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METHOD OF PURIFYING PETROLEUM OILS

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This invention relates to an improved process of purifying petroleum oils derived by distillation or cracking of mineral oils, such as lubricating oil stocks, lamp oil distillates, gasoline or naphtha stocks, or distillates derived from shale oil, and more specifically refers to the treatment of gasoline or naphtha stocks produced by cracking an asphalt or mixed base crude petroleum oil 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 unstable hydrocarbons (such as diolefines and acetylenes) may be present or formed during said distillation or cracking operation. For the purpose of simplifying the description of my invention, reference will be made to gasoline 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 permanganate in a water solution of caustic soda may be employed to convert corrosive sulphur compounds into non-corrosive 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 stock, to use a purifying agent which in itself will not form chlorinated oils and one which will remove a high percentage of the sulphur compounds from a gasoline stock and polymerize the unstable hydrocarbons so that the same may be separated therefrom by a subsequent distillation.

Now, I have discovered that a concentrated solution, or a substantially concentrated water solution of a caustic alkali, such as caustic soda, caustic potash, or the carbonates of sodium or potassium, are suitable agents to employ for this purpose on a gasoline or naphtha stock or other petroleum oil distillate, at temperatures between 350 and 500 degrees F., under a pressure sufficient to prevent any substantial vaporization of the petroleum oil stock under treatment, by means of which a gasoline stock so treated is rendered "sweet" to the "doctor test", the unstable hydrocarbons are polymerized, a high percentage of the sulphur bearing compounds are removed and on distillation a purified gasoline stock is obtained which is water white in color and may be stored for a period of time without any substantial change in color.

The process described briefly consists in passing the hydrocarbon oil product, such as gasoline stock in a liquid phase, concomitantly with a substantially concentrated water solution of caustic soda or caustic potash, through a heating coil under a pressure sufficient to prevent any substantial vaporization therein, at a temperature between 350 and 500 degrees F., and then immediately releasing the pressure and separating by distillation the purified gasoline stock from the caustic alkali, the extracted impurities and the products of polymerization or condensation.

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

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

Another object of the invention is to provide a continuous, rapid and economical process for purifying gasoline stocks produced by the thermo-decomposition of higher boiling petroleum oils, by treating the same under super-atmospheric pressure sufficient to maintain a liquid phase with a substantially concentrated water solution of an alkali at temperatures of approximately 350 to 500 degrees F., to polymerize substantially all of 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 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 drawings which is a diagrammatical representation of the apparatus in which the invention may be carried out.

In the drawing, 3 represents generally a tank for holding a supply of the gasoline or other petroleum oil stock to be processed. Pipe 1, controlled by the 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, 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 16, connects the jet mixer 8 to heater coil 38.

The heater coil 38 is stationed in the furnace 17. The heater 17 is provided with a burner 18 which leads to a supply of fuel not shown. Pipe 39, controlled by pressure relief valve 19, connects the heater coil 38 to distillation tower 20. The distillation tower 20 is provided with bubble trays 21. Pipe 22, controlled by valve 23, connect the distillation tower 20 near the bottom to a source of water supply not shown. Pipe 25, controlled by the valve 24 connects distillation tower 20 at the bottom to tank 26. Pipe 28 controlled by valve 27 connects the 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 the condenser box 30 and is provided with a water inlet pipe 32 and a water outlet pipe 37. The pipe 32 leads to a source of water not shown and the water outlet pipe 37 leads to a waste receiver not shown. Pipe 33 connects the condenser coil 31 to treated gasoline tank 34. Pipe 36 controlled by valve 35 connects the treated gasoline tank 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 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 under a pressure of approximately 150 to 1000 pounds gauge into jet mixer 8, wherein the gasoline stock is continuously commingled with the necessary quantity of a substantially concentrated water solution of caustic soda or caustic potash coming from the caustic soda supply tank 13.

The water solution of caustic soda or caustic potash contained in the 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 to 1000 pounds gauge through pipe 9 and into the said jet mixer 8, the rate of flow being governed by operation of valve 12.

The quantity of water solution of caustic soda or caustic potash 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 sulfuric acid, as much as 10 per cent by volume or more of a concentrated water solution of caustic soda or caustic potash may be employed. The pressure maintained on the system by means of pumps 6 and 10 is regulated so that the commingled mixture of the water solution of caustic alkali and gasoline stock under treatment will be maintained in a substantially liquid phase, such pressure depend-
ing upon the boiling points of the gasoline stock and the temperature employed. From jet mixer 8 the gasoline stock commingled with the water solution of the alkali passes through heater coil 35, pipe 39, pressure relief valve 19, where the pressure is reduced to atmospheric, or approximately atmospheric, and then into distillation tower 20. The commingled mixture passing through heater coil 35 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 stocks. However, with some grades of petroleum oil 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, are vaporized and separated from the products of the alkali reaction and the caustic alkali employed. The purified gasoline stock mixed with water vapor, passes out of distillation tower 20, through pipe 29 into condenser coil 31 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. From the 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 the reaction which separate in the bottom of distillation tower 20 are intermittently or continuously drawn into tank 26 through pipe 28 controlled by valve 24, water being continuously or intermittently introduced into the lower section of distillation tower 20, through the pipe 22, controlled by valve 28, 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 the reaction in a fluid condition.

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

While the process herein described is well adapted for carrying out the objects of this invention, various modifications may be made such as the employment of various 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 which appear within the scope of the appended claims.

What I claim is:

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 coil at temperatures of approximately 350 to 500 degrees F., under a pressure sufficient to prevent substantial vaporization therein, then releasing the pressure and separating a purified naphtha stock by vaporization from products of reaction and excess caustic alkali.

2. 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 coil at temperatures of approximately 350 to 500 degrees F., under a pressure sufficient to prevent substantial vaporization therein, then releasing the pressure and separating by vaporization and fractionation, a purified naphtha stock from products of reaction and excess caustic alkali.

3. A process of purifying naphtha stocks, comprising, contacting a naphtha stock with a substantially concentrated water solution of a caustic alkali, at a temperature of approximately 350 to 500 degrees F., under a pressure sufficient to prevent substantial vaporization, then reducing the pressure and separating purified naphtha stocks by vaporization and fractionation, from products of reaction and excess caustic alkali.

4. A continuous process for purifying gasoline stocks, derived from cracking higher boiling petroleum oils, comprising, continuously commingling a gasoline stock with a substantially concentrated water solution of caustic soda, continuously passing the commingled mixture through a heating element to heat the same to a temperature of approximately 350 to 500 degrees F., under a pressure sufficient to prevent substantial vaporization therein, releasing the pressure and separating by vaporization a purified gasoline stock from products of reaction and excess caustic soda.

5. A process of removing unstable unsaturated hydrocarbons and corrosive sulphur bearing hydrocarbons from a gasoline stock containing the same, comprising, contacting the gasoline stock with a substantially concentrated water solution of a caustic alkali, while passing through a restricted passageway, at temperatures ranging from 350 to 500 degrees F., under a pressure sufficient to prevent any substantial vaporization therein, then reducing the pressure to approximately atmospheric and separating by vaporization a purified gasoline stock from products of reaction and excess caustic alkali.
6. A process of removing gum-forming constituents from cracked gasoline stock, comprising, contacting a cracked gasoline stock with a water solution of a caustic alkali at temperatures of approximately 400 to 500 degrees F., under a pressure sufficient to prevent substantial vaporization thereof, while passing through a heating coil for a period of time sufficient to cause 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 purified gasoline stock from products of reaction, polymerization and excess caustic alkali.

7. A process of purifying naphtha stocks, comprising, contacting a naphtha stock with a water solution of caustic alkali at temperatures of approximately 400 to 500 degrees F., under a pressure sufficient to prevent substantial vaporization thereof, while passing through an elongated passageway, then reducing the pressure and passing the treated naphtha, products of reaction and excess water solution of caustic alkali into a passageway of larger diameter, vaporizing, fractionating, condensing and collecting purified naphtha free from the products of reaction and excess caustic alkali.

8. A continuous process for purifying gasoline stocks derived by the thermo-decomposition of higher boiling petroleum oils, comprising, continuously commingling a gasoline stock in a jet mixer with a water solution of a caustic alkali, continuously passing the commingled mixture from the jet mixer through a heating coil 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 substantially vaporization therein, continuously releasing the pressure after the commingled mixture of the gasoline stock and water solution of caustic alkali has passed through the said heating coil and has been heated to a temperature of approximately 400 degrees F., continuously passing the said heated mixture of gasoline stock and water solution of alkali into a vaporizing tower, continuously vaporizing and separating purified gasoline stock mixed with water vapor from higher boiling products of reaction and excess caustic alkali, continuously introducing water into the said vaporizing tower in quantities sufficient to replace water of vaporization, continuously withdrawing products of reaction and introduced water containing excess caustic alkali, substantially as described.

9. A continuous process for purifying gasoline stocks derived by the 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 coil 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 the gasoline stock and water solution of caustic alkali has passed through the said heating coil and has been heated to a temperature of approximately 400 degrees F., continuously passing the said heated mixture of gasoline stock and water solution of alkali into a vaporizing tower, continuously vaporizing and separating purified gasoline stock mixed with water vapor from higher boiling products of reaction and excess caustic alkali.

In testimony whereof I affix my signature.

DAVID E. DAY.