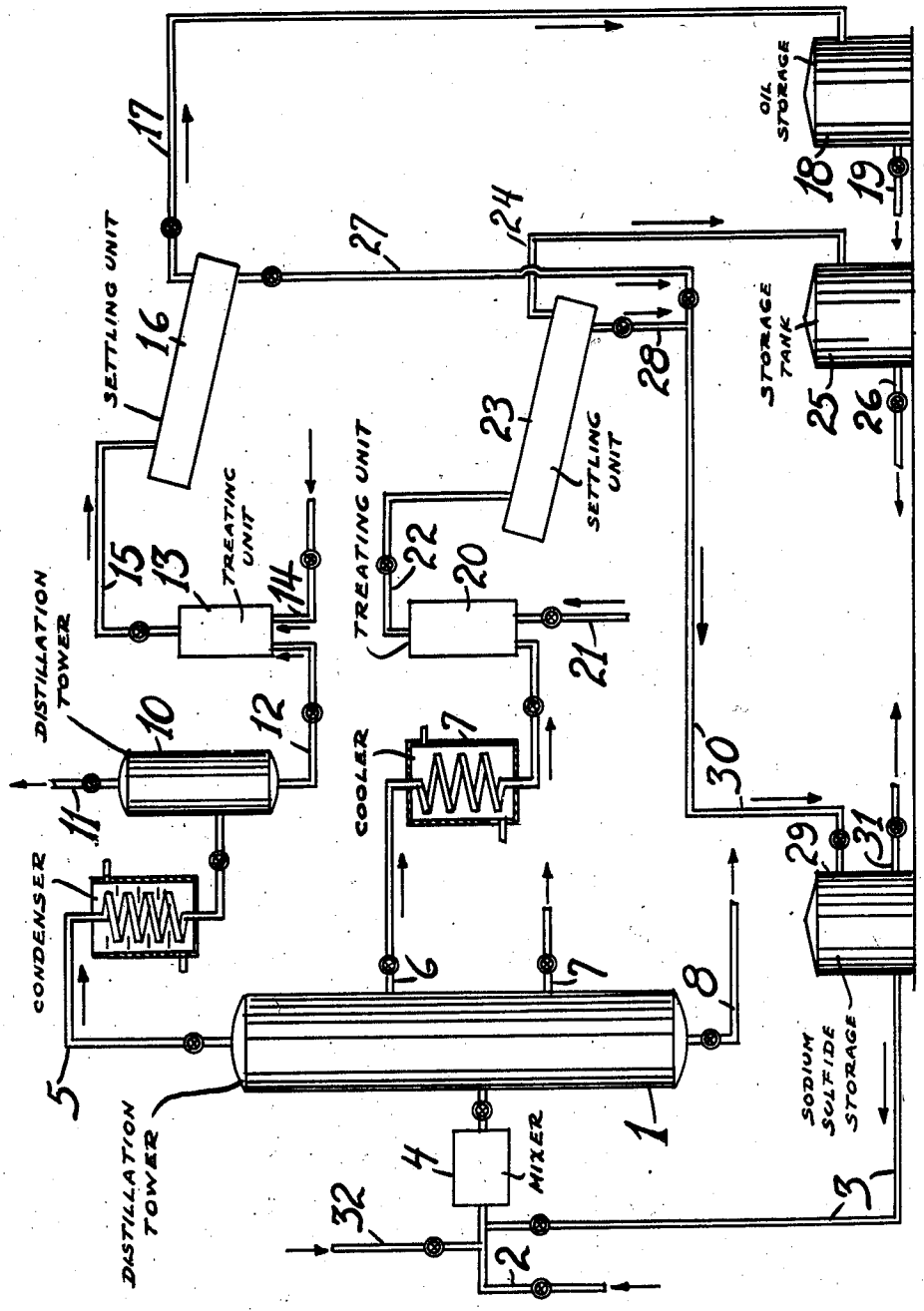
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PROCESS FOR THE DISTILLATION OF OIL CONTAINING SALTS OF HYDROCHLORIC ACID

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PROCESS FOR THE DISTILLATION OF OIL CONTAINING SALTS OF HYDROCHLORIC ACID

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The present invention relates to the refining of mineral oils. The invention is more particularly concerned with a method for the prevention of corrosion of the refining equipment. In accordance with the present process, petroleum oils which tend to cause excessive corrosion are distilled in the presence of a reagent which serves to substantially completely eliminate prohibitive corrosion of the equipment. A special modification of the invention is directed to an improved process for the production of hydrogen sulfide-free petroleum oils boiling in the motor fuel boiling range from petroleum crude oils containing acid-forming constituents. In accordance with the present process, petroleum oils containing acid-forming constituents are distilled in the presence of a sulfide selected from the class of sulfides which are characterized by the fact that they form stable salts which do not decompose under distillation conditions into harmful acidic substances.

It is known in the art that various petroleum crude oils contain appreciable amounts of constituents which, upon distillation of the oil, form corrosive acids which materially decrease the life of the distillation and related equipment, resulting in a substantial increase in operating costs. Particularly harmful acidic-forming constituents contained in unrefined petroleum oils are relatively unstable salts of hydrochloric acid, as for example, magnesium, calcium and iron chloride which hydrolize to form free hydrochloric acid. Thus numerous suggestions have been made that various reagents be added to petroleum oils prior to distilling the same in order to prevent the formation of or to neutralize free acids which may be formed. Substances which have been employed for this purpose are, for example, aqueous solutions of sodium hydroxide and sodium carbonate. These materials due in part to their cost are not entirely satisfactory. Furthermore, sodium hydroxide under distillation conditions tends to fuse on the metallic surfaces of the shell and on the various metallic distributing, heating and cooling means. This decreases the life of the equipment, lowers heat transfer rates, increases operating difficulties and thus further substantially raises the cost of the overall operations.

I have now discovered a process by which it is possible to efficiently and economically distill petroleum oils containing acid-forming constituents utilizing a reagent which will substantially entirely prevent corrosion of the equipment and which will not fuse with the metallic surfaces of the same. My process comprises distilling mineral oils which tend to cause excessive corrosion of the distillation and related equipment in the presence of a sulfide selected from the class of sulfides which are characterized by the fact that they form salts which are entirely substantially stable under the temperature and pressure conditions prevailing in the distillation operation. Substances of this type are, for example, ammonium sulfide, sodium sulfide and potassium sulfide. A preferred modification of my invention comprises a novel sequence and arrangement of stages which is particularly adapted for the production of a refined hydrogen sulfide-free petroleum oil boiling in the motor fuel boiling range from an unrefined petroleum oil containing sulfur compounds and acidic forming materials as for example, relatively unstable salts of hydrochloric acid such as magesium chloride, calcium chloride and iron chloride. In accordance with my preferred adaptation of the invention, these unrefined crude oils are distilled in the presence of sodium sulfide solutions which are secured in the removal of hydrogen sulfide from the lower boiling constituents of said crude oils by treating said lower boiling constituents with a sodium hydroxide solution. The lower boiling constituents preferably boil in the motor fuel boiling range.

My process may be readily understood by reference to the attached drawing illustrating modifications of the same. For purposes of description it is assumed that the feed oil is an unrefined petroleum oil containing appreciable quantities of acidic forming substances such as magnesium and calcium chloride. The feed oil is introduced into distillation tower 1 by means of feed line 2. Prior to introducing the feed oil into distillation tower 1 it is mixed with a sulfide solution which is introduced into feed line 2 by means of line 3. For purposes of description it is assumed the sulfide solution is an aqueous sodium sulfide solution. Efficient mixing of the feed oil and reagent is secured by means of mixer 4. Temperature and pressure conditions are maintained in distillation tower 1 adapted to remove overhead by means of line 5 lower boiling hydrocarbon fractions preferably boiling in the motor fuel boiling range. Under certain conditions it may be desirable to withdraw as a side stream by means of line 6 a relatively high boiling fraction of hydrocarbons boiling substantially in the motor fuel boiling range. If this operation be employed the boiling range of this stream will be from about 250° to 420° F. Intermediate and higher boiling range streams, as for example gas oil fractions and reduced crude fractions are withdrawal by means of lines 7 and 8 respectively. The gas oil and reduced crude streams may be handled in any manner desirable. Generally they are processed by various cracking operations for the production of cracked motor fuels, heating oils and the like. The cracked products are then refined by various refining operations such as debutanization, stabilization, acid treating and the like in order to produce finished prod-

ucts. The distillate fraction removed overhead from distillation tower 1 by means of line 5 is condensed in condenser 9 and passed to distillate drum 10. Uncondensed and fixed gases are removed from distillate drum 10 by means of line 11 and handled in any desired manner. These gases may be processed for the recovery of valuable hydrocarbons which may be included in motor fuels or may be passed to a burning line. The condensed distillate containing various sulfur compounds, as for example hydrogen sulfide, is removed from distillate drum 10 by means of line 12, and passed through treating plant 13, in which it is contacted with an alkaline solution preferably a solution of sodium hydroxide. Treating plant 13 may comprise any number of stages arranged in any desirable manner. The sodium hydroxide solution is introduced into treating plant 13 by means of line 14. The mixture is withdrawn from treating plant 13 by means of line 15 and passed to settling unit 16, in which the spent sodium hydroxide solution comprising a sodium sulfide solution substantially free of sodium hydroxide separates from the treated oil. Hydrogen sulfide-free oil is withdrawn from settling unit 16 by means of line 17 and passed into storage tank 18. The oil is withdrawn from storage tank 18 by means of line 19 and handled in any manner desirable. Generally the oil is sweetened and blended into a finished refined product. If the operation be conducted under conditions to remove a relatively higher boiling fraction of hydrocarbons boiling in the motor fuel boiling range by means of line 6 this fraction is cooled in cooler 7 and passed to treating plant 20, which may comprise any suitable number of units arranged in any desirable manner. This oil in treating plant 20 is thoroughly contacted with an alkaline solution preferably with a sodium hydroxide solution which is introduced by means of line 21. The mixture is withdrawn from treating unit 20 by means of line 22 and passed to settling drum 23 from which a hydrogen sulfide-free oil is withdrawn by means of line 24 and passed to storage tank 25. The oil withdrawn from tank 25 by means of line 26 may be acid treated or reformed or further processed in any manner desired. The spent sodium hydroxide solution comprising sodium sulfide and substantially free of sodium hydroxide is withdrawn from settling drums 16 and 23 by means of lines 27 and 28 respectively. These solutions are passed into sodium sulfide storage 29 by means of line 30 from which it is withdrawn by means of line 3 and introduced into the unrefined feed oil. Excess solution may be withdrawn from storage tank 29 by means of line 31 and disposed of as desired. Under certain conditions it may be desirable to utilize or to employ in part, a sodium sulfide not produced in the manner described in which case the solution is introduced into the feed oil by means of line 32.

The present invention may be widely varied. The process may be applied to any distillation operation utilized in the refining of mineral oils containing sulfur and acid forming compounds. The process, however, is particularly adapted for the production of hydrogen sulfide-free refined oil produces boiling in the motor fuel boiling range from sulfur-containing crude oils which also contain acid-forming salts, such as magnesium chloride and calcium chloride. Although any sulfide which has the ability to prevent the formation of or to neutralize the free acids formed may be used. I have found that the preferred sulfides are the alkali metal sulfides particularly sodium sulfide.

The amount of the sulfide added to the unrefined oil will be a function to a large extent of the characteristic of the unrefined oil and of the particular sulfide employed. The quantity added should be at least sufficient to completely neutralize the acid-forming constituents present. In general, it is preferred that the quantity added should be several times the amount equivalent to secure theoretical complete neutralization. The concentration of the sulfide solutions may also vary considerably depending upon the various factors. For example, when employing spent sodium hydroxide solution the concentrations will vary depending upon the relative proportions of sodium sulfide and sodium hydrogen sulfide present. We have found, for example, that sodium sulfide solutions comprising from 0.01 lb. to 0.1 lb. of sodium sulfide and from 0.1 to 0.5 lb. of sodium hydrogen sulfide per gallon are very satisfactory. When employing the preferred modification of the invention in order to secure the desired concentration of sodium sulfide and sodium hydrogen sulfide and to substantially completely eliminate free sodium hydroxide, the spent sodium hydroxide solution may be processed or concentrated prior to introducing the same into the oil feed. The spent sodium hydroxide solution should comprise sodium sulfide and sodium acid sulfide and should preferably be substantially completely free of sodium hydroxide.

In order to further illustrate the invention, the following examples are given which should not be construed as limiting the invention in any manner whatsoever.

Example 1

Operations were conducted on West Texas crude oils and the quantities of hydrochloric acid evolved per unit quantity of oil determined. In one operation no sulfide was added to the oil. In a second operation a spent sodium hydroxide solution free of sodium hydroxide and secured from a plant operated for the removal of hydrogen sulfide from petroleum hydrocarbons boiling in the motor fuel boiling range was employed. In a third operation sodium sulfide was utilized. The amounts of the solutions utilized were controlled to theoretically neutralize 80% of the acidity. The quantities of acidic vapors evolved in the respective operations were as follows:

Operation	Feed stock	Relative amounts of hydrochloric acid evolved per barrel of oil taking operation 1 as 100
1	West Texas crude oil	100.0
2	West Texas crude oil plus spent sodium hydroxide solution.	25.8
3	West Texas crude oil plus sodium sulfide.	24.4

From the above it is to be noted that the sulfides were particularly effective and that by utilizing a somewhat greater quantity than the theoretical amount needed, substantially complete removal of the acidic constituents will be effected.

Example 2

In a commercial distillation operation when processing East Texas crude oil a visual inspection disclosed that considerable corrosion of the distillation equipment occurred. This corrosion was substantially completely prevented by employing a spent sodium hydroxide solution which was essentially free of sodium hydroxide and comprised about 0.1 lb. of sodium sulfide and about 0.1 lb. of sodium hydrogen sulfide per gallon.

What I claim as new and wish to protect by Letters Patent is:

1. Process for the distillation of petroleum oils containing salts of hydrochloric acid of the class consisting of magnesium chloride, calcium chloride and iron chloride comprising distilling said oils in the presence of a spent sodium hydroxide solution secured in the removal of hydrogen sulfide from petroleum oils said spent sodium hydroxide solution being substantially completely free of sodium hydroxide.

2. Process for the production of a hydrogen sulfide free refined petroleum oil boiling substantially in the motor fuel boiling range from an unrefined petroleum oil containing sulfur compounds and salts of hydrochloric acid selected from the class consisting of magnesium chloride, calcium chloride and iron chloride comprising distilling said unrefined petroleum oil in the presence of a spent alkali metal hydroxide solution secured in the removal of hydrogen sulfide from said refined petroleum oil derived from said unrefined petroleum oil, said spent alkali metal hydroxide solution being substantially completely free of alkali metal hydroxide constituents.

3. A process for the distillation of oil containing salts of hydrochloric acid of the class consisting of magnesium chloride, calcium chloride and iron chloride, comprising distilling said oil in the presence of an added solution containing a sulfide salt selected from the class consisting of sodium sulfide and potassium sulfide.

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