Oct. 27, 1942. M. C. K. JONES 2,300,158

REFINING MINERAL OIL

Filed Oct. 18, 1940 2 Sheets-Sheet 1

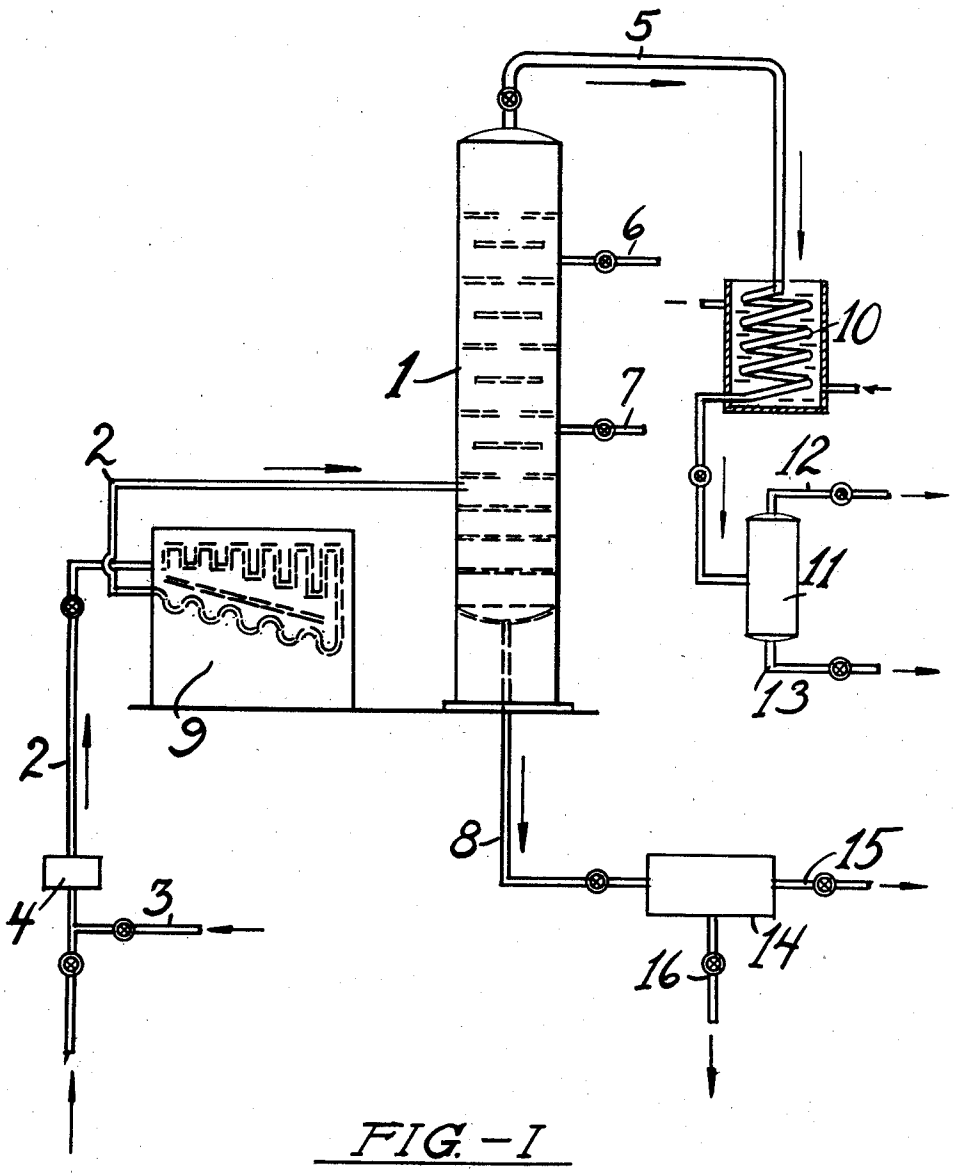


FIG. -1

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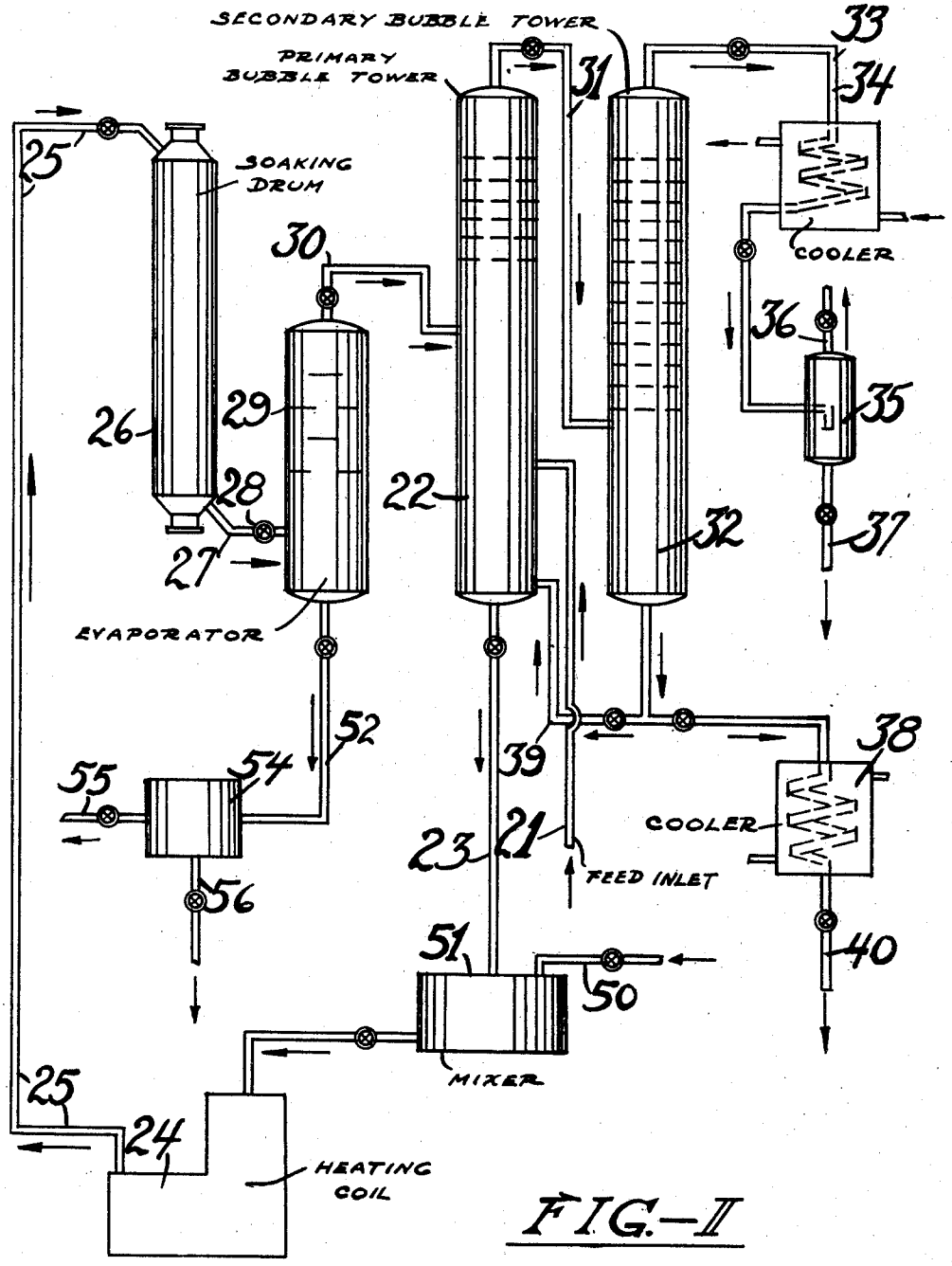


FIG.—II

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Patented Oct. 27, 1942

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UNITED STATES PATENT OFFICE

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REFINING MINERAL OIL

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9 Claims. (Cl. 196—35)

The present invention relates to the refining of mineral oils. The invention is more particularly concerned with an improved distillation operation in which deleterious corrosion of the refining equipment is substantially completely prevented. In accordance with the present process, petroleum oils which tend to cause excessive corrosion when distilled are distilled in the presence of a reagent which functions substantially completely to eliminate deterioration of the distillation equipment. A special modification of the invention is directed to an improved process for the production of substantially 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, feed petroleum oils containing acid-forming constituents are distilled in the presence of an alkali metal silicate which is characterized in that upon distillation a salt is formed which will 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 hydrolyze to form corrosive acids which react with and thus 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 petrolum oils are relatively unstable salts of hydrochloric acid, as for example, magnesium, calcium, and iron chlorides, which materials readily hydrolize under distillation conditions and form free hydrochloric acid. In order to overcome the resulting adverse results, suggestions have been made that various reagents be added to the feed petroleum oils prior to distilling the same which reagents act to prevent the formation of or to neutralize free acid which is formed. Substances which have been employed for this purpose are, for example, aqueous solutions of sodium hydroxide, sodium carbonate and the like. These substances are desirable since sodium chloride will not hydrolize under distillation conditions as is the case with magnesium chloride and calcium chloride.

It is known that sodium chloride does not hydrolize under distillation conditions as do magnesium and calcium chloride. These materials, however, due in part to their cost are not entirely satisfactory. Furthermore, sodium hydroxide under distillation conditions, particularly when relatively high temperatures are employed, tends to fuse on the metallic surfaces of the shell and on the various metallic distributing, heating, and cooling means. This materially decreases the life of the equipment, lowers heat transfer rates, increases operating difficulties and thus further substantially increases the cost of the over-all operation.

I have now discovered a process by which it is possible efficiently and economically to 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 an alkali metal silicate which is characterized in that a salt is formed which is entirely stable under the temperature and pressure conditions prevailing in the distillation operation. Substances of this class are, for example, potassium silicate and sodium silicate. By employing these substances which not only react and remove the hydrochloric acid but also function to prevent salts or carbonaceous material from adhering to metal tubes and surfaces an improved operation results.

My process may be readily understood by reference to the attached drawings illustrating modifications of the same. Referring specifically to Figure 1 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 passed through furnace 9 and introduced into topping still 1 by means of feed line 2. Prior to introducing the feed oil into topping still 1, it is mixed with a quantity of an alkali metal silicate which, for the purpose of description, is taken to be a sodium silicate. This material is introduced into feed line 2 by means of line 3 and the feed oil and reagent then passed through mixer 4. Temperature and pressure conditions are regulated in distillation tower 1 adapted to remove overhead by means of line 5 lower boiling hydrocarbon constituents which are condensed in condenser 10 and passed into separation zone 11. Uncondensed constituents are separated and removed by means of line 12 while the condensate is removed by means of line 13 and handled or further refined as desired. Under certain conditions it may be desirable to withdraw side streams by means of lines 6 and 7. These fractions may be further refined or handled in any desired manner. A bottoms stream comprising

the added reagent and the higher boiling constituents is withdrawn by means of line 8 and passed through filter 14, wherein the reagent is separated from the oil which is removed by means of line 15. The spent reagent is removed by means of line 16 and handled as desired.

Referring specifically to Figure 2, another modification of the present invention may be readily understood. My process as illustrated in this drawing is employed in conjunction with a typical reduced crude cracking operation. In this operation, the feed oil boiling in the range above about 500° F. to 700° F. is introduced by means of feed line 21 into the lower section of primary bubble tower 22. The feed oil, along with recycle oil is withdrawn from the bottom of primary bubble tower 22 by means of line 23 and introduced into heating coil or furnace 24 which is so designed as to secure optimum heat transfer rates and to raise the oil to the desired temperature and pressure. Prior to introducing the oil into heating coil 24 it is mixed with an amount of sodium silicate which is introduced by means of line 50. Complete mixing is secured by passing the sodium silicate and oil through mixer 51. The total feed along with the sodium silicate is passed through the tubes in the radiant and convection sections of furnace 24 in which the oil is raised to the desired cracking temperature. The heated oil is withdrawn from furnace 24 by means of line 25 and passed into soaking drum or reaction chamber 26 which, for the purposes of illustration is assumed to be a downflow type soaking drum. Reaction drum 26 is designed to permit maintaining the oil for an additional optimum time period under cracking conditions. The oil, along with the reagent, is withdrawn from reaction drum 26 by means of line 27 and passed through pressure release valve 28. The cracked products pass into evaporator 29 from the bottom of which tar or fuel oil of the desired gravity is removed. The flashed vapors pass overhead from evaporator 29 through line 30 and are introduced into the middle section of primary bubble tower 22. Cycle stock accumulates in the bottom of primary bubble tower 22 which is recycled with the fresh feed as described. Vapors pass overhead from bubble tower 22 by means of vapor line 31 and are introduced into a secondary bubble tower 32. The temperature maintained at the bottom of primary bubble tower 22 is usually adapted to secure the desired end point on the heating oil fraction which is withdrawn from the bottom of secondary bubble tower 32. The temperature at the top of secondary bubble tower 32 is controlled to produce an overhead distillate of the desired end point. This distillate is removed by means of line 33, condensed in cooler 34, and then passed into distillate drum 35. Uncondensed gases are removed from the top of distillate drum 35 by means of a line 36 and handled in any manner desirable, usually by passing to a high pressure burning line. The condensed distillate which usually comprises constituents boiling in the motor fuel boiling range is removed from distillate drum 35 by means of line 37, further stabilized and refined, and then blended to produce finished motor fuels. Higher boiling petroleum constituents, usually boiling in the heating oil boiling range, are removed from the bottom of secondary bubble tower 32, passed through cooler 38, and withdrawn from the system by means of line 40.

Tar or heavy fuel oil containing the reagent and the product of reaction with the hydrochloric acid evolved from hydrolyzable chlorides in the crude oil is removed from the bottom of evaporator 29 by means of line 52 and passed into separator 54 which may comprise any suitable number of units of any desired design in which reagent reaction product may be separated from the heavy fuel oil or tar fraction. The tar or fuel oil fraction is withdrawn from the system by means of line 55 and handled in any manner desired. The silicate reagent reaction product is withdrawn from separator 54 which may comprise a filter by means of line 56 and disposed of by suitable means.

The present invention may be widely varied. The process may be applied to any distillation operation employed in the refining of mineral oils containing sulfur and acid-forming compounds. The process, however, is particularly adapted for the production of refined oil products from sulfur-containing crude oils which contain acid-forming salts such as magnesium chloride and calcium chloride.

The invention essentially comprises adding an alkali silicate to the crude petroleum oil which is to be distilled. By the present process an alkali metal silicate preferably a sodium silicate, is injected with the crude petroleum which will react with the hydrogen chloride which is formed by the hydrolysis of magnesium and calcium chlorides under the conditions existing in distillation equipment. Sodium silicate of appropriate SiO_2 to Na_2O ratio may be added as a finely divided solid or as a water solution of appropriate gravity. The reaction which occurs is as follows:

$$Na_2Si_4O_9+HCl+H_2O \rightarrow NaCl+mSiO_2 \cdot nH_2O$$
$$Na_2Si_4O_9+HCl \rightarrow NaCl+SiO_2$$

The reaction of sodium silicate in the presence of water with hydrochloric acid from the hydrolyzable chlorides in the crude oil will yield silicic acid as a hydrogel, of the general formula $mSiO_2 \cdot nH_2O$. Upon heating, dehydration will occur with the formation of silicon dioxide. This material exerts an abrasive action, thereby keeping interior metal surfaces of distillation and cracking equipment clean and bright and free from carbon or salt deposits.

The amount of silicate added will depend on the character of the feed oil and the particular silicate added. In general, it is preferred to add about 100% to 200% of the silicate based upon the quantity of hydrolyzable chlorides, determined by analysis, in the feed oil. The silicate may be added in a finely divided form, or may be added in an aqueous solution. However, in general, it is preferred that the silicate be added as an oil slurry, particularly in order to expedite the ready introduction of the relatively small quantities required in relation to the oil fed for distillation.

Sodium silicate in excess of that which reacts with the hydrochloric acid formed may also be used to provide an adherent and chemically inactive film that renders the metallic equipment non-corrosive to acidic gases and promotes easy removal of materials tending to accumulate during the processing of the oil.

In order further to illustrate the invention, the following example is given which should not be construed as limiting the same in any manner whatsoever:

Example

A petroleum crude oil fed to a distillation unit and then to a reduced crude cracking unit contained 30 lbs. of hydrolyzable chlorides as equiv-

alent hydrochloric acid per thousand barrels of oil. This oil when distilled in a conventional manner results in excessive corrosion of the refining equipment. However, when the oil is distilled in the presence of about 250 lbs. of sodium silicate per thousand barrels of oil, at least 90% to 95% of the hydrochloric acid is neutralized and corrosion substantially completely prevented.

What I claim as novel 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 a feed petroleum oil in the presence of an alkali metal silicate uniformly distributed throughout the body of the oil.

2. Process in accordance with claim 1, in which said alkali metal silicate is sodium silicate.

3. Process for the refining of petroleum oils containing salts of hydrochloric acid of the class consisting of magnesium chloride, calcium chloride, and iron chloride, comprising refining the oils in the presence of a finely divided alkali metal silicate uniformly distributed throughout the body of the oil.

4. Process in accordance with claim 3, in which said alkaline metal silicate is sodium silicate.

5. Process in accordance with claim 3, in which said sodium silicate is added as an aqueous solution.

6. Process in accordance with claim 3, in which said sodium silicate is added as an oil slurry.

7. Process in accordance with claim 3, in which 100% to 200% of sodium silicate theoretically required to react with hydrolyzable chlorides present is added.

8. A process for the distillation of mineral oils containing acid forming constituents which comprises adding an alkali metal silicate to the oil in an initial stage, followed by distilling the oil in a secondary stage in the presence of said added alkali metal silicate uniformly distributed throughout the body of the oil.

9. Process as defined by claim 8 in which said alkali metal silicate comprises sodium silicate which is added to the feed oil as an oil slurry.

MINOR C. K. JONES.