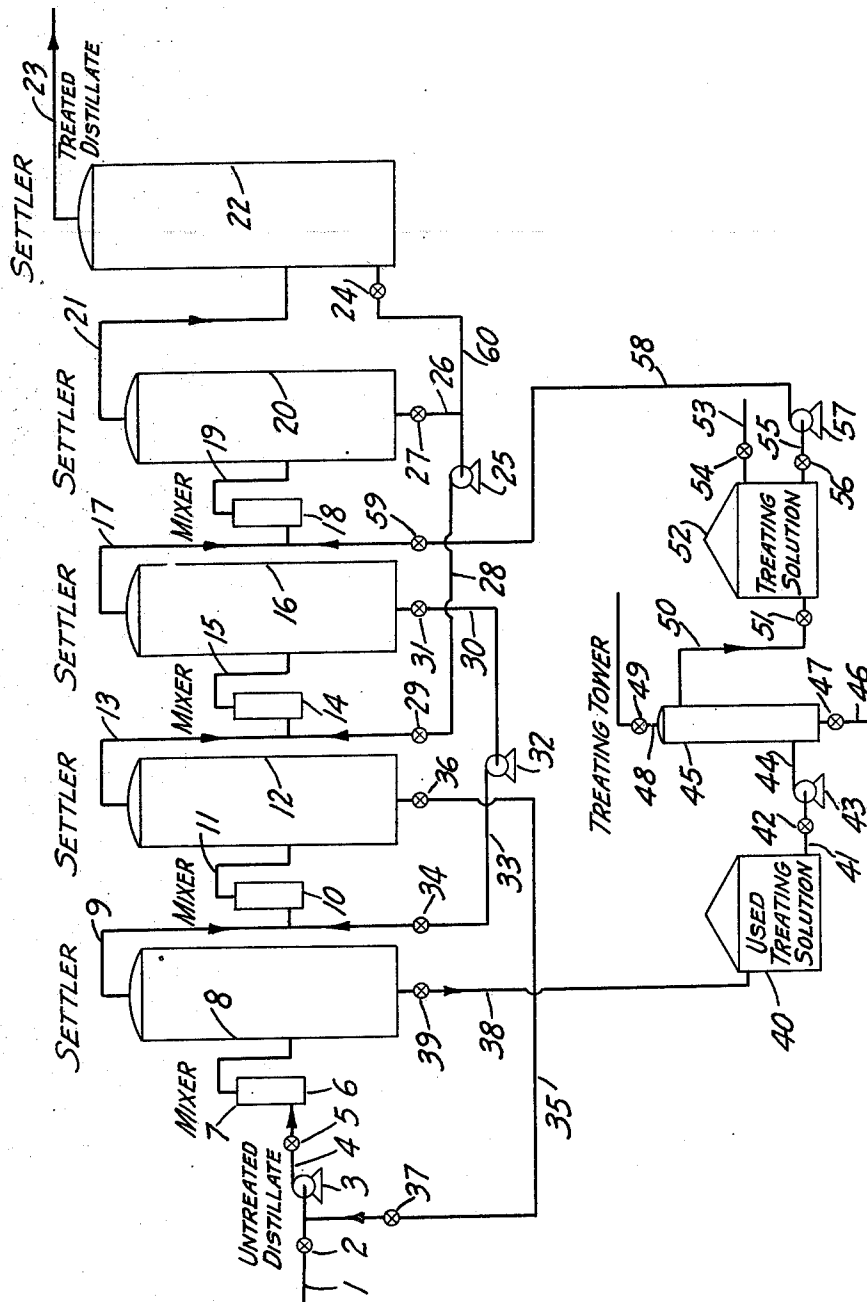


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PROCESS OF REFINING GASOLINE CONTAINING MERCAPTANS

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This invention pertains to the removal of sulphur compounds from hydrocarbon oils. More specifically, it pertains to the removal of hydrogen sulphide, mercaptans, and other similar sulphur compounds which are contained in petroleum distillates produced by distillation or cracking of hydrocarbon oils.

The benefits obtained by washing untreated cracked gasoline stocks or other petroleum oil distillates for the removal of hydrogen sulphide and mercaptans with solutions of alkali hydroxide are generally known in the art, by means of which hydrogen sulphide can be completely separated from the oil. However, by such treatments the mercaptans can be only partially removed, the percent removal depending upon the relative solubility or affinity of the mercaptans to remain with the oil in relationship to their solubility in the wash liquor or alkali solution employed. Various degrees of removal of mercaptans from an average cracked distillate can be obtained up to about 75% by varying the concentration of the alkali wash, the quantity of wash used, and the method of applying the wash by continuous counter-current extraction or batch operation processes.

It is also known in the art that alkali hydroxide solutions will remove acidic compounds, such as the so-called petroleum or naphthenic acids usually contained in asphalt base petroleum oils, such as the distillates derived from California crude petroleum oils, and also compounds of a phenolic nature. A mixture of these naphthenic and phenolic hydrocarbons, dissolved in alkali liquor, is readily recovered by blowing the spent alkali liquor with carbon dioxide and/or neutralizing with acid, and thereafter separating the oily layer which rises to the top of the liquor.

Heretofore, alkali washes, such as a water solution of sodium hydroxide, have been used principally for hydrogen sulphide removal, because the number of alkali washes necessary for a partial removal of the mercaptans is so great that other methods of treatment have been considered more economical. Regeneration of the spent alkali wash has been developed to reduce the cost of treating with alkali hydroxide solutions, but due to the fact that such treatments will not remove all of the mercaptans, the commercial development thereof has been retarded.

For example, when a four stage counter-current treatment is employed, and cracked gasoline stock is washed with 25% of its volume of caustic soda solution, containing 165 grams of sodium hydroxide per liter of solution, the mer-

captan removal amounts to only 65-75% of the total mercaptans contained in the cracked gasoline before treatment. With such a treatment, approximately 14.5 pounds of caustic soda per barrel of gasoline are used, and from an economical point of view, it is necessary to recover a high percentage of the caustic soda to commercially compete with other known processes. Furthermore, since the gasoline after treatment with caustic soda solution must be further treated to remove the remaining mercaptans or convert them to sulphur compounds that are not corrosive to obtain a sweet product, as is done by the known treatment with sodium plumbite solution, such an operation is not always commercially profitable to the petroleum refiner. However, since the caustic soda treatment removes the major portion of the mercaptans and other sulphur compounds from the gasoline stock, whereas the conventional methods of sweetening with sodium plumbite solutions have no marked effect in the reduction of the sulphur content of the oil being treated, the former treatment would be preferred if the cost of the treatment does not substantially exceed the cost of the later sodium plumbite treatment. Consequently, any means of increasing the amount of sulphur which is removed from the gasoline is advantageous.

Now I have discovered that a more efficient removal of the mercaptans from hydrocarbons or cracked gasoline stock can be obtained by extraction or contacting such stock with a water or alcohol water solution of an alkali hydroxide to which petroleum or naphthenic acids and/or petroleum phenolic compounds have been added. I have discovered that the ability of such solutions to remove mercaptans improves as the concentration of the alkali hydroxide and petroleum acids and/or petroleum phenolic bodies increases.

I have further discovered that the treating solution, after use and separation from the treated oil stock, can be repeatedly revived for reuse by blowing with air or other oxygen containing gas, whereby the mercaptans which have been removed from the oil stock are converted to disulphides and can be separated from the solution by decantation, distillation or extraction.

An object of the invention is to produce a treating agent that will substantially completely extract all the mercaptans from an average cracked distillate by a plurality of counter-current contacts therewith.

Another object of the invention is to extract mercaptans and hydrogen sulphide from petro-

leum oil products by substantially complete solution thereof in a treating agent capable of being recovered for reuse.

Another object of the invention is to effect substantially complete separation of corrosive constituents from petroleum oil products without the use of oxidizing agents on the oil stock treated.

Various other objects and advantages of the present invention will be apparent from the description of the preferred method or example of the process for extracting sulphur compounds from hydrocarbon oils, embodying the invention. For this purpose, reference is made to the accompanying drawing, in which there is illustrated one form of apparatus in which the invention may be performed. The drawing represents a diagrammatical view of the apparatus, in which the parts are in vertical section.

In the drawing, 1 represents generally a pipe for conveying the hydrocarbon oil or distillate to be treated from a source of supply to pump 3, controlled by valve 2. Pipe 4, controlled by valve 5, connects the discharge side of pump 3 to mixer 6 near the bottom. Pipe 7 connects mixer 6 at the top to settling tank 8 near the center section thereof. Pipe 9 connects settling tank 8 at the top to mixer 10. Pipe 11 connects mixer 10 at the top to settling tank 12 near the center section. Pipe 13 connects settling tank 12 at the top to mixer 14. Pipe 15 connects mixer 14 at the top to the center section of settling tank 16. Pipe 17 connects settling tank 16 at the top to mixer 18. Pipe 19 connects mixer 18 at the top to the middle section of settling tank 20. Pipe 21 connects settling tank 20 at the top to the middle section of settling tank 22. Pipe 23 connects settling tank 22 at the top to a storage tank not shown.

Pipe 60, controlled by valve 24, connects settling tank 22 at the bottom to the inlet of pump 25. Pipe 26, controlled by valve 27, connects settling tank 20 at the bottom to pipe 60. Pipe 28, controlled by valve 29, connects the discharge side of pump 25 to pipe 13. Pipe 30, controlled by valve 31, connects settling tank 16 at the bottom to pump 32. Pipe 33, controlled by valve 34, connects the discharge side of pump 32 to pipe 9. Pipe 35, controlled by valves 36 and 37, connects settling tank 12 at the bottom to pipe 1.

Pipe 38, controlled by valve 39, connects settling tank 8 at the bottom to used treating solution tank 40. Pipe 41, controlled by valve 42, connects used treating solution tank 40 near the bottom to the inlet side of pump 43. Pipe 44 connects the discharge side of pump 43 to the lower section of treating tower 45. Pipe 46, controlled by valve 47, connects treating tower 45 at the bottom to a source of compressed air. Pipe 48, controlled by valve 49, connects treating tower 45 at the top to the atmosphere.

Pipe 50, controlled by valve 51, connects the top section of treating tower 45 to treating solution tank 52. Pipe 53, controlled by valve 54, connects treating solution tank 52 to a source of treating solution. Pipe 55, controlled by valve 56, connects treating solution tank 52 near the bottom to the inlet of pump 57. Pipe 58, controlled by valve 59, connects the discharge side of pump 57 to pipe 17.

The preferred operation of the counterflow treating apparatus just described is as follows:

Tank 52 is filled with the treating solution to be used by opening valve 54 in pipe 53, which is connected to a source of supply not shown. The

treating solution is prepared by dissolving phenolic and other acidic oils, which have been extracted from asphalt base petroleum oils, in a water solution of potassium or sodium hydroxide. Preferably, a solution containing approximately 485 grams of sodium hydroxide per liter of water is used, to which is added one volume of the petroleum acidic and phenolic oils or naphthenic acid products per volume of sodium hydroxide solution. Preferably, the phenolic and other acidic oils are obtained by extracting cracked naphtha derived from asphalt or mixed base petroleum oil with a water solution of sodium or potassium hydroxide.

Untreated, hydrogen sulphide-mercaptan-containing distillate, such as cracked gasoline or naphtha stock, is caused to flow through pipe 1 and into the inlet side of pump 3, the rate of flow being governed by operation of valve 2. At the same time a regulated flow of the treating solution from settler 12 passes through pipe 35, controlled by valves 36 and 37, and is mixed therein with the distillate under treatment in pipe 1. From pipe 1 the mixed distillate and solution passes through pump 3, pipe 4, valve 5, mixer 6, pipe 7, and then into settler 8, during the passage of which the said distillate and solution are thoroughly commingled, with the extraction of the hydrogen sulphide and a portion of the mercaptan content of the distillate by the solution.

In settler 8 the once treated distillate separates from the solution and passes therefrom through pipe 9 and into mixer 10 for the second stage treatment, while the spent solution passes continuously from the bottom of settler 8 through pipe 38, controlled by valve 39, and collects in used treating solution tank 40. In mixer 10 the once treated distillate is mixed with the treating solution coming from settler 16 through pipe 30, pump 32 and pipe 33, controlled by valves 31 and 34. From mixer 10 the commingled solution and distillate passes through pipe 11 into settler 12, wherein the twice treated distillate separates from the solution and passes through pipe 13 into mixer 14, and is therein again mixed with solution coming from the bottom of settler 20 through pipe 26, pump 25 and pipe 28, controlled by valves 27 and 29.

From mixer 14 the commingled solution and distillate passes through pipe 15 and into settler 16, wherein the thrice treated distillate separates from the solution and passes through pipe 17 into mixer 18. In mixer 18 the thrice treated distillate is mixed with fresh or regenerated solution, coming from treating solution tank 52 through pipe 55, pump 57 and pipe 58, controlled by valves 56 and 59. From mixer 18 the commingled solution and distillate passes through pipe 19 and into settler 20, wherein the treated distillate, now substantially free of mercaptans and hydrogen sulphide, separates from the once used treating solution, the treated distillate passing from settler 20 through pipe 21 and into settler 22. From settler 22 the treated distillate passes through pipe 23 to a storage not shown, and any treating solution that separates in settler 22 may be returned to the system through pipe 60, which is connected to pump 25, controlled by valve 24.

The spent treating solution which collects in tank 40 is continuously revived for reuse by blowing with air at temperatures which may range from about 70 to as high as 200° F. or a little higher, which converts the dissolved mercaptides into disulphides, which are separated partly

by vaporization along with the air, and the remainder by separation and withdrawal from the revived solution through a swing pipe attached to the suction side of a pump not shown. This revivification operation is carried out by causing a regulated flow of the used treating solution to pass from tank 40 through pipe 41, valve 42, pump 43, pipe 44, and into the lower section of treating tower 45. A stream of air or heated air is continuously introduced into the lower section of tower 45 through pipe 46, controlled by valve 47, which converts the mercaptides into disulphides. The air and products of vaporization, including the lower boiling disulphides, pass out of tower 45 through pipe 48, controlled by valve 49. If desired, a superatmospheric pressure may be maintained on tower 45. The revived solution, containing unvaporized disulphides, passes from treating tower 45 through pipe 50, controlled by valve 51, into treating solution tank 52, wherein the unvaporized disulphides collect, forming a top layer which may be removed at intervals, as heretofore described.

While the process herein described is well adapted for carrying out the objects of the present invention, various modifications and changes

may be made without departing from the spirit of the invention, such, for example, as the use of any of the known mechanical mixers and centrifugal separating devices, and the invention includes all such modifications as appear within the scope of the appended claims. 5

I claim:

1. In the process of refining gasoline containing mercaptans to substantially completely remove the mercaptans without conversion to disulphides, the improvement which comprises, commingling the gasoline with a treating solution consisting of a water solution of sodium hydroxide containing alcohol and approximately 50% by volume petroleum naphthenic acid products dissolved therein, and then separating purified gasoline substantially free of mercaptans from the treating solution containing the mercaptans dissolved therein as mercaptides. 10 15

2. A solvent to substantially completely remove mercaptans from mercaptan containing gasoline stock which comprises, a water solution of sodium hydroxide containing alcohol and approximately 50% by volume added petroleum acids dissolved therein. 20 25

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