Patented May 12, 1953 2,638,439

UNITED STATES PATENT OFFICE

2,638,439

TREATMENT OF PETROLEUM DISTILLATES

John G. Browder, Houston, and Alvin R. Smith, Baytown, Tex., assignors, by mesne assignments, to Standard Oil Development Company, Elizabeth, N. J., a corporation of Delaware

No Drawing. Application April 18, 1951, Serial No. 221,718

4 Claims. (Cl. 196—29)

1

The present invention is directed to a method for treating sour petroleum distillates. More particularly, the invention is directed to the sweetening of sour petroleum distillates in the presence of an alkali metal hydroxide and a mild oxidizing agent.

This invention is an improvement over the invention described and claimed in co-pending application Serial No. 77,447, filed February 19, 1949, for John G. Browder, now U. S. Patent 2,552,399.

The present invention may be briefly described as involving the treatment of a sour petroleum distillate containing mercaptans and boiling in the range from about 50° to 750° F. by contacting the distillate with a solution of an alkali metal hydroxide. Prior to contacting the distillate with an alkali metal hydroxide the distillate has added to it a small but effective catalytic amount of an organic fraction obtained by acidifying a solution of an alkali metal salt of crude petroleum phenol to at least 75% of a methyl orange end point to release an acidic fraction therefrom following which the released acidic fraction is discarded and the solution from which the acidic material has been released is retained. The retained solution is then further acidified to the methyl orange end point to release the organic fraction added to the sour distillate.

The sweetening operation is conducted in the presence of a mild oxidizing agent by adding an oxidizing agent to the contacted mixture to convert mercaptans in the sour distillate to disulfides and to obtain a sweetened distillate.

The organic fraction employed in the present invention is obtained by contacting a petroleum fraction boiling in the range from about 400° to 700°, which is in the heating oil boiling range, and obtained from thermal and catalytic cracking operations, with a strong alkaline solution, such as a sodium hydroxide solution, having a Baumé gravity in the range from about 40 to 50 degrees. This extraction causes the separation, as interface layer between the heating oil and the alkali metal hydroxide solution, of a solution of a sodium salt of crude petroleum phenols. The designation "crude petroleum phenols" is well known in the art and is believed to comprise a mixture of phenolic and naphthenic materials. In short the term "sodium salt of crude petroleum phenols" would contain a mixture of sodium salts of naphthenic and phenolic as well as other unidentified bodies. The organic fraction is obtained from the sodium salt of crude petroleum phenols by fractional acidification thereof.

2

It has been discovered that a particular fraction obtained by acidifying the sodium salt of crude petroleum phenols gives markedly superior results to the crude petroleum phenols themselves. In obtaining the organic fraction employed in the sweetening operation of the present invention, a solution of a sodium salt of crude petroleum phenol obtained as has been described is acidified to the methyl orange end point to release the crude petroleum phenols. The amount of mineral acid required to acidify to the methyl orange end point is thus determined. Another portion of the solution of sodium salt of crude petroleum phenols is then acidified to at least 75% of the methyl orange end point to release an acidic fraction from the solution of a salt of crude petroleum phenols. This fraction is discarded and the remaining solution is then acidified to the methyl orange end point to release the organic fraction employed in the present invention.

The organic fraction employed in the practice of the present invention may be used in amounts based on the sour distillates varying from 0.001 to 1.0% by volume, with a preferred range from 0.01 to 0.15% by volume. It is to be emphasized that the specified amount of the organic fraction should be added to the sour distillate and not to the alkaline solution.

The alkaline solution employed in the present invention should be a solution of an alkali metal hydroxide. Preferably the solution should be an aqueous solution having a Baumé gravity in the range from about 30° to 50° Bé. but solutions of lower strengths may be used under some conditions. A 40° Bé. aqueous solution of sodium hydroxide gives satisfactory results.

The alkali metal hydroxide may be lithium, sodium, or potassium hydroxide, but sodium hydroxide will be preferred on account of its availability.

The temperature at which the treating operation is conducted will usually be atmospheric temperature and may range from about 60° F. up to about 200° F. and sometimes higher depending on the boiling range and type of the stock being treated. A preferred temperature range will be from about 70° to about 95° F. Satisfactory results have been obtained at atmospheric temperatures encountered in the Texas Gulf Coast area.

The invention will be further illustrated by the following examples:

A heating oil fraction composed of hydrocarbons boiling in the range from 400° to 650° F. ob-

tained from thermally and catalytically cracked stocks as well as from crude petroleum components was treated with 40° Bé. sodium hydroxide solution. An interface layer was formed between the sodium hydroxide solution and the heating oil fraction. This interface layer was separated and was acidified to a methyl orange end point to release crude petroleum phenols. The amount of mineral acid required to acidify to the methyl orange end point was noted and a second portion of the interface layer was acidified to 62% of the methyl orange end point. This resulted in the release of an acid fraction which was separated and withdrawn. The remaining solution then had mineral acid added to it to acidify the solution up to 75% of the methyl orange end point which resulted in the release of a second acidic fraction which was withdrawn and retained. Following separation of the second acid fraction the remaining solution was then acidified to 87% of the methyl orange end point to release a third acid fraction which was separated and withdrawn. The solution remaining after release of the third acid fraction was further acidified to the methyl orange end point to obtain a fourth acid fraction.

These 4 acid fractions and the crude petroleum phenols were each added to separate portions of a high sulfur kerosene fraction which was a solvent raffinate having a copper number of 40. The amount of each of the acid fractions and the crude petroleum phenols added to the kerosene was 0.10 volume per cent of the solvent raffinate. The several portions of kerosene to which the various acid fractions and the crude petroleum phenols had been added were then contacted with 5 volume per cent of 45° Bé. sodium hydroxide solution in the presence of 300% of the theoretical amount of oxygen required to obtain a sweetened distillate. The contacting operation was conducted at a temperature of 95° F. and was conducted for two minutes. Following the contacting operation the caustic solution was separated from the contacted kerosene and the copper number of the contacted kerosene was obtained after 1, 4, and 20 hours. The results of these runs are shown in Table I which follows:

Table I

	Amount Added to Kerosene, Vol. Percent	Copper Number of Kerosene after Treatment		
		1 Hr.	4 Hrs.	20 Hrs.
First Acid Fraction	0.10	25	20	15
Second Acid Fraction	0.10	15	10	5
Third Acid Fraction	0.10	4	1	1
Fourth Acid Fraction	0.10	1	1	1
Crude Petroleum Phenols	0.10	8	2	1

From the data in Table I, it will be noted that the third and fourth acid fractions give superior results to the first and second acid fractions and to the crude petroleum phenols. It will thus be seen that the third and fourth acid fractions are superior additives to the fractions released by acidifying to 75% of the methyl orange end point and also are superior to the crude petroleum phenols which are released by acidification to the methyl orange end point. It is, therefore, contemplated that the fractions obtained after acidification to at least 75% and no more than 90% of the methyl orange end point followed by further acidification of the remaining solution will give superior results in the practice of the present invention.

Since, as pointed out before, it is known that the crude petroleum phenols contained naphthenic acids, a comparison was made between adding the several fractions employed in Table I and naphthenic acids to the sour distillate in the sweetening operation. To this end a naphthenic acid fraction was added in an amount of 0.10 volume per cent to the same kerosene employed in the previous runs. This kerosene was then treated as outlined above. In all instances, both in the runs reported in Table I and below, the contacting operation was conducted at 95° F. and 300% of the theoretical amount of oxygen required to sweeten was used. Also in the runs the results of which are given in Table I and following, the contacted kerosene was allowed to stand at 95° F. for the stated time before determination of the copper number. The sour kerosene to which nothing had been added was also contacted with the same amount of 45° Bé. sodium hydrogen solution in the presence of the same amount of oxygen as employed in the runs represented in Table I. The results of these runs are given in Table II.

Table II

	Amount Added to Kerosene, Vol. Percent	Copper Number of Kerosene after Treatment		
		1 Hr.	4 Hrs.	20 Hrs.
Naphthenic Acids	0.10	20	20	2
None		38	35	28

The copper number test used in evalulating the present invention is a measure of the mercaptan content of petroleum distillates. A description of the methods for determining copper number may be found in "U. O. P. Laboratory Test Methods for Petroleum and its Products," Universal Oil Products Company, Chicago, 1940, page H–61.

It will be noted comparing the data in Table I with that in Table II when employing the third and fourth fractions of the present invention obtained by fractional acidification of an alkali metal salt of crude petroleum phenols that superior results are obtained to crude petroleum phenols, naphthenic acids and to the first and second fractions released in the fractional acidification indicating that the additive is neither a pure phenolic material nor a pure naphthenic acid material. Since the identity of the organic fraction employed in the practice of the present invention is unknown, it is defined by the way it is produced.

Although not illustrated by the several examples, one of the particular advantages of the present invention resides in the catalytic effect of the alkali metal hydroxide solution. The alkali metal hydroxide appears to function as a true catalyst since the small amount used may be recycled to treat large quantities of the sour petroleum distillate. A small amount of the alkali metal hydroxide solution may be entrained in the treated naphtha, and, therefore, it may be necessary to replace the entrained amount with fresh solution. In short, it is contemplated in the practice of the present invention that the alkali metal hydroxide solution will be reused over and over again since it is not necessary to regenerate the alkali metal hydroxide solution.

The invention has been described and illustrated by employment of a mild oxidizing agent

such as oxygen. It is contemplated that mixtures of oxygen with other gases, such as air, may be employed. It is also contemplated that other mild oxidizing agents such as peroxides, permanganates, and the like may be used. For example, a hydrogen peroxide solution may be employed as the mild oxidizing agent.

In practicing the present invention, it is to be understood that the petroleum distillate may be subjected to a preliminary treatment for removal of hydrogen sulfide if the distillate contains hydrogen sulfide. Such preliminary treatment may include washing with a dilute alkali metal hydroxide solution or blowing with a free-oxygen containing gas such as air. If hydrogen sulfide or other acidic compounds are present and not removed, the alkali metal hydroxide solution employed as the catalyst may very quickly become seriously depleted in activity.

In the practice of the invention, it will be desirable to use an amount of oxygen in excess of the theoretical required to sweeten the sour petroleum distillate. Ordinarily, an amount of about 300% of the theoretical amount to sweeten may be employed. However, sweetening in accordance with the present invention may be obtained with considerably lesser quantities of oxygen. In fact, sweetening may be obtained in some cases by contact with the oxygen present in the treating vessel. It will be desirable to employ an amount of oxidizing agent at least equivalent to the theoretical amount required to sweeten.

The invention has been described and exemplified by employment of 5% by volume of the catalytic alkali metal hydroxide solution. It is contemplated that as little as 0.1 and as much as 5% by volume, or more, of the alkali metal hydroxide solution, based on the sour naphtha, may be employed. Very good results, however, are obtained with 1% by volume and this amount usually will be preferred.

The nature and objects of the present invention having been completely described and illustrated, what we wish to claim as new and useful and to secure by Letters Patent is:

1. A method for sweetening a sour petroleum distillate containing mercaptans and having a final boiling point no greater than 750° F. which comprises adding to said distillate a small but effective catalytic amount no greater than 1% by volume of said distillate of an organic fraction obtained by: acidifying a solution of an alkali metal salt of crude petroleum phenols to at least 75% of a methyl orange end point to release an acidic fraction therefrom, discarding said acidic fraction and retaining said solution from which acidic material has been released, acidifying the retained solution to the methyl orange end point to release said organic fraction, and then contacting the sour distillate containing the organic fraction with a catalytic amount no more than 5% by volume of a solution of an alkali metal hydroxide while adding a sufficient amount of a mild oxidizing agent to convert the mercaptans to disulfides and to obtain a sweetened distillate.

2. A method for sweetening a sour petroleum distillate containing mercaptans and having a final boiling point no greater than 750° F. which comprises adding to said distillate an amount in the range from 0.001% to 1.0% by volume of said distillate of an organic fraction obtained by: acidifying a solution of a sodium salt of crude petroleum phenols to at least 75% of a methyl orange end point to release an acidic fraction therefrom, discarding said acidic fraction and retaining said solution from which acidic material has been released, acidifying the retained solution to the methyl orange end point to release said organic fraction, then contacting the sour distillate containing the organic fraction with sodium hydroxide solution in an amount in the range between 0.1% and 5% by volume while adding a sufficient amount of air to convert the mercaptans to disulfides, and separating the contacted distillate from said sodium hydroxide solution to obtain a sweetened distillate.

3. A method for sweetening a sour petroleum distillate containing mercaptans and having a final boiling point no greater than 750° F. which comprises adding to said distillate an amount in the range from 0.001% to 1.0% by volume of said distillate of an organic fraction obtained by: acidifying a solution of a sodium salt of crude petroleum phenols to at least 75% and no more than 90% of a methyl orange end point to release an acidic fraction therefrom, discarding said acidic fraction and retaining said solution from which acidic material has been released, acidifying the retained solution to a methyl orange end point to release said organic fraction, then contacting the sour distillate containing the organic fraction with a sodium hydroxide solution in an amount in the range between 0.1% and 5% by volume while adding a sufficient amount of air to convert the mercaptans to disulfides and separating the contacted distillate from said sodium hydroxide solution to obtain a sweetened distillate.

4. A method for sweetening a sour petroleum distillate containing mercaptans and having a final boiling point no greater than 750° F. which comprises adding to said distillate an amount in the range from 0.001% to 1.0% by volume of said distillate of an organic fraction obtained by: acidifying an aqueous solution of a sodium salt of crude petroleum phenols to at least 37% of a methyl orange end point to release an acidic fraction therefrom, discarding said acidic fraction and retaining said solution from which acidic material has been released, acidifying the retained solution to the methyl orange end point to release said organic fraction, then contacting the sour distillate containing the organic fraction with a sodium hydroxide solution in an amount in the range between 0.1% and 5% by volume while adding a sufficient amount of air to convert the mercaptans to disulfides and separating the contacted distillate from said sodium hydroxide solution to obtain a sweetened distillate.

JOHN G. BROWDER.
ALVIN R. SMITH.

References Cited in the file of this patent

UNITED STATES PATENTS

Number	Name	Date
2,569,370	Browder et al.	Sept. 25, 1951