

July 3, 1956

C. A. PORTER ET AL
METHOD OF CONDUCTING ALKALINE TREATMENT
OF PETROLEUM PRODUCTS

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2 Sheets-Sheet 1

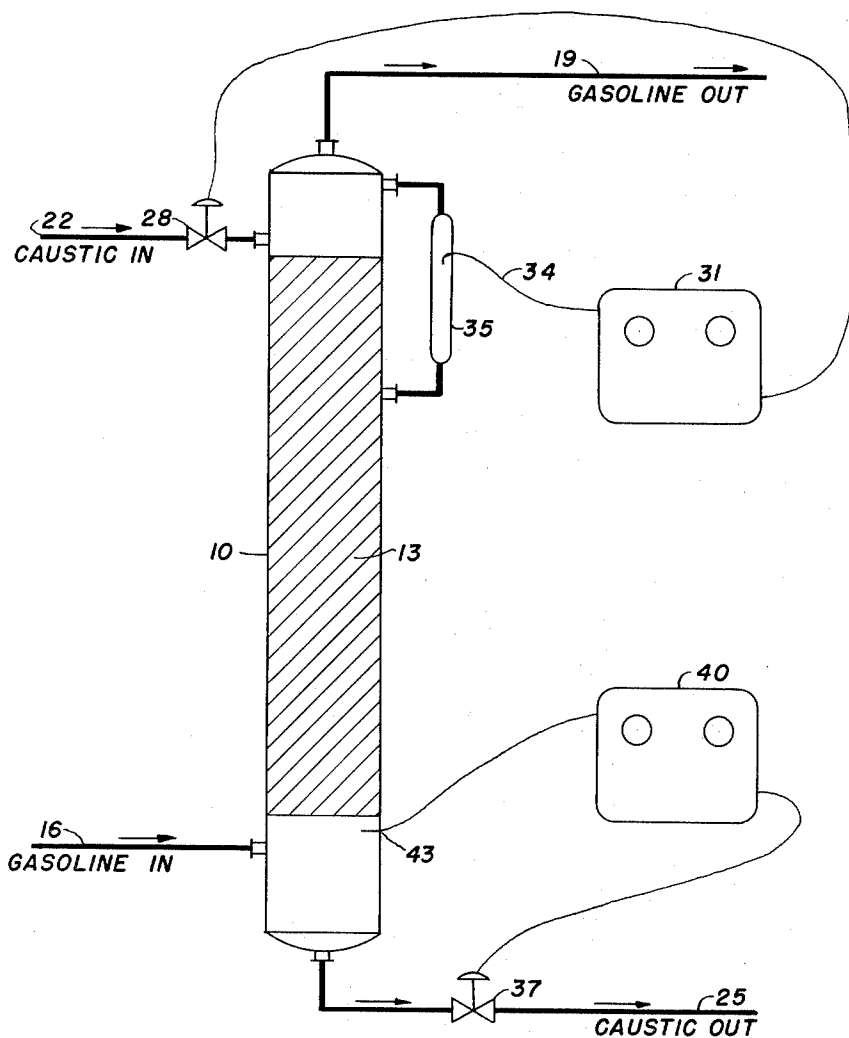


FIG. 1

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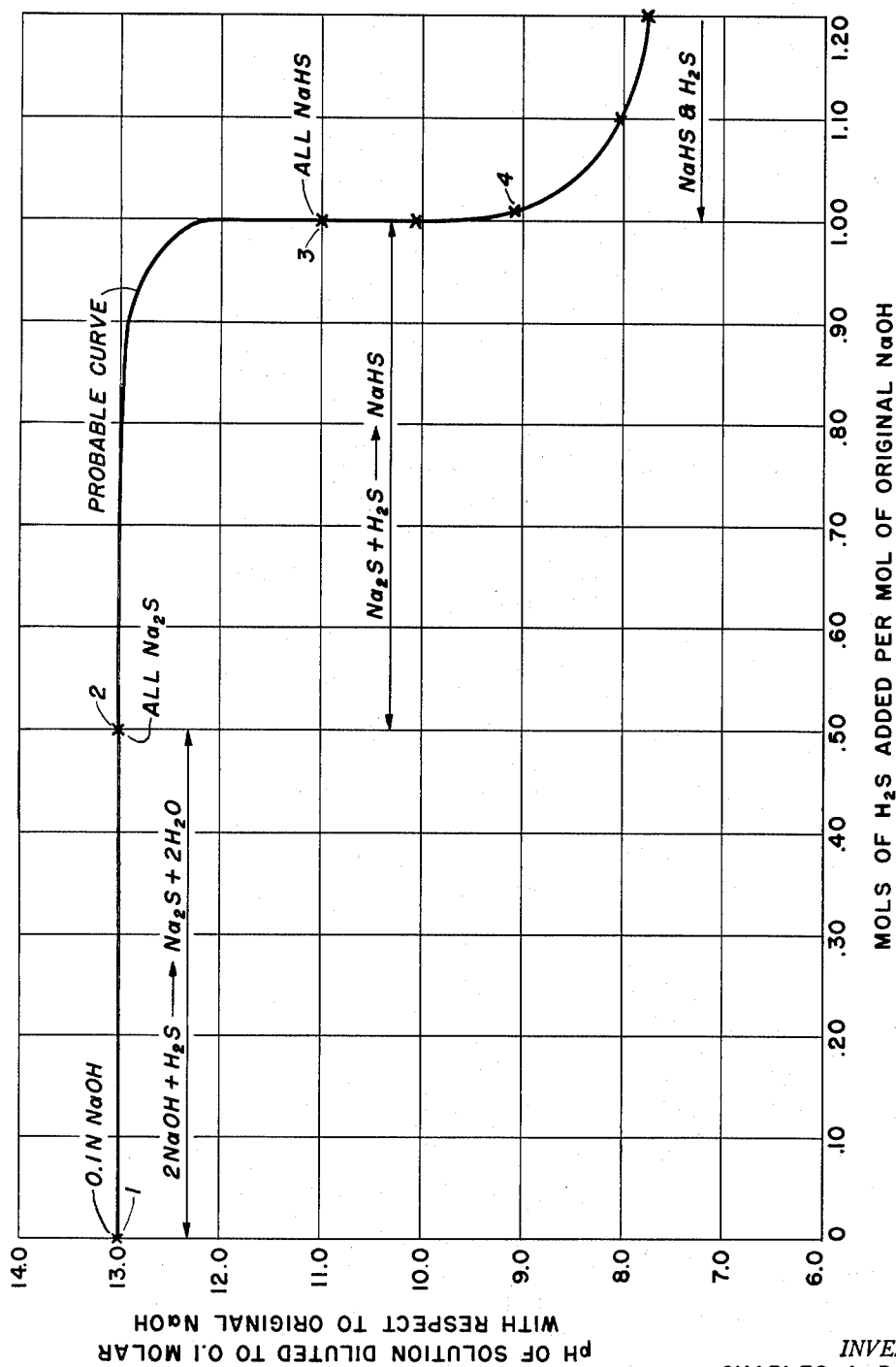


FIG. 2

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METHOD OF CONDUCTING ALKALINE
TREATMENT OF PETROLEUM PRODUCTS

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2 Claims. (Cl. 196—32)

This invention relates to the treatment of hydrocarbon materials containing acidic impurities with alkaline reagents. A more specific aspect of this invention relates to an improved method of treating light petroleum products with aqueous caustic solutions to remove impurities therefrom.

It is well known in the art that hydrocarbon materials can be treated to remove acidic constituents by contacting the hydrocarbon mixture with an aqueous solution of an alkaline reagent, such as sodium hydroxide, potassium hydroxide, etc. These acidic impurities can be grouped into two classes. We may designate as Class I those acidic compounds such as hydrogen sulfide, aryl mercaptans, and aliphatic, phenolic, and naphthenic acids, which can be removed with relative ease by aqueous alkaline solutions of moderate strength but whose alkali metal salts are not easily hydrolyzable. It is, therefore, not practical to revivify by steam stripping aqueous solutions of alkali metal hydroxides spent in the process of removing these more acidic compounds. Class II would consist of alkyl mercaptans and possibly other compounds, which are very weakly acidic and which require for their removal the use of relatively concentrated alkaline solutions, in some cases fortified with solubility promoters. Alkaline solutions spent in the process of removing this latter class of impurities can usually be revivified by steam stripping or by other simple means and used repeatedly. In general, Class I compounds must be removed from the hydrocarbon stream before it is processed for the removal or conversion of Class II compounds because otherwise the accumulation of certain Class I compounds in the permanent treating solution would soon render it unfit for use. From such necessity arises the general practice of employing a two-step process for the removal of acidic impurities from light petroleum products. It is the first step, that is to say, the removal of Class I compounds, toward which the present invention is directed. Some light petroleum products, for instance, liquefied petroleum gases, contain essentially no Class II compounds, so that only the removal of Class I compounds, to which this invention applies, is necessary.

Since a caustic solution used for the removal of Class I compounds cannot be revivified, it must usually be discarded, and, for economic reasons, it is therefore desirable that as much as possible of the available caustic be consumed prior to rejection of the solution. However, proper protection of the permanent treating solution used in the removal of Class II compounds requires substantially complete removal of certain Class I compounds. Consequently, the first step of the treating process to which our invention applies must be carried out with two main objectives in mind, namely: to obtain maximum utility of the caustic and to maintain continually the required degree of removal of certain Class I compounds. Prior art methods for carrying out the process to which this invention relates have accomplished either one or the other of these objectives in a simple manner, but pre-

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vious arrangements for accomplishing both objectives have been extremely cumbersome. For example, both complete utilization of the caustic and the required degree of removal of Class I compounds could be accomplished by the use of two or more mixer-settlers in series with the rerouting of the gasoline flow as the caustic solution becomes spent and is replaced in each settler in turn. This arrangement, however, is unduly cumbersome and would consume a large number of man-hours in its operation.

It is, therefore, an object of this invention to provide an improved method of treating hydrocarbon materials containing acidic impurities with alkaline reagents whereby more complete utilization of the alkaline reagent is attained.

A further object of this invention is to provide an improved method of treating light petroleum products with aqueous caustic solutions whereby more complete utilization of caustic is accomplished.

Another and further object of this invention is to provide an improved method of treating light petroleum products with aqueous caustic solutions whereby caustic is automatically discharged when its effectiveness has diminished to a predetermined point and the discharged caustic is automatically replaced by fresh caustic.

A still further object of this invention is to provide an improved method of treating light petroleum products with aqueous caustic solutions whereby caustic is automatically discharged when its pH reaches a predetermined value and fresh caustic is automatically added to maintain a constant level of caustic in the treating zone.

Still another object of this invention is to provide an improved method of washing a gasoline fraction with an aqueous sodium hydroxide solution whereby the wash solution is automatically discharged when its pH reaches a predetermined value and the level of wash solution in the treating zone is maintained constant by automatically adding fresh sodium hydroxide solution to replace the spent wash solution discharged.

Another and further object of this invention is to provide an improved apparatus for treating hydrocarbon materials containing acidic impurities with alkaline reagents.

These and other objects will be apparent from the following description of this invention.

In accordance with the present invention, it has been found that a considerable amount of alkaline treating reagents can be conserved in a process for the treatment of hydrocarbon materials containing acidic impurities with alkaline reagents by automatically discharging the alkaline reagent from the treating system when it has reached a pH value at which the solution is completely spent and is no longer effective in the removal of acidic materials, and automatically replacing the alkaline reagent discharged by adding sufficient fresh alkaline reagent to the treating system to maintain a predetermined height of treating solution in the system. In a preferred embodiment of this invention, the automatic discharge and replacement of alkaline treating solution is accomplished by providing a countercurrent caustic washing tower with a caustic discharge valve operated by a pH controller set to discharge treating solution when it has reached a predetermined pH value and an alkaline reagent feed valve operated by a liquid level controller set to admit alkaline reagent when the interface between the treating solution and the petroleum fraction being treating drops below a predetermined level.

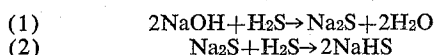
The novelty and utility of the present invention is further illustrated in the accompanying drawings wherein Figure 1 is a diagrammatic flow sheet illustrating a specific embodiment of the present invention. In the interest of simplicity, the following description of Figure 1 will

be limited to the treatment of a petroleum fraction boiling in the gasoline range with an aqueous caustic solution. Further, in the interest of simplicity, valves, pumps, and other conventional equipment familiar to one skilled in the art have been omitted from the flow sheet illustrated in Figure 1.

Figure 2 is a graphical representation of the manner in which the pH value of an aqueous sodium hydroxide solution can be expected to change as hydrogen sulfide is extracted from a petroleum fraction with a 0.1 normal solution of sodium hydroxide.

In accordance with Figure 1, a petroleum fraction boiling in the gasoline range is fed to a vertical tower 10 having a packed section 13, filled with conventional packing materials, such as Raschig rings, through line 16 at a point below packed section 13. The gasoline being treated passes upwardly through column 10 and is discharged through line 19 located at the top of tower 10. An aqueous caustic solution is fed to column 10 at a point just above packed section 13 through caustic charge line 22. The caustic solution passes downwardly through column 10, countercurrent to the flow of gasoline through the tower, and is discharged through draw-off line 25 located at the bottom of tower 10. Control valve 28 located on caustic charge line 22 is opened and closed in response to liquid level controller 31, which in turn is operated by liquid level sensing element 34, located in liquid level float case 35, at the interface between gasoline and the caustic treating solution. Control valve 37 located on caustic draw-off line 25 is opened and closed in response to pH controller 40, which in turn is operated by pH sensing element 43 located in the bottom of tower 10. In operation, fresh caustic solution is charged to tower 10 through line 22 and passes countercurrently to a gasoline fraction admitted through line 16. When the caustic treating solution at the bottom of tower 10 has attained a pH value below which its ability to remove acidic impurities from the gasoline is practically nil, pH controller 40 will open valve 37, discharging the spent caustic through line 25. At the same time, as the level of caustic solution in tower 10 begins to drop due to the discharge of spent caustic, liquid level controller 31 will open valve 28, thereby admitting fresh caustic to replace the spent caustic discharged.

Figure 2 illustrates the manner in which the pH value of a caustic treating solution would be expected to change as hydrogen sulfide is extracted from a petroleum fraction in accordance with the following reactions:



Although a 0.1 normal solution of sodium hydroxide might not be sufficiently strong to extract acidic materials from a gasoline fraction, this normality was chosen in order to simplify the calculations involved. However, it is to be observed that the same net result would be obtained with a more concentrated solution of sodium hydroxide.

Referring to Figure 2 and the equations shown above, point 1 represents the pH of the original NaOH solution, which in this case is 13.0. When one-half mol of hydrogen sulfide had been extracted for each mol of original sodium hydroxide, in accordance with Equation 1, the sulfur would be substantially all in the form of sodium sulfide and the solution would have a pH very slightly below 13.0, as represented by point 2 on Figure 2. At this point in the extraction, the solution, being still highly alkaline, would continue to take up hydrogen sulfide in accordance with Equation 2 until one mol of hydrogen sulfide had been extracted for each mol of the original sodium hydroxide. When this point in the extraction has been reached, the sulfur would be in the form of sodium hydrosulfide and the pH of the solution would be 10.98, is illustrated by point 3 on the graph. With continued addition of hydrogen sulfide, the solution pH would drop

very rapidly to point 4 where the pH value is approximately 9.0. A pH controller adjusted to discharge solution having a pH of 9.0 or below would insure practically complete utilization of the solution's capacity to extract hydrogen sulfide in this system. In addition, in a tower of sufficient height and with a gasoline velocity not too great, the presence of fresh caustic solution in the upper part of the tower will insure the complete removal of hydrogen sulfide.

In the operation of the present invention, any of the well known alkaline washing agents, such as sodium hydroxide, potassium hydroxide, sodium carbonate, etc., may be used. However, it is preferred to use a sodium hydroxide solution having a strength of about 10° to 20° Bé. However, concentrations as low as 0.3 per cent sodium hydroxide (2° Bé.) or as high as 30 per cent sodium hydroxide (35° Bé.) may be used, depending upon the type of petroleum fraction being treated.

The operating temperatures of the instant process are well known in the art of treating hydrocarbon materials with alkaline solutions. Normally, the lower limit of temperatures is dictated by the temperatures at which caustic solution will remain sufficiently fluid to accomplish adequate scrubbing of the petroleum product, and the upper limit of temperatures is dictated by the vapor pressure of the liquids involved and the type of equipment employed. Under ordinary climatic conditions, temperatures in the range of about 70° F. to 90° F. will be used. However, temperatures both above and below this range may be used, depending upon seasonal changes and climatic conditions. In some cases, it may be desirable to employ hot caustic solutions at temperatures considerably above the range indicated. The present invention would also be applicable to these higher temperatures.

Control of the level of alkaline solution and admission of fresh alkaline solution may be accomplished by the use of any one of a large number of commercially available liquid level controllers capable of responding to variations in the height of the interface between the alkaline solution and the petroleum fraction being treated. In its simplest form the liquid level controller would be a common float having its float arm directly connected to a suitable valve.

There are also a number of pH controllers on the market which are capable of responding to pH changes in the range existing within the treating system of the present invention. In order to accomplish the best possible control of the discharge of spent alkaline solution, a pH controller having a pH range of about 6 to 13 is preferred. Commercial pH controllers suitable for operation in this range, normally have a Calomel reference electrode and a glass sensing electrode, and are equipped with a temperature compensator and an electronic amplifier to which an electrically operated valve may be connected.

Although the present invention has been illustrated by examples wherein a gasoline fraction is treated, it is universally applicable to the purification of any other hydrocarbon material containing acidic materials, such as hydrocarbon gases containing hydrogen sulfide, etc. Therefore, the present invention is not to be considered as limited by any of the examples described herein, which are given by way of illustration only, but is to be limited solely by the terms of the appended claims.

We claim:

1. A continuous non-regenerative process for removing hydrogen sulfide, mercaptans and other weakly acidic compounds from a light petroleum fraction boiling within the gasoline boiling range which comprises maintaining an elongated column of aqueous caustic soda solution, containing from 0.3 to 30% by weight of sodium hydroxide, in a contact tower, feeding the light petroleum fraction to be treated into contact with said solution at the lower portion of said column and passing the fraction upwardly through said column, continuously electrometrically determining the change in hydrogen ion concentration of said

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solution adjacent the locus where the petroleum fraction is fed into contact with said solution, automatically withdrawing spent solution from the bottom of said body when the pH of said solution adjacent the aforesaid locus is about 9 and stopping withdrawal thereof when pH rises above about 9, maintaining an interface at the top of said column between said solution and said fraction, continuously withdrawing treated fraction from the top of said tower and automatically introducing fresh caustic soda solution into the upper portion of said tower when the said interface is lowered as a result of withdrawal of spent solution, whereby to increase the pH value of said solution and automatically stop withdrawal thereof.

2. An apparatus for countercurrently contacting a light hydrocarbon distillate containing hydrogen sulfide, mercaptans and other weakly acidic constituents with an aqueous caustic alkali solution wherein said alkali reacts with said acidic constituents to produce difficulty hydrolyzable reaction products, which comprises in combination, an elongated vertical contacting tower, a distillate inlet means positioned adjacent the bottom of said tower, an alkali solution inlet means disposed adjacent the top of said tower, an intermediate contacting section containing therein a plurality of means for increasing the liquid-liquid contacting area of said section, a means for discharging said hydrocarbon distillate from the top of

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said tower, a means for discharging alkali solution from the bottom of said tower, a first flow controller interconnected to said alkali solution inlet means, a liquid level controller operatively connected to the top section of said tower and cooperating with said first flow controller to control the top level of said solution and the flow of alkali solution through said alkali inlet means, a second flow controller connected to said alkali discharge means, a pH meter operatively connected to open and close said second flow controller in accordance with a predetermined pH of said solution adjacent said distillate inlet means, whereby said liquid level controller functions to open and close said first flow controller in fixed relation to the opening and closing of said second flow controller.

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