reduced to atmospheric or approximately atmospheric, and then passes into distillation tower 20. The commingled mixture passing through heater coil 38 is heated to the reaction temperature. Preferably, a temperature ranging from approximately 300 to 400 degrees F. is suitable to employ in treating ordinary gasoline stocks. However, with some grades of petroleum oil distillates, as high as 600 degrees F. or a little higher may be employed.

In distillation tower 20, the purified gasoline stock, at a temperature ranging from approximately 300 to 400 degrees F., together with a portion of the water content of the salt solution, are vaporized and separated from the products of the 25 reaction and the metallic salt or salts employed. The purified gasoline stock, mixed with water vapor, passes out of distillation tower 20, through pipe 39, into condenser coil 40, stationed in condenser box 30, wherein the said purified gasoline stock and water vapor are condensed to a liquid passing through pipe 33 and into the treated gasoline tank 34. A cooling fluid such as water is employed to condense the gasoline vapors, passing through condenser coil 40, coming from a source not shown through pipe 32 and passing out of condenser box 30 through pipe 37. From the purified gasoline stock, in the treated gasoline tank 34 the purified gasoline stock may be conducted to a storage by not shown through pipe 36, controlled by valve 35. The purified gasoline stock so obtained may be thereby treated, if necessary, by other methods known in the art, or may be subjected to a distillation operation to separate fractions having any desired range of boiling points.

The metallic salts and products of reaction which separate in the bottom of distillation tower 20 are intermittently or continuously drawn into tank 26 through pipe 26, the flow being controlled by valve 24, water being continuously or intermittently introduced into the lower section of distillation tower 20 through pipe 22, controlled by valve 23, in quantities sufficient to replace the vaporized water from the metallic salt water solution, so as to maintain the used metallic salts or compounds and products of reaction in a fluid condition.

From tank 26 the excess water solution of metallic salt or salts and products of reaction are conducted to a storage not shown through pipe 26, controlled by valve 21, and the metallic salts or compounds are separated from the reaction products and purified for re-use.

As illustrated in Figures I and II, if it is desired to treat a gasoline stock coming directly from a fractionating tower or other distillation apparatus, in a vapor or semi-vapor state, valve 5 is closed and valve 41 is open, wherein the gasoline stock coming from a source not shown, in a vapor or semi-vapor state, to flow 80 through pipe 40 and into the inlet side of pump 6, wherein the gasoline stock is completely condensed to a liquid by the applied pressure maintained on the system and the introduction of the cool water solution of a metallic salt or salts in 75...
Figure I, and by the application of pressure in Figure II.

The process as carried out in the apparatus described in Figure II is substantially the same as the process heretofore described for Figure I, except that the petroleum oil or gasoline stock to be treated and the water solution of a metallic salt or salts are first separately heated to the reaction temperature by heating coils 38 and 44, at a pressure sufficient to prevent any substantial vaporization thereof, after which the heated gasoline stock and heated water solution of a metallic salt or salts, as heretofore enumerated, are commingled in jet mixer 8 and pass through pipe 16, reaction chamber 46, pipe 47, pressure release valve 18, and into distillation tower 20.

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 invention, such as the use of centrifugal or other mechanical mixers, or the employment of any of the well known contact towers wherein a water solution of a metallic salt or salts, either organic or inorganic, heretofore enumerated, may be commingled with or brought into contact with a petroleum oil at a pressure sufficient to prevent substantial vaporization at the reacting temperature, and the invention includes all such modifications and changes as come within the scope of the appended claims.

I claim:

1. A process of purifying a petroleum oil product which comprises, causing the said product to vaporize from a heated commingled mixture of the said product and a maintained water solution of an aluminum salt at a reaction temperature.

2. A process of purifying a petroleum oil product which comprises, heating and commingling said product with a water solution of an aluminum salt, under pressure sufficient to prevent substantial vaporization, therefrom releasing the pressure and causing the product to vaporize from the heated commingled mixture at a reaction temperature while maintaining the aluminum salt in solution by the addition of water.

3. A process of purifying petroleum oil products, comprising, commingling a petroleum oil product with a substantially concentrated water solution of an aluminum salt, passing the commingled mixture through a heating coil and heating the mixture to a reaction temperature, under pressure sufficient to prevent substantial vaporization, releasing the pressure and separating by vaporization, fractionation and condensation a purified petroleum oil product from products of reaction and excess treating agent.

4. A process of purifying petroleum oil, comprising, commingling the petroleum oil with a substantially concentrated water solution of aluminum salt, passing the commingled mixture through a heating coil and heating the mixture to a temperature of approximately 300-600°F., under pressure sufficient to prevent substantial vaporization, releasing the pressure and separating by vaporization and condensation a purified petroleum oil product from products of reaction and excess treating agent.

5. A continuous process for purifying gasoline stocks, comprising, continuously commingling gasoline stock with a substantially concentrated water solution of aluminum salt, continuously passing the commingled mixture through a heating element and heating the mixture to a temperature of approximately 300-600°F., under pressure sufficient to prevent substantial vaporization, releasing the pressure and separating by vaporization, fractionation and condensation a purified gasoline stock from products of reaction and excess treating agent.

6. A process of removing gum forming constituents from cracked gasoline stock, comprising, commingling cracked gasoline stock with a water solution of aluminum salt, and heating the commingled mixture to a temperature of approximately 300-600°F., under pressure sufficient to prevent substantial vaporization, continuously passing through a heating zone, for a period of time sufficient to cause the unstable hydrocarbons contained in the cracked gasoline stock to polymerize with the formation of gums, then reducing the pressure to approximately atmospheric, and separating by vaporization, fractionation and condensation a purified gasoline stock from products of reaction and polymerization, and excess treating agent.

7. A continuous process for purifying gasoline or naphtha derived by thermo decomposition of high boiling oil, comprising, continuously commingling the gasoline or naphtha with a water solution of aluminum chloride, continuously passing the commingled mixture through a heating zone and heating the commingled gasoline or naphtha and water solution of aluminum chloride to a temperature of approximately 300-600°F., under pressure sufficient to prevent substantial vaporization, continuously releasing the pressure after the commingled mixture of gasoline or naphtha and water solution of aluminum chloride has passed through said heating zone, continuously passing the treated gasoline or naphtha, products of reaction and excess treating agent into a vaporizing zone, continuously vaporizing, fractionating and separating a purified gasoline or naphtha and water vapor from higher boiling reaction products and excess treating agent.

8. A continuous process of purifying gasoline or naphtha derived by the thermo-molecular decomposition of higher boiling mineral oils, comprising, continuously commingling the gasoline or naphtha with a water solution of aluminum salt, continuously passing the commingled mixture through a heating zone and heating the commingled gasoline or naphtha and water solution of aluminum salt to a temperature of approximately 300-600°F., under pressure sufficient to prevent substantial vaporization, continuously releasing the pressure and continuously passing the treated mixture of gasoline or naphtha, water solution of aluminum salt and products of reaction into a vaporizing zone, continuously vaporizing and separating by fractionation and condensation a purified gasoline or naphtha with water from higher boiling reaction products of reaction and excess treating agent, continuously introducing water into the vaporizing zone in quantities sufficient to replace the water of vaporization, continuously withdrawing products of reaction and introduced water and separating excess treating agent, substantially as described.

9. A process of purifying gasoline or naphtha, comprising, contacting the gasoline or naphtha with a water solution of aluminum salt while passing through a heating zone, under a pressure substantially greater than atmospheric, and continuously passing the mixed gasoline or naphtha and water solution of aluminum salt to a temperature of...
approximately 300-600° F., releasing the pressure after the gasoline or naphtha mixed with the water solution of aluminum salt has passed through the heating zone, and separating by vaporization, fractionation and condensation a purified gasoline or naphtha stock from higher boiling products of reaction and excess treating agent.

5. A process of purifying petroleum oil, comprising, commingling the petroleum oil with a water solution of aluminum salt, passing the commingled mixture through a heating zone and heating the commingled mixture to a reaction temperature, under a pressure sufficient to prevent substantial vaporization, releasing the pressure and passing the treated petroleum oil, products of reaction and water solution of aluminum salt into a vaporizing zone, maintaining the aluminum salt in a fluid condition by the addition of water, vaporizing, fractionating and separating a purified petroleum oil mixed with water vapor from higher boiling reaction products and excess treating agent.

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