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PROCESS OF PURIFYING NAPHTHA STOCKS

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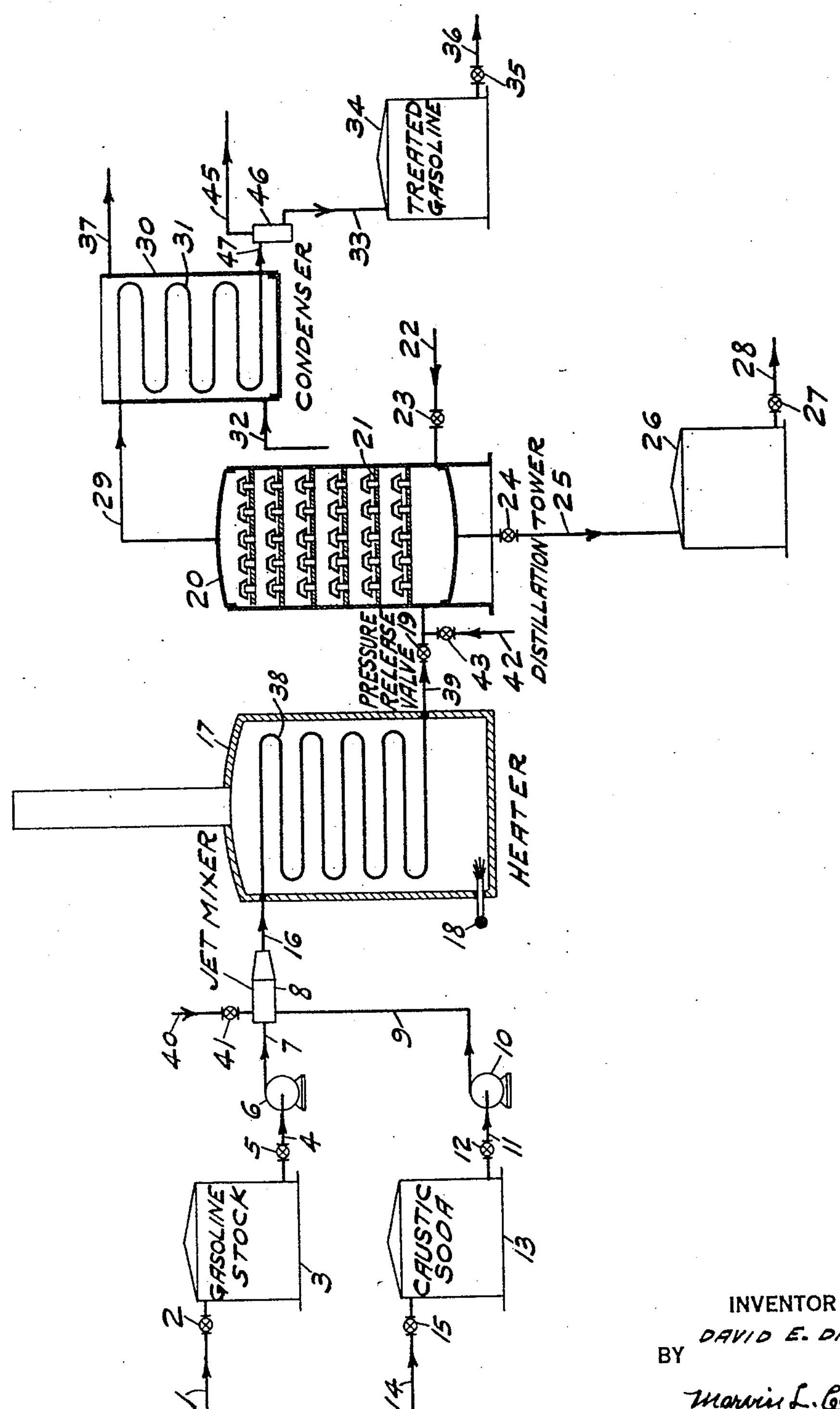

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PROCESS OF PURIFYING NAPHTHA STOCKS

Application filed December 5, 1931. Serial No. 579,237.

This application is a continuation in part of my application Serial No. 370,325, filed June 12, 1929, for method of purifying petroleum oils.

This invention relates to an improved method for purifying hydrocarbon oils derived by distillation or cracking of mineral oils or mineral oil products, such as lubricating oil stocks, lamp oil distillates, gasoline or naphtha stocks, or any other distillates produced in general refinery practice, and more specifically refers to the treatment of gasoline or naphtha stocks produced by cracking petroleum oils or distillates derived from relatively high sulphur bearing crude petroleum oils, in which hydrogen sulphide, mercaptans and other sulphur bearing compounds, as well as varying percentages of phenols and unsaturated hydrocarbons (such as diolefines and acetylenes) may be present or formed during a distillation or cracking operation.

For the purpose of simplifying the description of the invention, reference will be made to gasoline or naphtha stocks mainly.

By well known methods, gasoline stocks derived from cracking petroleum oils or from distilling high sulphur bearing crude petroleum oils are usually purified by varying treatments with sulphuric acid, followed by neutralization with a water solution of an alkali, a sweetening operation and a final distillation. In the sweetening operation hypochlorite of soda or sodium plumbite in a water solution of caustic soda may be employed to convert corrosive sulphur compounds into noncorrosive bodies, so that the treated gasoline stock will be "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. Also all the sulphur bearing hydrocarbons remaining in the gasoline stock after the purification operation form corrosive acid compounds during combustion, and if in appreciable amounts, may attack the metal parts of an engine. Therefore, it is advantageous in the purification of gasoline or naphtha stocks to use a purifying agent which in itself will not form chlorinated oils, and one which will remove a certain percentage of the sulphur compounds from a gasoline or naphtha stock and polymerize the unstable hydrocarbons so that the same may be separated therefrom by a subsequent distillation.

In my pending application, Serial No. 370,325, filed June 12, 1929, for method of purifying petroleum oils, it has been disclosed that hydrocarbon oils, such as gasoline or naphtha stocks, may be purified by passing the same, commingled with a substantially concentrated water solution of caustic soda, caustic potash, sodium carbonate or potassium carbonate, through a heating coil under a pressure sufficient to prevent substantial vaporization, at a temperature between 350 and 500 degrees F., then releasing the pressure and separating by distillation and fractionation a purified gasoline or naphtha from the excess caustic alkali, the extracted impurities and the products of polymerization or condensation. Water is continuously or intermittently introduced into the lower section of the distillation and fractionating apparatus in quantities sufficient to replace the vaporized water from the caustic alkali solution, so as to maintain the used caustic alkali or carbonate and products of reaction in a fluid state.

Now I have discovered an improvement thereto, in which I have determined that it is an advantage to mix air with the gasoline or naphtha stock during the treating operation, in quantities sufficient to oxidize the corrosive sulphur compounds contained therein into compounds that may be extracted to a certain extent with the caustic alkali or carbonate treating solution; also that the introduction of air into the gasoline or naphtha stock assists in the polymerization of the unstable hydrocarbons and thereby produces gasoline or naphtha which is lower in sulphur content, "sweet" to the "doctor test", and contains substantially no gums or gum forming constituents. The air may be mixed with the gasoline or naphtha stock as it is being commingled with the treating solution, or it may be introduced into the commingled mixture of gasoline or naphtha stock and treating solution at any convenient point in the treating system.

The hydrocarbon oil 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. In the case of gasoline or naphtha stocks produced by cracking high sulphur bearing crude petroleum oils or residuums, it may be advantageous to treat such gasoline or naphtha stocks with sulphuric acid at low temperatures, ranging from approximately 0 to 32 degrees F., before the treatment with the concentrated water solution of caustic alkali or carbonate at the elevated temperatures and pressures heretofore given.

One of the principal objects of this invention is to accomplish a partial desulphurization and purification of gasoline or naphtha stocks produced by thermo-molecular decomposition of high boiling petroleum oils, by a treatment with a substantially concentrated water solution of an alkali hydroxide or carbonate and air, under a pressure sufficient to prevent substantial vaporization of the gasoline or naphtha stock, and at a temperature of approximately 350–500 degrees F., followed by a distillation and fractionation operation to separate the products of reaction and higher boiling polymerized products from purified gasoline or naphtha.

Another object of the invention is to provide a continuous, rapid and economical process for purifying gasoline or naphtha stocks by treating the same, under superatmospheric pressure sufficient to maintain the gasoline or naphtha stock in a liquid phase, with a substantially concentrated water solution of an alkali hydroxide or carbonate and air, at temperatures of approximately 350–500 degrees F., to polymerize substantially all the unstable hydrocarbons contained therein, and at the same time remove oxygenated hydrocarbons and render the gasoline or naphtha "sweet" to the "doctor test".

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

Other objects and advantages will be apparent from the preferred embodiment of this invention, which will now be more fully explained by reference to the accompanying drawing, which is a diagrammatical representation of an apparatus in which the invention may be performed.

In the drawing, 3 represents generally a tank for holding a supply of gasoline, naphtha or other petroleum oil stocks to be processed. Pipe 1, controlled by valve 2, connects 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 connects pump 6 to jet mixer 8.

13 represents generally a caustic soda tank for holding a concentrated solution of a caustic alkali such as caustic soda or caustic potash. Pipe 14, controlled by valve 15, connects caustic soda tank 13 near the top to a source of supply not shown. Pipe 11, controlled by valve 12, connects caustic soda tank 13 near the bottom to the inlet side of pump 10. Pipe 9 connects the discharge side of pump 10 to jet mixer 8. Pipe 40, controlled by valve 41, is connected to jet mixer 8 and leads to a source of compressed air.

Pipe 16 connects jet mixer 8 to heater coil 38. Heater coil 38 is stationed in furnace 17. Furnace 17 is provided with a burner 18, which leads to a supply of fuel oil not shown.

Pipe 39, controlled by pressure release valve 19, connects heater coil 38 to distillation tower 20. Pipe 42, controlled by valve 43, connects pipe 39 to a source of compressed air. 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 or steam supply not shown. Pipe 25, controlled by valve 24, connects distillation tower 20 at the bottom to tank 26. Pipe 28, 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, and is provided with a water inlet pipe 32 and a water outlet pipe 37. Pipe 32 leads to a source of water not shown, and water outlet pipe 37 leads to a waste receiver not shown.

Pipe 47 connects condenser coil 31 to air separator 46. Pipe 45 connects air separator 46 near the top to an absorber not shown. Pipe 33 connects air separator 46 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 preferred process as carried out in the apparatus just described is as follows:

Petroleum oil distillate, such as gasoline or naphtha 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 discharges the gasoline stock through pipe 7, under a pressure of approximately 150—1000 pounds gauge, into jet mixer 8, wherein the gasoline stock is continuously commingled with the necessary quantity of air, and a substantially concentrated water solution of caustic alkali coming from the caustic soda supply tank 13.

The air introduced into jet mixer 8 comes from a source of compressed air through pipe 40, controlled by valve 41, and may range from approximately one-half volume to four volumes of air per volume of liquid gasoline under treatment.

The water solution of caustic alkali contained in supply tank 13 is permitted to flow through pipe 11 and into the inlet side of pump 10, which discharges the same, under a pressure ranging from approximately 150—1000 pounds gauge, through pipe 9 and into jet mixer 8, the rate of flow being governed by operation of valve 12. The quantity of water solution of caustic alkali employed may range from as low as approximately 1 per cent to as high as 10 per cent by volume or more, depending upon the stock to be treated. For example, if a crude gasoline stock contains a high percentage of impurities to be extracted, or has had a preliminary treatment with sulphuric acid, as much as 10 per cent by volume or more of a concentrated water solution of caustic alkali may be employed.

The pressure maintained on the system by means of pumps 6 and 10 is regulated so that the commingled mixture of water solution of caustic alkali and gasoline or naphtha stock under treatment will be maintained in a substantially liquid phase, such pressure depending upon the boiling points of the gasoline or naphtha stock and the temperature employed.

From jet mixer 8 the gasoline stock, commingled with the water solution of caustic alkali and air, passes through pipe 16, heater coil 38, pipe 39, pressure release valve 19 where the pressure is reduced to atmospheric or approximately atmospheric, and into distillation tower 20. The commingled mixture passing through heater coil 38 is heated to a temperature greater than 350 degrees F. Preferably, approximately 400 degrees F. is a suitable temperature to employ in treating ordinary gasoline or naphtha stocks, however, with some grades of petroleum distillates as high as 500 degrees F. or a little higher may be employed.

In distillation tower 20 the purified gasoline stock, at a temperature of approximately 400 degrees F., together with a portion of the water content of the alkali solution, is vaporized and separated from the products of reaction and the caustic alkali employed. The purified gasoline stock, mixed with water vapor and air, passes out of distillation tower 20, through pipe 29, into condenser coil 31, which is stationed in condenser box 30, wherein the major portion of the purified gasoline stock and water vapor is condensed to a liquid and passed through pipe 47 into air separator 46.

In separator 46 the air, containing a small percentage of the treated gasoline stock, is separated from the condensed purified gasoline or naphtha and passes from the top of separator 46 through pipe 45, which leads to an absorber, not shown, wherein the gasoline retained by the air is recovered by absorption methods known in the art, and may be thereafter returned and mixed with the treated gasoline stock in tank 34.

From separator 46 the treated gasoline passes through pipe 33 into tank 34. From treated gasoline tank 34 the purified gasoline stock may be conducted to a storage not shown through pipe 36, controlled by valve 35. The purified gasoline stock so obtained may be thereafter 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 caustic alkali and products of reaction, which separate in the bottom of distillation tower 20, are intermittently or continuously withdrawn into tank 26 through pipe 25, 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 caustic alkali water solution, so as to maintain the used caustic alkali and products of reaction in a fluid condition.

From tank 26 the excess water solution of caustic alkali and products of reaction are conducted to a storage not shown through pipe 28, controlled by valve 27, and the caustic alkali may be separated from the reaction products and recovered for reuse.

The air used in the treatment may be introduced into the treating system through pipe 42, controlled by valve 43, which is connected to pipe 39, and leads to a source of compressed air not shown.

While the process herein described is well adapted for carrying out the objects of this invention, various modifications and changes may be made, such as the employment of various types of fractionating equipment known in the art to effect any desired separation of the treated gasoline stock into fractions having a desired range of boiling points, and the invention includes all such changes and modifications as appear within the scope of the appended claims.

I claim:

1. A process of purifying naphtha stocks, comprising, commingling a naphtha stock with a substantially concentrated water solution of a caustic alkali, passing the commingled mixture through a heating zone at temperatures of approximately 350–500 degrees F., under a pressure sufficient to prevent substantial vaporization of the naphtha stock, releasing the pressure and introducing air

into the commingled mixture, and separating a purified naphtha by vaporization, fractionation and condensation from products of reaction, excess caustic alkali and aeriform products.

2. A process of removing gum forming constituents from cracked gasoline stock, comprising, contacting the cracked gasoline stock with a water solution of a caustic alkali, at temperatures of approximately 350–500 degrees F., under a pressure sufficient to prevent substantial vaporization thereof, while passing through a heating zone, for a period of time sufficient to cause unstable hydrocarbons contained in the gasoline stock to polymerize with the formation of gums, then reducing the pressure to approximately atmospheric, introducing air, and separating by vaporization, fractionation and condensation purified gasoline stock from reaction and polymerization products, excess caustic alkali and aeriform products.

3. A continuous process for purifying gasoline stocks derived by thermo-molecular decomposition of higher boiling petroleum oils, comprising, continuously commingling a gasoline stock with a water solution of a caustic alkali; continuously passing the commingled mixture through a heating zone to heat the commingled gasoline stock and water solution of caustic alkali to a temperature of approximately 400 degrees F., under a pressure sufficient to prevent substantial vaporization therein; continuously releasing the pressure after the commingled mixture of gasoline stock and water solution of caustic alkali has passed through the said heating zone and has been heated to a temperature of approximately 400 degrees F.; continuously introducing air into the heated mixture of gasoline stock and water solution of alkali; continuously passing the same into a vaporizing zone and vaporizing, fractionating, condensing and separating purified gasoline stock mixed with water from higher boiling products of reaction, excess caustic alkali and aeriform products; continuously introducing water into the said vaporizing zone in quantities sufficient to replace water of vaporization; and continuously withdrawing products of reaction and introduced water containing caustic alkali, substantially as described.

In testimony whereof I affix my signature.

DAVID E. DAY.