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METHOD FOR SWEETENING 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.

It has also been known, in the prior art, to employ alcohols in a non-oxidative sweetening process in which small quantities of alcohol are added to the solutions of sodium hydroxide and to the petroleum distillate being sweetened to extract mercaptans from the sour hydrocarbons. In such processes the alcohol is either used as aqueous alcohol dissolved in the alkali metal hydroxide, or the alcohol is added to the caustic solution in large concentrations to provide a solvent which will remove the mercaptans

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in solution. Thus the prior art teachings have been to the effect in the employment of substantially anhydrous alcohol in conjunction with caustic or in the employment of alcohol in non-oxidative sweetening processes. Such art, on the face, would appear disadvantageous in obtaining a sweetened product in requiring expensive equipment in view of using large amounts of solvent or in not completely sweetening the product.

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 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 employed compounds such as phenol, amines and alcohols in sweetening processes in which alkaline solutions were used to treat sour naphthas. We have now found that improved results may be obtained in oxidative sweetening processes in which an alkali metal hydroxide is employed by adding a catalytic amount of pyridine to the sour distillate which is to be sweetened. Thus, in accordance with the present invention the foregoing objects may be achieved by adding pyridine to a sour petroleum distillate and then contacting the sour distillate to which pyridine has been added with a catalytic amount of a solution of an alkali metal hydroxide while maintaining in contact therewith 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. to which has been added a small amount of pyridine in catalytic quantity with a solution of an alkali metal hydroxide to form a mixture thereof and maintaining the mixture undergoing contacting in the presence of a mild oxidizing agent in an amount sufficient to sweeten said distillate, following which the alkali metal hydroxide is separated from the contacted distillates.

The pyridine may be employed in amounts based on the sour distillate varying from 0.1 to 5% by volume, with a preferred range of about 0.5 to 1% by volume. The pyridine is preferably added to the petroleum distillate, but may be added to the mixture of the alkali metal hydroxide and sour petroleum distillate undergoing the sweetening reactions.

The alkali metal hydroxide employed in the present invention preferably should be a solution of an alkali metal hydroxide. Preferably the solution should be an aqueous solution having a Baumé gravity in the range of from about 30° to about 50° Baumé, but solutions of lower strength may be used under some conditions. An aqueous solution of sodium hydroxide of 40° 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 range from about 60° F. up to 200° F. and sometimes higher temperatures may be employed depending on the boiling range and the type of feed stock being treated. 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 our invention may be carried out in suitable equipment which will allow contact of the sour distillate to which pyridine has been added with the alkali metal hydroxide and the mild oxidizing agent. For example, pumps, jet mixers, incorporators and contacting towers may be used. Such towers may be equipped with packing, bell cap trays and other similar well known expedients, for insuring contact between liquids and between liquids and gaseous material.

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

EXAMPLE I

A sour petroleum distillate boiling in the 350° to 540° F. boiling range was divided into two portions; one portion was contacted with a 50° Baumé sodium hydroxide solution in the presence of 300% of the theoretical amount of oxygen required to sweeten said sour distillate. The second portion had added to it 0.5% of pyridine and was likewise contacted with a solution of sodium hydroxide having a Baumé gravity of 50°. After the contacting operation, the sodium hydroxide solution was separated from the contacted distillate and the copper number of the contacted distillate, determined immediately and after 1, 3, 5, and 20 hours' settling time. The operation was conducted at substantially room temperature.

Pertinent information with regard to the amount of reagents employed and inspection data on the said naphtha before and after the

contacting operation are presented in the table which follows:

Table

Treatment:		
50° Bé. caustic, per cent-----	1.0	1.0
Oxygen, per cent of theoretical--	300	300
Pyridine, per cent-----	---	0.5
Copper No. before treat-----	65	65
Copper No. after treat:		
Immediately after-----	49	55
1 hour after-----	29	6
3 hours after-----	17	---
5 hours after-----	15	6
20 hours after-----	10	3

From the foregoing data it will be apparent that the copper number of the distillate without the addition of pyridine was lowered from 65 to 10 after 20 hours' setting time. On the other hand, the copper number of the distillate to which pyridine was added was reduced to 6 one hour after the treatment had been concluded and to 3 after twenty hours' settling time.

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.

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

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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.

It is to be understood that after separation of the alkali metal hydroxide solution the contacted naphtha may be washed with water, if desired, to remove any alkali metal hydroxide which may be entrained therein, although in most instances it will be unnecessary to treat the contacted naphtha with water or other aqueous solutions.

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 which comprises contacting a sour petroleum distillate boiling below 750° F. with a solution of an alkali metal hydroxide in the presence of pyridine and a mild oxidizing agent to obtain a sweetened distillate, said alkali metal hydroxide being present in an amount in the range of 0.1% to 5.0% by volume based on the sour petroleum distillate and said pyridine being present in an amount in the range of 0.1% to 5.0% by volume based on the sour petroleum distillate.

2. A method for sweetening a sour petroleum distillate boiling below 750° F. which comprises adding to said distillate an amount of pyridine in the range from 0.1 to 5% by volume based on said distillate, forming a mixture of an aqueous solution of an alkali metal hydroxide and said sour petroleum distillate to which pyridine has been added, and agitating the mixture in the presence of a mild oxidizing agent to obtain a

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sweetened distillate, said solution of alkali metal hydroxide being present in the mixture in an amount in the range of 0.1% to 5.0% by volume based on the sour petroleum distillate.

3. A method for sweetening a sour petroleum distillate boiling below 750° F. which comprises adding to said distillate an amount of pyridine in the range from 0.1 to 5% by volume based on said distillate, forming a mixture of an aqueous solution of sodium hydroxide and said sour petroleum distillate to which pyridine has been added, the aqueous solution of sodium hydroxide being present in the mixture in an amount in the range of 0.1% to 5.0% by volume based on the sour petroleum distillate, agitating the mixture in the presence of air to cause sweetening of said distillate, separating sodium hydroxide solution from said distillate and recovering said distillate.

4. A method for sweetening a sour petroleum distillate which comprises adding 0.5% by volume of pyridine to said sour petroleum distillate, forming a mixture of said sour petroleum distillate to which pyridine has been added with an aqueous solution of sodium hydroxide having a Baumé gravity of 50° A. P. I., the aqueous solution of sodium hydroxide being present in the mixture in an amount in the range of 0.1% to 5.0% by volume based on the sour petroleum distillate, agitating the mixture in the presence of air to cause sweetening of said distillate, separating said sodium hydroxide solution from said agitated distillate, and recovering said agitated distillate.

5. A method in accordance with claim 4 in which the amount of sodium hydroxide solution is 1% by volume based on the sour distillate.

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