Patented May 9, 1939 2,157,223

UNITED STATES PATENT OFFICE

2,157,223

METHOD FOR SWEETENING HYDROCARBON OILS

Earl D. Sutton, Newark, Ohio, assignor to The Pure Oil Company, Chicago, Ill., a corporation of Ohio

No Drawing. Application June 17, 1935, Serial No. 26,957

15 Claims. (Cl. 196—33)

This invention relates to sweetening of hydrocarbon oils and particularly to doctor treatment for the removal of certain sulfur compounds from light hydrocarbon distillates.

The present invention finds application in the treatment of sour gasoline, naphtha, kerosene, and other hydrocarbon distillates for the removal of sulfur compounds, such as mercaptans, which are undesirable owing to their objectionable smell or corrosiveness.

Doctor treatment, as usually employed, may consist of intimately mixing a hydrocarbon oil with an alkaline solution of sodium plumbite in water to form lead mercaptides and subsequently adding sulfur to precipitate lead sulfide. Said precipitation is often a matter of some difficulty and may require the use of excess sulfur to complete the reaction which renders the oil corrosive or may entail extensive washing of the oil with water and an attendant loss of lead.

The object of my invention is the sweetening of hydrocarbon oils by an improved doctor treatment, the improvement residing in the facility and completeness with which lead sulfide, lead mercaptides, and suspended bodies are precipitated and separated from the oil.

A further object of my invention is to sweeten hydrocarbon oils by doctor treatment and to render the sweetened product free from discoloration or cloudiness.

Still another object of my invention is to obtain a good "break" after treatment of hydrocarbon oils with doctor solution without the necessity of adding excessive amounts of free sulfur.

In carrying out my invention, doctor treatment is employed in the usual manner, the process comprising mixing a stream of hydrocarbon oil with at least a sufficient quantity of alkaline sodium plumbite solution to react with the sulfur compounds which are to be removed. A quantity of sulfur may be added to the stream in amount sufficient to initiate the "break" but insufficient to provide any excess of free sulfur in solution in the oil. The quantity of sulfur necessary will vary with different types of oil but in general, should be sufficient to react with the oil soluble lead mercaptides formed upon treatment of the oil with the doctor solution to convert them to lead sulfide. There is also injected into the stream a quantity of water soluble soap. The soap may be any soap obtained by the saponification of animal or vegetable oils with alkali metal bases such as stearates, oleates, or palmitates, or any soap which is soluble in or miscible with water but insoluble in the oil undergoing treatment. The soap may be added in any convenient way, as for example, by dissolving the soap in water so as to make a solution containing about one-quarter pound of soap per gallon of water. The strength of the solution may be varied to any extent, being limited only by the solubility of the soap in water. The soap may be injected separately into the stream as a solution either before or after addition of the doctor, or it may be dissolved in the proper amount in the doctor solution itself and injected into the hydrocarbon oil stream therewith. The soap may also be added to the stream in a solid form such as flake or powder. The quantity of soap that is used in any case is determined by the character of the hydrocarbon oil, and particularly by the character and quantity of lead salts and other suspended bodies that will be precipitated.

Sulfur may be added in small amounts either before or after introduction of the doctor solution and/or soap, or may be added simultaneously with either or both.

The process is preferably carried out in a continuous manner. The stream of hydrocarbon oils containing doctor solution and soap is forced by a pump or a suitable device through a mixer, which will insure intimate contact of all the constituents. Samples of the mixed stream may be taken from time to time and the rapidity of the "break", and the color and clarity of the supernatant oil are observed. If the "break" is sluggish the quantity of soap that is present in the stream is inadequate and should be increased. The stream then passes into a settling tank wherein the doctor solution and soap carrying the precipitated lead salts are allowed to settle to the bottom, the hydrocarbon oil forming the supernatant layer. The two layers are separated by withdrawing them from the tank at suitable points. If the color of the separated hydrocarbon oil is materially darker than the oil originally charged, the condition may be the result of colored lead mercaptides in solution or in suspension in the oil. These may be precipitated by increasing the sulfur in the mixed stream, which will complete conversion of the oil soluble lead mercaptides to insoluble lead sulfide. However, another frequent cause of discoloration and cloudiness of the gasoline is lead sulfide in suspension which will not be removed by the further addition of sulfur to the stream, and in fact, addition of sulfur in this case will render the oil corrosive. It has been found that a further addition of soap to the mixed stream will agglomerate these fine suspensions into larger par-

ticles which will settle rapidly. Furthermore, the use of sulfur is reduced because it is not necessary to add sufficient sulfur to precipitate all the lead mercaptides but only those that are soluble in the oil. The insoluble lead mercaptides that formerly had to be converted to lead sulfide before they would settle may now be agglomerated by soap and their removal thereby simplified. As a result the presence of excess free sulfur and its attendant corrosiveness is completely avoided.

In the past these suspensions of lead salts have been removed by long settling or prolonged washing with water, which will eventually yield a satisfactory product but will usually entail a loss of lead. By the addition of soap, the use of sulfur as a precipitant is reduced to a minimum, the separation of lead salts from the oil is practically complete without the necessity of extended water washing, and the consequent loss of lead is avoided.

For carrying out the invention, a laundry or household soap such as Chipso, Fels Naphtha or Ivory soap, has been found satisfactory. When the gasoline, naphtha or similar distillates are to be doctor treated, soap may be added conveniently to the doctor solution when it is made up out of the usual ingredients comprising sodium hydroxide solution and litharge. The amount of soap added may be from 1 to 3 pounds per 1000 gallons of doctor solution. The treatment is preferably continuous and the doctor solution may be recirculated through the process and may treat from 7000 to 25,000 barrels of gasoline and the like. The efficacy of the soap will not materially decrease throughout the life of the doctor solution, but further quantities of soap may be added at such times as difficulties in completely precipitating the lead salts present themselves.

In cases where the gasoline, naphtha or the like that is being treated has a particularly high sulfur content or one from which lead sulfide is precipitated in a form which does not separate readily, a soap solution containing one-quarter of a pound per gallon may be introduced into the stream of hydrocarbon oil being treated at the rate of one to three pounds of soap per 1000 barrels of hydrocarbon oil.

Additions of soap solution from time to time into the stream of hydrocarbon oil during the life of a batch of doctor solution will cause eventually, a considerable accumulation of soap therein. This may rise as high as 50 pounds per 1000 gallons of doctor solution, more or less, without in any way impairing the solution as a treating agent.

Owing to the coagulant effect of the soap, the quantity of sulfur that has to be used in order to get a good "break" is considerably less than is necessary when the doctor treatment is performed without the improvement effected by the addition of soap. In the case of gasolines, which are only slightly sour or which contain free sulfur in solution, it may not be necessary to use sulfur at all.

The complete precipitation of the lead salts out of the oil into the used doctor solution that is affected by the soap causes a material lengthening of the life of the doctor solution. The revivification of doctor solution, comprising heating and blowing with air as is usually employed, is not affected in any adverse way by the presence of soap, and the full benefit of a complete recovery of lead may be enjoyed.

In winter weather the temperature of hydrocarbon oils to be doctor treated may reach 32° F. or less. Under these low temperature conditions, the reaction velocities obtained in the interaction of the treating agent with the sulfur compounds in the oil is materially reduced, and the complete precipitation and separation of lead salts from the oil is thereby made more difficult. The present invention is particularly well suited for overcoming these difficulties. The addition of a suitable quantity of soap solution will, even under the most adverse conditions, result in a satisfactory separation and recovery of lead. Furthermore, the cloudiness and discoloration of the treated hydrocarbon oil that is so often encountered, especially when the temperatures at which the treatment is performed are low, can be completely eliminated by the improved method disclosed in the present invention.

The present invention also provides that doctor treatment with or without soap may be performed upon hydrocarbon oil and a treatment of the sweetened oil with soap may be made subsequently. In this case the sweetened oil separated from the used doctor solution may be intimately mixed or agitated with an aqueous solution of soap in any convenient quantity or strength, to remove lead salts and other bodies in suspension which will be coagulated and settle out of the oil into the soap solution on allowing the mixture to come to rest.

Experiments have shown that certain well known de-emulsifying agents such as "Tretolite", which are prepared for use in breaking hydrocarbon oil-water emulsions, are not suitable to the purpose of the present invention and may not be satisfactorily substituted for soap when used as disclosed herebefore.

Certain commercial soaps may contain unsaponified oil or unsaponifiable oils which are soluble in the hydrocarbon oil that it is desired to treat. When these soaps are to be used for the purpose of the present invention it is preferable to make aqueous solutions thereof and to separate the unsaponified or unsaponifiable oil therefrom before introducing them into the treating system. Likewise oil soluble soaps should be avoided since such soaps, like unsaponified oils, will contaminate the oil undergoing treatment.

Although specific amounts of soap have been disclosed as applicable to the process, it is to be understood that the amount may be varied within wide limits without departing from the scope of the invention.

What I claim is:

1. A method of sweetening sour hydrocarbon oils containing free sulfur which comprises adding thereto sufficient aqueous doctor reagent to react with the mercaptans present in the oil and adding to the mixture sufficient water-soluble soap which is insoluble in the oil, to cause a rapid break between the oil and reaction products, the sulfur being present in amounts sufficient to initiate the "break".

2. In the method of sweetening sour hydrocarbon oils containing free sulfur with aqueous doctor reagent, the step which consists in adding to the oil sufficient water-soluble soap which is insoluble in the oil, to agglomerate suspended reaction products contained therein, the sulfur being present in amounts sufficient to react with soluble mercaptides that are formed.

3. A method of sweetening hydrocarbon oils which comprises mixing with the oil sufficient doctor reagent to react with the mercaptans contained therein, treating the oil with sufficient sul-

fur to convert oil soluble mercaptides to lead sulfide, and adding sufficient water-soluble soap which is insoluble in the oil, to precipitate suspended reaction products.

4. A method of sweetening hydrocarbon oils which comprises mixing with the oil sufficient doctor reagent to react with the mercaptans contained therein, treating the oil with sufficient sulfur to initiate the "break", and adding sufficient water-soluble soap which is insoluble in the oil, to agglomerate reaction products held in suspension in the oil.

5. A method of sweetening hydrocarbon oils which comprises mixing with the oil sufficient alkali plumbite reagent to react with the mercaptans contained therein, treating the oil with sufficient sulfur to react with the oil soluble mercaptides but insufficient to react with the total mercaptides formed, and mixing the oil with sufficient water-soluble soap which is insoluble in the oil, to agglomerate the reaction products which remain suspended in the oil.

6. In the method of sweetening sour oil containing free sulfur with aqueous alkali plumbite reagent, the step which consists in adding water-soluble soap which is insoluble in the oil, to the plumbite prior to treatment of the oil therewith in sufficient quantity to agglomerate reaction products which remain suspended in the oil, the sulfur being present in amounts sufficient to react with soluble mercaptides that are formed.

7. The method of sweetening sour hydrocarbon oil containing free sulfur which comprises mixing the oil with alkali plumbite reagent, separating the reagent from the oil, mixing the separated oil with a water solution of oil-insoluble soap in sufficient quantity to agglomerate reaction products remaining suspended in the oil, and separating the oil from the soap solution and precipitated reaction products, the sulfur being present in amounts sufficient to react with soluble mercaptides that are formed.

8. The method of sweetening hydrocarbon oil which comprises mixing the oil with alkali plumbite reagent, in the presence of sufficient sulfur to initiate the "break", separating the reagent from the oil, mixing the separated oil with a water solution of oil-insoluble soap in sufficient quantity to agglomerate reaction products remaining suspended in the oil, and separating the oil from the soap solution and precipitated reaction products.

9. The method of sweetening hydrocarbon oil which comprises mixing the oil with alkali plumbite reagent in the presence of sufficient sulfur to react with oil soluble mercaptides but insufficient to react with oil insoluble mercaptides, separating the reagent from the oil, mixing the separated oil with a water solution of oil-insoluble soap in sufficient quantity to agglomerate reaction products remaining suspended in the oil, and separating the oil from the soap solution and precipitated reaction products.

10. The method of sweetening sour hydrocarbon oil containing free sulfur which comprises treating the oil with an aqueous alkali plumbite solution containing oil-insoluble soap in solution, the soap being present in amounts of from 1 to 3 pounds per 1000 gallons of plumbite solution, the sulfur being present in amounts sufficient to initiate the "break".

11. The method of sweetening sour hydrocarbon oil containing free sulfur which comprises treating the oil with alkali plumbite reagent and with a water solution of oil-insoluble soap, in the amount of 1 to 3 pounds of soap per 1000 barrels of oil, the soap solution containing approximately ¼ pound of soap per gallon of solution, the sulfur being present in amounts sufficient to initiate the "break".

12. A method for sweetening hydrocarbon oils containing dissolved sulfur which comprises mixing therewith sufficient aqueous doctor reagent to react with the mercaptans in the oil and a fatty acid soap capable of producing a rapid break between the oil and reaction products, the sulfur being present in amounts sufficient to initiate the "break".

13. A method for sweetening hydrocarbon oils which comprises mixing therewith sufficient aqueous doctor reagent to react with the mercaptans in the oil, sufficient sulfur to initiate the "break" and a fatty acid soap capable of accelerating the "break".

14. A method for sweetening sour hydrocarbon oils in the presence of free sulfur in sufficient quantity to initiate the "break" which comprises mixing therewith aqueous doctor reagent, adding to the mixture a small amount of soap capable of accelerating separation of oil and reaction products, separating the doctor reagent from the oil and recycling for treatment of further quantities of oil, and adding further quantities of soap to the oil-doctor mixture.

15. The method of facilitating the removal of lead-sulfur compounds formed in the sweetening of hydrocarbon oil by means of an alkali solution of a lead compound and sulfur which comprises adding to the oil containing such lead-sulfur compounds, sufficient water-soluble, oil-insoluble soap to coagulate the lead compounds and cause them to separate with the soap.

EARL D. SUTTON.