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SWEETENING OF 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, some 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 sweetening 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 discussion of the prior art, it will be seen that the prior workers in this field have added compounds such as phenols, amines and alcohols to sweetening processes in which alkaline solutions were employed to treat sour distillates. We have now found that in distinction to the prior art workers improved results may be obtained in an oxidative sweetening process in which an alkali metal hydroxide is employed by adding catalytic amounts of amides such as an aliphatic or aromatic amide to the sour distillate to be sweetened in the oxidative sweetening process. Thus, in accordance with the present invention the foregoing objects may be achieved by adding to a sour petroleum distillate a catalytic amount of an amide; the petroleum distillate to which the amide has been added is then contacted with a small, catalytic amount of a solution of an alkali metal hydroxide while maintaining the mixture of the petroleum distillate containing the amide and the solution of alkali metal hydroxide in contact with a mild oxidizing agent.

Accordingly, the present invention may be described briefly as involving contacting a sour petroleum distillate having a boiling range of about 50° to 750° F. with a solution of an alkali metal hydroxide in the presence of a catalytic amount of an amide which has previously been added to the sour petroleum distillate and adding to the mixture undergoing contacting with the alkali metal hydroxide a mild oxidizing agent in an amount sufficient to sweeten said distillate, following which the alkali metal hydroxide is separated from the contacted distillate.

The amides finding employment in the present invention may be an aliphatic or an aromatic amide. As examples of the aliphatic amides may be mentioned formamide, normal butyramide, propionamide, acetamide, isovaleramide and the secondary and tertiary amides. As examples of the aromatic amides may be mentioned benzamide, N-butylbenzamide, N-isopropylbenzamide, N-ethylbenzamide and N-methylbenzamide. Other aliphatic and aromatic amides may be employed in the practice of the present invention and the foregoing members are to be understood to be illustrations. As a general statement it may be mentioned that the low molecular weight aliphatic amides are to be preferred since they are the more effective of the aliphatic amides employed in the practice of the present invention. Of the aromatic amides it will be preferred to

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employ the aromatic amides having aliphatic substituents on the nitrogen atom since it appears that the substituent groupings on the nitrogen atom increase the effectiveness with increasing molecular weight of the compound.

The amides may be employed in amounts based on the sour distillate or naphtha varying from 0.1 to 5% by volume with a preferred range from about 0.5 to 1.0% by volume. It is to be emphasized that the specified amount of amides may be added to the petroleum distillate or to the mixture of petroleum distillate and alkali metal hydroxide while in contact therewith. It is preferred, however, to add the amide to the petroleum distillate since the amides are largely insoluble in the alkali metal hydroxide solutions.

The alkali metal hydroxide employed in the present invention preferably should be a solution of an alkali metal hydroxide and the solution should preferably be an aqueous solution having a Baumé gravity in the range from about 30° to 50° Baumé, but solutions of lower strengths may be used under some conditions. An aqueous solution of sodium hydroxide from 40° to 50° Baumé has been found to give satisfactory results in the practice of the present invention. Other alkali metal hydroxides besides sodium hydroxide may be used. For example, lithium and potassium hydroxides may be used in lieu of sodium hydroxide, but the latter is to be preferred.

The temperature at which the treating operation is conducted will usually be atmospheric temperature and may be in the range from about 60° up to about 200° F. Under some conditions higher temperatures may be employed depending on the boiling range and type of feed stock being treated. Of course, it will be understood that pressure may be superimposed on the vessel in which the treating is taking place to maintain the hydrocarbon in the liquid phase and to prevent evaporation of water from the solution of alkali metal hydroxide. A preferred temperature range may be from about 70° to about 95° F. Satisfactory results have been obtained at atmospheric temperatures encountered in the Texas Gulf Coast area.

The process of the present invention may be conducted in various types of equipments. For example, the contacting operation may be conducted in incorporators, mixing devices, pumps, jet mixers and the like. It may be desirable to cause contact of the mixture of a petroleum distillate, alkali metal hydroxide and mild oxidizing agent in a suitable tower containing packing equipment to cause contact between the reagents and the distillate being sweetened. The skilled workman will find numerous contacting and mixing devices on the market and available in the modern petroleum refinery in which the process of our invention may be carried out. It is to be expressly understood that we do not wish to be limited to any specific apparatus for conducting the operation.

The present invention will be further illustrated by the following examples:

Example I

A sour petroleum distillate which had been freed of hydrogen sulfide and which boiled in the 350° to 540° F. boiling range was divided into two portions. One portion was contacted with an aqueous solution of 50° Baumé sodium hydroxide in the presence of 300% by volume of the theoretical amount of oxygen required to sweeten.

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The second portion was also contacted with 50° Baumé sodium hydroxide solution but the distillate had added to it, prior to contact with the sodium hydroxide, 0.5% of formamide based on the distillate. Similarly, it was contacted in the presence of 300% by volume of the theoretical amount of oxygen required to sweeten. In each instance the sodium hydroxide solution was separated from the treated distillate and the treated distillate was then tested for copper number.

The following table presents the results of the foregoing runs with column 1 presenting the data on the distillate treated with sodium hydroxide in the absence of formamide, whereas column 2 presents the results obtained when 0.5% by volume of formamide was present.

TABLE I

Treatment:

50° Bé. sodium hydroxide, percent	1.0	1.0
Oxygen, percent of theoretical	300	300
Formamide, volume percent	--	0.5
Copper No. before treat	40	40
Copper after treat:		
Immediately after	35	36
1 hour after	25	30
3 hours after	--	--
5 hours after	25	--
20 hours after	20	5

It will be seen from the data in the foregoing table that the addition of formamide to the sour distillate exerted a beneficial effect in promoting the sweetening. In the case where formamide was absent, the copper number of the treated product had been reduced from 40 to 20 after 20 hours after the treating operation had been conducted, whereas in the practice of the present invention the copper number was 5 after 20 hours of settling time, a four-four decrease in copper number over that obtained where the formamide was absent.

In each instance the copper number was determined immediately after the treat and after 1, 3, 5, and 20 hours settling time.

Example II

In this example a 40 copper number high sulfur refined oil fraction which had been freed of hydrogen sulfide was divided into nine portions. One portion was treated as is, while the remaining other portions had added to them different aliphatic and aromatic amides. The treats were conducted by contacting the high sulfur refined oil with 1% by volume of 50° Baumé sodium hydroxide solution in the presence of 300% by volume of the theoretical amount of oxygen required to sweeten. The amide was added to the hydrocarbon prior to contact in the amount of 0.5%. The conditions for the treats are summarized in Table II.

TABLE II

Caustic: 1.0 vol. % 50° Bé. NaOH
Oxygen: 300% Theoretical
Promoter: 0.5 vol. %
Hydrocarbon: A 40 copper number high sulfur refined oil
Following the treatment described the sodium hydroxide solution was separated from the contacted refined oil and tested for copper number after 0, 3, and 20 hours settling time. Table III which follows lists the promoters added and shows the copper number of the contacted oil

after the aforesaid settling times after the treating operation had been conducted.

TABLE III

Promoter	Copper Number After Settling		
	0 Hours	3 Hours	20 Hours
None	38	35	31
n-Butylamide	24		0.5
Propionamide	38		2
Acetamide	37	20	5
Isovaleramide	38		7
N-Butylbenzamide	38	30	10
N-Isopropylbenzamide	40	25	12
N-Ethylbenzamide	39	27	19
N-Methylbenzamide	38	28	20

It will be apparent that contacting the 40 copper number refined oil with 50° Baumé sodium hydroxide in the presence of 300% of theoretical oxygen required to sweeten resulted in a very slight reduction of copper number immediately after treatment and a total reduction after 20 hours of settling of only 7 copper numbers whereas n-butylamide and acetamide showed a reduction respectively from 24 to 0.5 and from 37 to 5. The reduction obtained when using the aromatic amides was not as great, reductions from 40 to 10, 12, and 19 being obtained respectively for N-butylbenzamide, N-isopropylbenzamide, and N-ethylbenzamide. These reductions, however, are appreciable and allow the obtaining of beneficial results.

In the foregoing example, the improvement obtained by the practice of the present invention has been illustrated by the copper number test. This is a well known analytical procedure 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 Co., Chicago, 1947. This test is a measure of the mercaptan sulfur content of the oil being tested.

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.

Although not described in the foregoing examples, it will be understood that the petroleum distillate, after treating in accordance with the present invention and separation from the alkali metal hydroxide solution, may be washed with water or aqueous solutions to remove any alkali metal hydroxide which may be entrained therewith.

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 ex-

ample, 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 other instances as much as 500% of the theoretical amount required to sweeten may be employed. 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 0.5 to 1% 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 small but effective catalytic amount of an amide and then contacting the sour distillate containing the amide with 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 amide is an aliphatic amide.

3. A method in accordance with claim 2 in which the aliphatic amide is normal butylamide.

4. A method in accordance with claim 2 in which the aliphatic amide is propyl amide.

5. A method in accordance with claim 2 in which the aliphatic amide is acetamide.

6. A method in accordance with claim 1 in which the amide is an aromatic amide.

7. A method in accordance with claim 6 in which the aromatic amide is N-butylbenzamide.

8. A method in accordance with claim 6 in which the aromatic amide is N-isopropylbenzamide.

9. A method for sweetening a sour petroleum distillate containing mercaptans and boiling below 750° F. which comprises adding to said distillate an amide in an amount in the range from 0.1 to 5% by volume based on said distillate and then contacting said sour petroleum distillate to which amide has been added with an aqueous

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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.

10. A method in accordance with claim 9 in which the amide is an aliphatic amide.

11. A method in accordance with claim 9 in which the amide is an aromatic amide.

12. A method for sweetening a sour petroleum distillate containing mercaptans and boiling below 750° F. which comprises adding to said sour petroleum distillate an amount of an aliphatic amide in the range from 0.1 to 5% by volume based on said distillate and then contacting the sour petroleum distillate to which amide has been added with a catalytic amount no more than 5% by volume based on said distillate of an aqueous solution of sodium hydroxide while adding a sufficient amount of a mild oxidizing agent to convert the mercaptans to disulfides and to obtain a sweetened distillate.

13. A method for sweetening a sour petroleum distillate containing mercaptans and boiling below 750° F. which comprises adding to said distillate an aliphatic amide in an amount in the range from 0.1 to 5% by volume based on said distillate, then agitating said sour petroleum distillate to which amide has been added with a catalytic amount in the range of 0.1 to 5% by volume based on said distillate of an aqueous

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solution of sodium hydroxide while adding a sufficient amount of air to convert the mercaptans to disulfides and to cause sweetening of said distillate, separating sodium hydroxide solution from said distillate, and recovering said contacted distillate.

14. A method in accordance with claim 13 in which the aliphatic amide is normal butyramide.

15. A method in accordance with claim 13 in which the aliphatic amide is propyl amide.

16. A method in accordance with claim 13 in which the aliphatic amide is acetamide.

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