Patented Jan. 28, 1936

2,028,998

UNITED STATES PATENT OFFICE

2,028,998

METHOD OF SWEETENING HYDROCARBON OILS

Walter A. Schulze and Lovell V. Chaney, Bartlesville, Okla., assignors to Phillips Petroleum Company, Bartlesville, Okla., a corporation of Delaware

No Drawing. Application December 2, 1933, Serial No. 700,700

10 Claims. (Cl. 196—30)

This invention relates to a method of treating hydrocarbon fluids and the like, with particular reference to sweetening petroleum hydrocarbon oils.

One object of this invention is to convert certain malodorous sulfur compounds occurring in petroleum hydrocarbon mixtures into less obnoxious substances.

A further and most important object is to accomplish said conversion of these obnoxious sulfur compounds by means of alkali and alkaline earth hypochlorite solutions and obtain a "sweetened" product which is free from corrosive substances and which is more stable in sunlight, particularly when in the presence of hydrocarbons having been subjected to pyrolysis.

The term "sweetening" is usually applied to processes involving the conversion of malodorous mercaptans, occurring in petroleum hydrocarbon mixtures, into less odorous substances. Since one of the accepted characteristics of a good motor fuel is its freedom from obnoxious odors, substances responsible for such odors are accordingly usually either completely removed from the petroleum oil being processed, at some stage of the refining process, or are converted by some means to more agreeable smelling substances. The latter method is employed in many cases and the conversion is accomplished by some oxidizing agent, the mercaptans being converted principally to disulfides. The extent of this conversion is usually determined by the well-known "doctor", or sodium plumbite, test.

Hypochlorite solutions, such as sodium and calcium hypochlorites, are used many times for sweetening petroleum hydrocarbon fluids. In many instances, however, the sweetened product is very corrosive to the well-known copper strip test and becomes much darker in color when exposed to sunlight, particularly if the sweetened product has been produced by cracking, or pyrolysis, or is mixed with a petroleum oil which has been subjected to cracking conditions.

We have discovered a means by which we can treat petroleum hydrocarbon fluids such as natural gasoline, liquefied petroleum gases, straight run and cracked refinery gasolines, and the like, which have been treated with sodium hypochlorite, for example, and have been rendered such as to be very corrosive to a copper strip in contact therewith and to be unstable towards sunlight—so that following our treatment they will be substantially non-corrosive to a copper strip in contact therewith in sunlight or when heated to moderate temperatures, and their stability towards sunlight will be substantially increased. We accomplish these results by means of acting on the hypochlorite-sweetened oil with alkaline solutions of reducing agents of the group sodium sulfite (Na_2SO_3), sodium stannite (Na_2SnO_2) and sodium cyanide (NaCN).

It is believed that the compounds which are responsible for these undesirable properties of the oil treated with hypochlorite in the usual manner are the alkyl sulfur chlorides. In these compounds the chlorine has a valence of +1, therefore such compounds have oxidizing properties. These alkyl sulfur chlorides are converted to the stable and unreactive disulfides by treatment with the reducing solutions of sodium sulfite, sodium stannite, or sodium cyanide, substantially as described.

As one example, we have found that a West Texas natural gasoline, containing 0.02 per cent mercaptan sulfur, when sweetened with an alkaline sodium hypochlorite solution (2.5 g. per liter NaOCl; 6 g. per liter excess NaOH) and subsequently treated with a slightly alkaline sodium sulfite solution was only slightly corrosive to a copper strip in contact with the copper in sunlight for two hours, and gave only a slight darkening in color of the composite in sunlight for two hours when mixed with a highly cracked naphtha. Without the sodium sulfite treatment, portions of the same hypochlorite sweetened natural gasoline were very corrosive to a copper strip in sunlight in less than two hours and made the composite much darker in color when mixed with a portion of the same cracked gasoline and placed in the sunlight two hours. We obtained equally beneficial results, with reference to a less corrosive product and one more stable to light, upon sweetening a highly cracked naphtha from high-sulfur crude oil with a similar sodium hypochlorite solution and subsequently treating the sweetened naphtha with a similar sodium sulfite solution.

The sodium sulfite solution which we employed in these examples contained 65 grams of Na_2SO_3 per liter of aqueous solution but the concentration of Na_2SO_3 in the treating solution is not critical. We have employed concentrations ranging from 10 grams to 330 grams of Na_2SO_3 per liter and found them all to accomplish the same beneficial results, the solutions of low Na_2SO_3 concentrations obviously requiring a somewhat longer contacting time than those of higher concentrations. Likewise, there is little if any difference in operative results when the alkalinity of the solution is varied over a considerable range.

We have obtained practically identical results with approximately neutral sodium sulfite solutions as with solutions containing 300 grams of NaOH per liter. In fact, we have obtained good results with acid solutions, as with $NaHSO_3$, but to avoid contaminating the hydrocarbon oil treated with sulfur dioxide we find it advantageous to maintain the treating solution slightly alkaline. Addition of sodium carbonate to the sodium sulfite treating solution, we have found, serves well to impart and maintain this alkalinity and we employ it in our preferred method of working.

Synthetic mixtures of methyl, normal, secondary and tertiary butyl, normal heptyl, phenyl and benzyl mercaptans (0.04 per cent mercaptan sulfur) in naphtha were sweetened with sodium hypochlorite solutions and then treated with slightly alkaline sodium sulfite solutions. Before treatment with sodium sulfite, all were more or less corrosive to a copper strip in sunlight. Contacting with sodium sulfite solutions rendered them all less corrosive and in the majority of cases entirely non-corrosive to copper.

We have also discovered that sodium stannite and alkaline sodium or potassium cyanide, as group examples, react in a substantially analogous manner to sodium sulfite to render corrosive, light-unstable hypochlorite-treated mercaptan mixtures and naphthas non-corrosive and light-stable. As examples of their utility, a very corrosive sodium hypochlorite-sweetened mixture of tertiary butyl mercaptan in naphtha was made relatively non-corrosive to the sunlight copper strip test by contacting it with an aqueous solution containing 40 grams of stannous chloride ($SnCl_2$) and 125 grams of sodium hydroxide (i. e., alkaline sodium stannite) per liter. An aqueous solution comprising 160 grams of potassium cyanide (KCN) and 140 grams of sodium hydroxide per liter accomplished a similar result. The concentrations of stannous chloride, potassium cyanide and sodium hydroxide were varied over quite wide ranges and very satisfactory results were obtained. A substantial excess alkalinity was, however, found to be advantageous.

In carrying out our method of sweetening hydrocarbon oils we intimately contact the oils with an aqueous hypochlorite solution containing approximately 1 gram of sodium hypochlorite per liter and one gram or more of excess sodium hydroxide per liter. After washing the sweetened oil with a dilute sodium hydroxide solution, we then intimately contact the sweetened oil with an aqueous sodium sulfite solution containing approximately 60 grams of Na_2SO_3 per liter (0.5 pound per gallon) and 20 grams of Na_2CO_3 (or NaOH) per liter (0.17 pound per gallon), finally washing the sulfite treated oil with water and allowing the water to separate out in a settling tank. Any of the well-known methods of obtaining intimate contact between the oil to be treated and the hypochlorite, sodium hydroxide and sodium sulfite treating solutions may be used and the oil and aqueous solutions may be separated by decantation and/or any mechanical means.

It is to be understood that other water soluble alkali and alkaline earth sulfites, stannites and cyanides are equivalents.

What we claim and desire to secure by Letters Patent is:

1. An improved method for sweetening a mercaptan-bearing petroleum hydrocarbon fluid, comprising treating said fluid with a hypochlorite solution in the absence of oxygen carriers, whereby a part of the mercaptans are converted to disulfides and the rest to alkyl sulfur chlorides, said alkyl sulfur chlorides remaining in the hydrocarbon fluid, separating said fluid from the hypochlorite solution, treating the fluid with a strong reducing solution of a water soluble alkaline salt selected from the group consisting of the alkali and alkaline earth sulfites, cyanides and stannites, whereby the alkyl sulfur chlorides are reduced to disulfides, and separating the improved sweetened hydrocarbon fluid from the reducing solution.

2. An improved method for sweetening a mercaptan-bearing petroleum hydrocarbon oil, comprising treating said oil with a hypochlorite solution in the absence of oxygen carriers, whereby a part of the mercaptans are converted to disulfides and the rest to alkyl sulfur chlorides, said alkyl sulfur chlorides remaining in the hydrocarbon oil, separating said oil from the hypochlorite solution, treating the oil with a strong reducing solution of a water soluble alkaline salt selected from the group consisting of the alkali and alkaline earth sulfites, cyanides and stannites, whereby the alkyl sulfur chlorides are reduced to disulfides, and separating the improved sweetened hydrocarbon oil from the reducing solution.

3. An improved method for sweetening a mercaptan-bearing petroleum hydrocarbon fluid, comprising treating said fluid with a hypochlorite solution in the absence of oxygen carriers, whereby a part of the mercaptans are converted to disulfides and the rest to alkyl sulfur chlorides, said alkyl sulfur chlorides remaining in the hydrocarbon fluid, separating said fluid from the hypochlorite solution, contacting the fluid with a strong reducing solution of an alkali and a water soluble alkaline salt selected from the group consisting of the alkali and alkaline earth sulfites, cyanides and stannites, whereby the alkyl sulfur chlorides are reduced to disulfides, and separating the improved sweetened hydrocarbon fluid from the reducing solution.

4. An improved method for sweetening a mercaptan-bearing petroleum hydrocarbon oil, comprising treating said oil with a hypochlorite solution in the absence of oxygen carriers, whereby a part of the mercaptans are converted to disulfides and the rest to alkyl sulfur chlorides, said alkyl sulfur chlorides remaining in the hydrocarbon oil, separating said oil from the hypochlorite solution, contacting the oil with a strong reducing solution of sodium hydroxide and a water soluble alkaline salt selected from the group consisting of the alkali and alkaline earth sulfites, cyanides and stannites, whereby the alkyl sulfur chlorides are reduced to disulfides, and separating the improved sweetened hydrocarbon oil from the reducing solution.

5. An improved method for sweetening a mercaptan-bearing petroleum hydrocarbon oil, comprising treating said oil with a hypochlorite solution in the absence of oxygen carriers, whereby a part of the mercaptans are converted to disulfides and the rest to alkyl sulfur chlorides, said alkyl sulfur chlorides remaining in the hydrocarbon oil, separating said oil from the hypochlorite solution, contacting the oil with a strong reducing solution of an alkali and a water soluble alkaline sulfite, whereby the alkyl sulfur chlorides are reduced to disulfides, and separating the improved sweetened hydrocarbon oil from the sulfite reducing solution.

6. An improved method for sweetening a mercaptan-bearing petroleum hydrocarbon oil, comprising treating said oil with a hpyochlorite

solution in the absence of oxygen carriers, whereby a part of the mercaptans are converted to disulfides and the rest to alkyl sulfur chlorides, said alkyl sulfur chlorides remaining in the hydrocarbon oil, separating said oil from the hypochlorite solution, contacting the oil with a strong reducing solution of an alkali and a water soluble alkaline stannite, whereby the alkyl sulfur chlorides are reduced to disulfides, and separating the improved sweetened hydrocarbon oil from the stannite reducing solution.

7. An improved method for sweetening a mercaptan-bearing petroleum hydrocarbon oil, comprising treating said oil with a hypochlorite solution in the absence of oxygen carriers, whereby a part of the mercaptans are converted to disulfides and the rest to alkyl sulfur chlorides, said alkyl sulfur chlorides remaining in the hydrocarbon oil, separating said oil from the hyprochlorite solution, contacting the oil with a strong reducing solution of an alkali and a water soluble alkaline cyanide, whereby the alkyl sulfur chlorides are reduced to disulfides, and separating the improved sweetened hydrocarbon oil from the cyanide reducing solution.

8. An improved method for sweetening a mercaptan-bearing petroleum hydrocarbon oil, comprising treating said oil with a hypochlorite solution in the absence of oxygen carriers, whereby a part of the mercaptans are converted to disulfides and the rest to alkyl sulfur chlorides, said alkyl sulfur chlorides remaining in the hydrocarbon oil, separating said oil from the hypochlorite solution, contacting the oil with a strong reducing solution of sodium hydroxide and a water soluble alkaline sulfite, whereby the alkyl sulfur chlorides are reduced to disulfides, and separating the improved sweetened hydrocarbon oil from the sulfite reducing solution.

9. An improved method for sweetening a mercaptan-bearing petroleum hydrocarbon oil, comprising treating said oil with a hypochlorite solution in the absence of oxygen carriers, whereby a part of the mercaptans are converted to disulfides and the rest to alkyl sulfur chlorides, said alkyl sulfur chlorides remaining in the hydrocarbon oil, separating said oil from the hypochlorite solution, contacting the oil with a strong reducing solution of sodium hydroxide and a water soluble alkaline stannite, whereby the alkyl sulfur chlorides are reduced to disulfides, and separating the improved sweetened hydrocarbon oil from the stannite reducing solution.

10. An improved method for sweetening a mercaptan-bearing petroleum hydrocarbon oil, comprising treating said oil with a hypochlorite solution in the absence of oxygen carriers, whereby a part of the mercaptans are converted to disulfides and the rest to alkyl sulfur chlorides, said alkyl sulfur chlorides remaining in the hydrocarbon oil, separating said oil from the hypochloride solution, contacting the oil with a strong reducing solution of sodium hydroxide and a water soluble alkaline cyanide, whereby the alkyl sulfur chlorides are reduced to disulfides, and separating the improved sweetened hydrocarbon oil from the cyanide reducing solution.

WALTER A. SCHULZE.
LOVELL V. CHANEY.