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METHOD FOR TREATING PETROLEUM DISTILLATES

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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.

Prior to the present invention, it has been known to treat sour petroleum distillates with aqueous alkaline solutions, such as solutions of alkali metal hydroxide, to remove hydrogen sulfide and other acidic bodies, following which the sour distillates were treated with sodium plumbite solution to convert deleterious sulfur compounds to compounds which are largely innocuous. This and other prior art processes relied on the addition of sulfur to cause the conversion of the sulfur compounds from mercaptans to disulfides. Other processes convert the undesirable compounds by means of lead sulfide which is then separated from the gasoline. Frequently, the separation of lead sulfide from the gasoline was not complete, and, consequently same was carried over into storage, which was disadvantageous. Furthermore, the addition of sulfur to gasoline frequently impaired the octane number level of the gasoline since it is well known that sulfur and its compounds affect gasoline detrimentally.

Efforts have been made in the prior art to remedy this situation, and the workers in the field have turned to adding certain compounds, such as phenols and amines, to alkaline solutions, such as sodium hydroxide, to cause conversion through an oxidation mechanism of the deleterious compounds in the sour naphtha. Frequently such expedients are unsatisfactory in not completely sweetening the product, and an after-treatment, by one of the well known procedures, becomes necessary.

From the foregoing discussion of the prior art, it will be seen that the petroleum refining industry has been faced with a problem of converting deleterious sulfur compounds present in petroleum distillates to those which do not detrimentally affect the quality of the product.

It is, therefore, the main object of the present invention to provide a treating process in which improved results are obtained in converting objectionable sulfur compounds to harmless bodies.

Another object of the present invention is to provide an improved sweetening process in which an active material is added to the petroleum distillate being sweetened to catalyze the conversion of deleterious sulfur compounds.

Another object of the present invention is to

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provide an improved sweetening process in which small amounts of catalytic reagents are employed.

In the foregoing description of the prior art, it will be seen that the prior art workers added compounds such as phenols and amines to the alkaline solutions which were employed to treat sour petroleum distillates. We have now found that, in distinction to the prior art workers, improved results may be obtained by adding catalytic amounts of a naphthenic acid to the sour petroleum distillate. Therefore, in accordance with the present invention the foregoing objects may be achieved by adding to sour petroleum distillates small amounts of naphthenic acids and then contacting the sour distillates containing the naphthenic acid with a very small catalytic quantity of a solution of an alkali metal hydroxide while maintaining in contact therewith a mild oxidizing agent.

Accordingly, it may be seen that the present invention may be described briefly as involving treating a sour petroleum distillate boiling in the range from about 50° to 750° F. by contacting the distillate with a solution of an alkali metal hydroxide while maintaining in the sour distillate a catalytic amount of a naphthenic acid and adding to the contacted mixture a mild oxidizing agent sufficient to sweeten said distillate, following which the alkali metal hydroxide is separated from the contacted distillate.

The naphthenic acids employed in the practice of the present invention are those naphthenic acids usually derived from petroleum and having from 6 to 16 carbon atoms in the molecule. The naphthenic acids containing up to 12 carbon atoms are usually monocyclic compounds and those having more than 12 carbon atoms are usually di- or polycyclic compounds. The naphthenic acids from petroleum will usually comprise the naphthenic acids employed in the practice of the present invention. The constitution of such naphthenic acids has been discussed extensively by Ellis, in "The Chemistry of Petroleum Derivatives," volume 2, Reinhold Publishing Corporation, New York, 1937, page 1110.

Ordinarily, it will be desirable to employ naphthenic acids in the present invention which have been extracted from petroleum fractions boiling in the range from 400° to 700° F., and particularly from thermally cracked petroleum fractions in this boiling range. The naphthenic acids may be obtained by contacting a petroleum fraction containing them with a solution of an alkali metal hydroxide having a Baumé gravity

of about 40° to form an aqueous layer and an oily layer. The aqueous layer may be partially acidified to release phenolic bodies, the phenolic bodies separated therefrom, and the aqueous layer further acidified to release the naphthenic acids which then may be used in the practice of the present invention.

These compounds may be employed in amounts, based on the naphtha, varying from 0.001 to 1.0 per cent by volume, with a preferred range from about 0.01 to 0.15 per cent by volume. It is to be emphasized that the specified amount of the naphthenic acids should be added to the naphtha 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 strength may be used under some conditions. For example, 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 120° F. although temperatures up to 200° F. or higher may sometimes be used. 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 present invention will be further illustrated by the following specific example.

EXAMPLE

A hydrogen sulfide free high sulfur petroleum distillate boiling in the kerosene boiling range, having a copper number of 50, was divided into two portions. One portion was contacted with 1% by volume of 40° Bé. sodium hydroxide solution in the presence of 300% of the theoretical amount of oxygen necessary to sweeten naphtha, while the other portion had added to it 0.1% by volume of naphthenic acids and was then contacted with 1% by volume of 40° Bé. sodium hydroxide solution in the presence of 300% by volume of the theoretical amount of oxygen required to sweeten. After separation of the alkali metal hydroxide from the two treated portions, copper number tests were determined immediately and after 1, 3, 5, and 20 hours' settling. The results of these tests are shown in the following table:

Table

Copper Number After Settling For—	1	2
0 Hour	55	47
1 Hour	53	28
3 Hours	51	19
5 Hours	50	19
20 Hours	49	17

The data in column 1 presents the results of the treatment with sodium hydroxide solution and oxygen in the absence of naphthenic acids, while the data in column 2 illustrate the practice of the present invention. It will be seen from the foregoing data that the addition of naphthenic acid to the kerosene in the presence of a catalytic quantity of sodium hydroxide and oxygen resulted in reduction of the copper number after treatment from 50 to 47 which dropped to 28 after 1 hour and then slowly to 17 whereas in the absence of naphthenic acids substantially little sweetening was obtained even after 20 hours' standing. It will also be apparent from the foregoing data that the kerosene treated in accordance with the present invention will slowly sweeten itself on standing.

In the foregoing example, the improvement obtained in the present invention has been illustrated by the copper number test. This is a well known analytical procedure employed in the petroleum industry. A description of the method of test may be found in "U. O. P. Laboratory Test Methods for Petroleum and Its Products," third edition, page H–61, Universal Oil Products Company, Chicago, 1947. This test is a measure of the mercaptan sulfur content of the oil being tested.

In the practice of the present invention, it is to be understood that the sour petroleum distillates employed as feed stocks are free from or deficient in catalytic oxidation promoting compounds such as naphthenic acids and will not sweeten in contact with a mild oxidizing agent and alkali metal hydroxide. The great majority of petroleum distillates to be sweetened in general refinery practice will be found to fall in this category. Our invention is concerned with adding to and/or maintaining in such stocks the stated amounts of naphthenic acids.

Although not illustrated by the example, 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 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 are 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 ob-

tained 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 1.0% 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 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 naphthenic acid in a small but effective amount no greater than 1% by volume of said distillate and then contacting the distillate containing added naphthenic acid with a small amount no greater than 5% by volume of said distillate 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 in accordance with claim 1 in which the alkali metal hydroxide is sodium hydroxide and the mild oxidizing agent is a free oxygen containing gas.

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