Patented Feb. 10, 1948 2,435,732

UNITED STATES PATENT OFFICE

2,435,732

REFINING HYDROCARBON LIQUIDS

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No Drawing. Application December 18, 1944, Serial No. 568,776

6 Claims. (Cl. 196—30)

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This invention relates to refining of hydrocarbon liquids and is particularly directed to the removal of corrosive sulfur from hydrocarbon oils.

Free sulfur is frequently found in various petroleum oils and fractitons such as, straight-run gasoline or naphtha, cracked gasoline, kerosene, gas oil, furnace oil, Diesel fuel and heavy fuel oil. In order to pass the copper dish corrosion test, it is necessary to remove the free sulfur from the oil. One of the best-known methods for removing free sulfur from hydrocarbon oils is the use of alkali solution of sodium sulfide. Although such solutions will often render a mildly corrosive oil non-corrosive, they will frequently not render badly corrosive oils non-corrosive.

The problem of corrosive oils has been particularly acute in connection with gasoline stocks made by the "Thermofor" catalytic cracking process.

We have discovered that corrosive oils can be made non-corrosive by treating such oils with alkali solutions of alkali metal stannite.

An object of this invention is to provide a method for removing free sulfur from hydrocarbon oil.

Another object of this invention is to provide a method for making corrosive hydrocarbon oils non-corrosive.

A further object of the invention is to provide a method for removing higher organic polysulfides from hydrocarbon liquids.

Still another object of the invention is to provide a method for regenerating spent alkali metal stannite solutions.

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

In accordance with our invention, hydrocarbon liquid to be treated is contacted with an aqueous solution of alkali, such as sodium or potassium hydroxide containing in solution alkali metal stannite, such as sodium or potassium stannite. Contact between the oil and the treating solution may be carried out in any conventional manner such as by batch agitation in a tank or continuous counter-current contact in a tower provided with contacting surfaces, such as bubble plates or Raschig rings. In carrying out the process, we prefer to use solutions containing not less than about 10% of alkali metal hydroxide and not less than approximately 2% of tin in the form of alkali metal stannite. Solutions containing over 13% by weight of alkali metal hydroxide and over 2% by weight of tin in the form of sodium stannite have been found to be very satisfactory.

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The upper limit of alkali metal hydroxide is fixed only by the viscosity of the solution. Solutions should not be so concentrated as to be so viscous as to cause emulsion difficulty during the treatment. The amount of alkali metal stannite which may be present is limited only by its solubility in the alkali solution.

In order to demonstrate the efficacy of alkali solutions of alkali metal stannites in the removal of elementary sulfur from hydrocarbon oils, a solution of sulfur in naphtha was prepared by dissolving flowers of sulfur in V. M. & P. naphtha so that the naphtha contained 0.0066% of elementary sulfur by weight. A series of treating solutions was prepared by mixing different amounts of sodium hydroxide, stannous chloride and water. Each solution was tested by shaking two volumes of the naphtha containing elementary sulfur with one volume of the treating solution and after separating the treated naphtha from the solution, 2 to 3 cc. of the treated naphtha was shaken with five drops of mercury for one minute. Coloration of the mercury or formation of black precipitate indicates the presence of elementary sulfur in the naphtha.

In preparing the treating solutions, the sodium hydroxide was added to the water and the solution cooled to room temperature before adding the stannous chloride dihydrate. This precaution was taken to prevent heating of the solution to a temperature which would result in conversion of the stannite to a stannate solution and to insoluble stannous oxide or metallic tin.

The results of the various tests are given in the following table:

Table I

Total Per cent NaOH Used	Per cent $SnCl_2$-$2H_2O$ Used	Per cent Tin in Treating Solution (calcd. from Amount of $SnCl_2$-$2H_2O$ used)	Duration of Shaking, min.	Result of Mercury Test for Elementary Sulfur in the Treated Gasoline
12	4	2.1	20	sulfur present.
13	4	2.1	20	Do.
14	4	2.1	20	sulfur absent.
14	4	2.1	10	sulfur present.
15	4	2.1	10	sulfur absent.
15	4	2.1	5	sulfur present.
16	4	2.1	5	Do.
17	4	2.1	5	Do.
20	4	2.1	5	sulfur absent.
20	4	2.1	2	sulfur present.
18	5	2.6	2	Do.
19	5	2.6	2	trace of sulfur present.
20	5	2.6	2	sulfur absent.
25	5	2.6	2	Do.
13	10	5.2	15	Do.

The data in the foregoing table shows that with a given concentration of sodium stannite in solution, as the concentration of the sodium hydroxide increases, the sulfur is more readily removed. The data further shows that with a given concentration of sodium hydroxide, as the concentration of sodium stannite increases, the sulfur is more readily removed. The data further shows that for a given concentration of sodium hydroxide and sodium stannite, increase in contact time results in more complete removal of sulfur.

Tests similar to those made and reported in Table I were made with solutions of potassium hydroxide containing potassium stannite. The results of these tests are given in the following table:

Table II

Per cent Total KOH Used	Per cent $SnCl_2$-$2H_2O$ Used	Per cent Tin in Treating Soln. (Calcd. from Amount of $SnCl_2$-$2H_2O$ used)	Duration of Shaking, min.	Result of Mercury Test for Elementary Sulfur in the Treated Gasoline
20	5	2.6	2	sulfur present.
23	5	2.6	2	Do.
25	5	2.6	2	trace sulfur present.
25	6	3.2	2	sulfur absent.
20	6	3.2	2	trace sulfur present.

It will be seen from the results in Table II that a solution containing 3.2% by weight of tin in the form of potassium stannite and 25% of potassium hydroxide completely removed the sulfur from the sulfur-containing naphtha solution by shaking for two minutes.

In order to demonstrate the efficacy of the solution for rendering corrosive gasoline from a "Thermofor" catalytic cracking unit non-corrosive, a 200 cc. sample of very corrosive aviation gasoline stock from a "Thermofor" unit was shaken mechanically for fifteen minutes with 100 cc. of alkaline stannite solution prepared by mixing 25% by weight of sodium hydroxide, 6% by weight of stannous chloride dihydrate and 69% of water. The treated gasoline showed no free sulfur with the mercury test and exhibited a negative copper dish corrosion test for free sulfur.

In preparing the alkaline stannite solution used in the foregoing tests, we used hydrated stannous chloride known as "tin crystals" because it is available commercially and is admirably suited to the preparation of the solution. Care should be taken to keep the "tin crystals" out of contact with air since they slowly oxidize to insoluble oxychloride. Anhydrous stannous chloride, known as "Stannchlor" is also available commercially and can be used in the preparation of this solution. Other water soluble and alkali soluble stannous compounds may be used in preparing the reagent.

In preparing the solution, upon addition of stannous chloride to the alkali solution, stannous hydroxide is first precipitated as a white solid, which readily dissolves in excess alkali to form the stannite solution according to the following equation:

$$SnCl_2+2NaOH \rightarrow Sn(OH)_2+2NaCl$$
$$Sn(OH)_2+2NaOH \rightarrow Na_2SnO_2+2H_2O$$

The alkaline sodium stannite takes up elementary sulfur at room or atomspheric temperature to form sodium sulfostannate (Na_2SnS_3).

Potassium stannite reacts similarly. Since alkaline stannite solutions are strong reducing agents and will oxidize upon standing in the presence of air to form the stannate, care should be taken to keep the solutions out of contact with air or to inhibit such solutions against oxidation by the addition of a small amount of an oxidation inhibitor such as sodium arsenite or hydroquinone.

Alkali metal stannite solutions can be used for long periods in removal of elementary sulfur from hydrocarbon oils before the solution becomes spent. The solution is readily regeneratable by contacting it with magnesium and can be regenerated indefinitely. Regeneration may be effected by merely permitting the spent solution to stand in contact with magnesium or by mixing the spent solution with or passing it through powdered or finely comminuted magnesium. The magnesium forms magnesium sulfide during the regeneration of the spent stannite solution and eventually must be discarded and replaced with fresh magnesium.

In order to demonstrate the ability of the magnesium to regenerate spent stannite solution, 10 grams of elementary sulfur was shaken mechanically with 400 cc. of an alkaline stannite solution prepared by mixing together 200 grams of sodium hydroxide, 50 grams of stannous chloride dihydrate and 750 grams of water. The yellow solution was filtered from the excess sulfur. The filtrate was tested to determine whether it would remove the elementary sulfur from the V. M. & P. naphtha containing 0.0066% of sulfur and it was ineffective. Twenty cubic centimeters of the spent solution prepared as just described, was shaken mechanically for fifteen minutes at room temperature with four grams of magnesium powder and the mixture was then filtered. The filtrate was then shaken for fifteen minutes with twice its volume of V. M. & P. naphtha containing 0.0066% elementary sulfur. All of the sulfur was removed from the naphtha as determined by the mercury test, thus showing that shaking of the spent solution with magnesium powder regenerated it rapidly. The magnesium powder which had been used in the regeneration was then acidified with hydrochloric acid causing an evolution of hydrogen sulfide.

Thus it is possible to carry on a continuous process in which the oil, from which sulfur is to be removed, is contacted on one tower with alkaline alkali metal stannite solution using the counter-current method, and the stannite solution which is withdrawn from the bottom of the treating tower is passed through a regeneration tower packed with finely divided magnesium or passed through an agitating device where the spent solution is agitated with powdered magnesium and then to settling chamber where the powdered magnesium is allowed to settle and returned to the regenerating step. Where intermittent or batch operation is practiced, it is merely necessary to permit the spent stannite solution to remain in contact with magnesium turnings or other form of magnesium for a period of time sufficient to regenerate the stannite solution. Magnesium alloys may also be used for regeneration.

In the regeneration step powdered magnesium may be used supported on a carrier such as activated alumina, pumice, active charcoal, silica gel, fuller's earth or co-precipitated silica-alumina complex.

The treating agent is effective at usual atmospheric temperatures and pressures in removing sulfur from hydrocarbon liquids.

It will be seen, therefore, that we have succeeded in developing a new method for removing elementary sulfur from hydrocarbon liquids and rendering such liquids non-corrosive and that we have discovered a novel method for regenerating the alkalin alkali metal stannite solution used in the treating step so that the process can be operated continuously or intermittently.

In addition to removing the free sulfur from hydrocarbon liquids we have found that alkali metal stannite solutions will reduce organic polysulfides having more than two sulfur atoms in the molecule to mercaptans. These higher organic sulfides are found in small amounts when hydrocarbon liquids are "doctor" sweetened. These higher organic polysulfides are objectionable in that they not only are corrosive, but adversely affect the lead susceptibility of gasoline to a greater extent than do alkyl mono- or disulfides. By contacting hydrocarbon liquid containing these higher organic polysulfides with alkali metal stannite solution, the polysulfides are reduced to mercaptans which can then be removed from the liquid either by extraction with an aqueous alkali solution containing a solubility promoter such as isobutyric acid, cresol or cresol and naphthenic acids; or by means of methanol alkali solution; or the mercaptans can be converted to disulfides by treating with oxygen or air in the presence of cupric chloride.

In order to demonstrate the effectiveness of alkali metal stannite solution in reducing organic polysulfides having more than two sulfur atoms in the molecule to mercaptans, an alkaline stannite solution was prepared by dissolving sodium hydroxide in water, cooling the resulting solution and adding solid stannous chloride dihydrate to the cooled solution. In preparing the solution, the following materials were added in the amounts indicated:

	Parts by weight
Sodium hydroxide	25
Stannous chloride dihydrate	6
Water	69

200 cc. of sour Stoddard solvent was sweetened by agitation with 50 cc. of "doctor" solution and such sufficient sulfur to obtain a "break." The resulting Stoddard solvent was sweet to the doctor test but contained free sulfur. A mixture of 175 cc. of doctor-sweet Stoddard solvent and 94 cc. of the alkali stannite solution was shaken mechanically for 15 minutes, but elementary sulfur was still present in the Stoddard solvent. Two further similar treatments with alkaline stannite solution were necessary to remove all the elementary sulfur from the Stoddard solvent. The Stoddard solvent after the alkaline stannite solution treats was slightly doctor sour and gave an unsatisfactory corrosion test as determined by the distillation-corrosion test described in Industrial & Engineering Chemistry, analytical edition, volume 12, pages 1 to 3, 1940, in an article entitled "Effect of sulfur and sulfur compounds in naphtha upon certain corrosion tests" by Henderson, Agruss and Ayers. The sourness can be accounted for by the fact that during doctor-sweetening a small amount of polysulfides having more than two sulfur atoms in the molecule were formed and these polysulfides were reduced to mercaptans during the alkaline stannite treatment.

In another example sour Stoddard solvent was "doctor" treated to render it sweet and all the free sulfur present was removed by treatment with alkaline stannite solution. The resulting Stoddard solvent was "doctor" sweet and contained .03% total sulfur. The sulfur-free Stoddard solvent was then agitated with additional alkaline stannite solution for 16 hours after which it became slightly sour, thereby showing the presence of mercaptans. The total sulfur content was still .03%.

The alkaline stannite solution is valuable as a test to indicate the presence of organic polysulfides having more than two sulfur atoms per molecule. By agitating a hydrocarbon liquid, which is doctor sweet, with alkaline stannite solution for a long period of time, as for example approximately 15 hours or less, the presence of higher organic polysulfides is indicated by the fact that the hydrocarbon liquid is sour to the doctor test or shows the presence of mercaptans by any other test, as for example by means of the silver nitrate-potassium thiocyanate titration method.

We claim:

1. The method of regenerating spent alkali metal stannite solution resulting from the removal of sulfur from sulfur-containing hydrocarbon liquids comprising contacting said solution with magnesium.

2. The method in accordance with claim 1 in which the magnesium is in powdered form.

3. The method of removing elemental sulfur and organic polysulfides containing more than two sulfur atoms per molecule, from hydrocarbon liquid comprising contacting said liquid with alkali metal stannite solution until the sulfur is removed and the polysulfides are converted to mercaptans.

4. Method in accordance with claim 3 in which the hydrocarbon liquid is treated to remove mercaptans after the alkali metal stannite treatment.

5. The method of removing organic polysulfides having more than two sulfur atoms per molecule from hydrocarbon liquid comprising contacting said liquid with alkali metal stannite solution until the polysulfides are converted to mercaptans.

6. Method in accordance with claim 5 in which the hydrocarbon liquid is treated to remove mercaptans subsequent to the alkali metal stannite treatment.

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