This invention relates to a method for removing sulfur compounds from hydrocarbon oils. Hydrocarbon oils frequently contain various sulfur compounds, particularly mercaptans and disulfides. I have discovered that the various sulfur compounds present in hydrocarbon oils can be removed by treating the oil with alkali solution in the presence of an alloy of a metal which is readily attacked by aqueous alkali solution, and a metal which is capable of functioning as a hydrogenation catalyst.

An object of the invention is to provide a method for removing sulfur compounds from hydrocarbon oils.

Another object of the invention is to render hydrocarbon oils containing sulfur compounds sweet to the "doctor" test.

A further object of the invention is to convert sulfur compounds present in hydrocarbon oils to hydrocarbons.

Other objects of the invention will become manifest from the following description.

In accordance with my invention hydrocarbon oil, containing sulfur compounds, is contacted with aqueous alkali solution in the presence of an alloy of an element which is attacked by the alkali solution, and a metal which is capable of functioning as a hydrogenation catalyst. In the preparation of the alkali solution alkali metal hydroxides and/or carbonates may be used, as for example sodium or potassium hydroxide or carbonate, or mixtures thereof. I prefer to use alkali solutions at least equivalent in alkali concentration to 10% by weight sodium hydroxide solution.

As elements which are readily attacked by the alkali solution and which may be used in the alloy may be mentioned aluminum, silicon, beryllium and zinc. As metals which act as hydrogenation catalysts and which may be incorporated in the alloy may be mentioned copper and nickel. Alloys which are useful in carrying out my invention are disclosed in Patents Nos. 1,563,937, 1,629,130 and 1,915,743. An alloy of nickel and aluminum known as Raney nickel-aluminum alloy is particularly effective.

The alkali solution and alloy contacted with the hydrocarbon oil to be treated should be present in amounts sufficient to generate enough hydrogen to substantially remove the entire mercaptan content of the gasoline, and preferably in amount sufficient to remove substantially the entire sulfur content of the gasoline. In the reaction the alloy is attacked by the alkali with formation of hydrogen and an active hydrogenation catalyst. In the presence of the active hydrogenation catalyst the hydrogen converts sulfur compounds to hydrocarbons and hydrogen sulfide. The hydrogen sulfide is absorbed in the alkali solution, or may react with the nickel or other hydrogenation catalyst to form nickel sulfide. The completion of the treatment can be determined by subjecting the oil to the well-known "doctor" test with alkali plumbite solution and free sulfur.

The process may be carried out in any desired manner. One way of carrying out the process is to mix powdered alloy with hydrocarbon oil and alkali solution in an open or closed vessel, until the oil has been sufficiently treated. Another method of carrying out the process is to pass alkali solution and hydrocarbon oil through a tower packed with comminuted alloy and continuously re-circulate the oil and solution therethrough until the treatment is completed as determined by the "doctor" test. The oil and alkali may be passed through the packed tower concurrently or counter-currently to each other. The reaction proceeds at atmospheric temperature and may be conducted at either atmospheric or superatmospheric pressure. Superatmospheric pressure accelerates the reaction and therefore cuts down the amount of time required to effect removal of the sulfur compounds.

Instead of using only alkali such as nickel-aluminum alloy, in carrying out the process, a mixture of an element readily attacked by alkali solution such as aluminum and alloy such as an aluminum-nickel alloy may be used, with the aluminum being present in the major proportion. Only a small amount of nickel, approximately 1 to 5% by weight of the oil undergoing treatment, is necessary to catalyze the reaction. After active nickel is formed as a result of the solution of a part, or all of the aluminum with which the nickel is alloyed, the nickel will remain in a highly active state as long as it is kept in the presence of the alkali solution. Thus it is necessary only to have sufficient aluminum or other metal present to insure an adequate supply of hydrogen. Since aluminum is cheaper than the nickel-aluminum alloy, it is more economical to use a mixture of aluminum and nickel-aluminum alloy instead of only nickel-aluminum alloy.

The treatment can be carried out satisfactorily at temperatures ranging from atmospheric to the boiling temperature of the alkali solution, and proceeds rapidly at temperatures above 38° C.

In carrying out the treatment hydrogen may be formed at a faster rate than it is consumed.
in the reaction. The unconsumed hydrogen may be recirculated to the oil undergoing treatment and thereby decrease the amount of alkali and aluminum or other metal necessary for removal of the sulfur compounds.

In order to demonstrate the invention 350 cc. of gasoline having a mercaptan sulfur content of 0.09% by weight was exposed to high pressure thermal cracking of petroleum gas oil was stirred with 30 grams of powdered Raney nickel-aluminum alloy and 25 cc. of aqueous caustic soda containing 10% by weight of sodium hydroxide. Before adding the caustic soda the gasoline was stirred with the nickel-aluminum alloy for about 25 minutes to determine if the gasoline could be sweetened in this manner. At the end of 25 minutes the gasoline was tested but substantially no mercaptans had been removed. After addition of the 25 cc. of aqueous caustic soda solution the mixture was stirred for about 5 minutes longer, at which time the reaction subsided and upon testing the gasoline it was determined that 92% of the mercaptans had been removed. Thereupon, 25 cc. of additional 10% aqueous caustic soda solution was added and the mixture again stirred for about 5 minutes, and again tested for mercaptans. It was determined that 97% of the mercaptans had been removed.

An additional 30 cc. of 10% caustic soda solution was added and stirred with the oil and after the reaction subsided the gasoline was again tested and it was found that 98.5% of the mercaptans had been removed, and that the gasoline was "doctor" sweet.

The foregoing tests were all conducted in an open vessel at room temperature and atmospheric pressure. It will be seen, therefore, that I have discovered an effective method for removing sulfur compounds from gasoline and other hydrocarbon oils, and of rendering such oils "doctor" sweet.

It is claimed:

1. The method of removing sulfur compounds from hydrocarbon oil comprising contacting said oil with an aqueous solution of a compound selected from the group consisting of copper and nickel and an element selected from the group consisting of silicon, beryllium, aluminum and zinc.

2. Method in accordance with claim 1 in which the alloy comprises nickel and an element selected from the group consisting of aluminum, silicon, beryllium and zinc.

3. Method in accordance with claim 1 in which the alloy is composed of aluminum and nickel.

4. The method in accordance with claim 1 in which the oil is contacted with the said solution and alloy at a temperature above approximately 38°C.

5. The method of removing sulfur compounds from hydrocarbon oil comprising contacting said oil with aqueous solution of a compound selected from the group consisting of alkali metal hydroxides and carbonates in the presence of commingled nickel-aluminum alloy at a temperature above approximately 38°C, the amount of alkali and alloy and the time of contact being sufficient to convert substantially all sulfur compounds present in the oil to hydrocarbons.

6. The method of removing mercaptans from hydrocarbon oil comprising contacting said oil with aqueous alkali metal hydroxide solution in the presence of commingled aluminum and a hydrogenation catalyst which is initially an aluminum-nickel alloy.

7. The method of removing sulfur compounds from hydrocarbon oil comprising contacting said oil with aqueous solution of a compound selected from the group consisting of alkali metal hydroxides and carbonates in the presence of commingled nickel-aluminum alloy, at a temperature between atmospheric and the boiling point of said solution, the quantity and concentration of said solution and the quantity of alloy being sufficient to generate sufficient hydrogen to react with all the sulfur present and the time of contact being sufficiently long to lower the sulfur content the required amount.

8. Method in accordance with claim 7 in which is present a commingled element readily attacked by said solution with liberation of hydrogen.

9. Method in accordance with claim 1 in which the element is aluminum.

10. Method in accordance with claim 6 in which the element and aluminum alloy are mixed together with the aluminum being present in major proportion.

GEORGE W. AYERS.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

<table>
<thead>
<tr>
<th>Number</th>
<th>Name</th>
<th>Date</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,930,216</td>
<td>Weber</td>
<td>Oct. 10, 1933</td>
</tr>
<tr>
<td>2,037,790</td>
<td>Ipatieff (A)</td>
<td>Apr. 21, 1936</td>
</tr>
<tr>
<td>2,037,792</td>
<td>Ipatieff (B)</td>
<td>Apr. 21, 1936</td>
</tr>
<tr>
<td>2,037,789</td>
<td>Ipatieff (C)</td>
<td>Apr. 21, 1936</td>
</tr>
<tr>
<td>2,128,385</td>
<td>Carmody</td>
<td>Sept. 6, 1938</td>
</tr>
<tr>
<td>2,371,641</td>
<td>Mozingo (A)</td>
<td>Mar. 20, 1945</td>
</tr>
<tr>
<td>2,371,642</td>
<td>Mozingo (B)</td>
<td>Mar. 20, 1945</td>
</tr>
</tbody>
</table>