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TREATMENT OF HYDROCARBON DISTILLATES

Robert H. Rosenwald, Western Springs, Ill., assignor to Universal Oil Products Company, Chicago, Ill., a corporation of Delaware

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This invention relates to the treatment of hydrocarbon distillates and more particularly to a novel method of effecting sweetening of sour hydrocarbon distillates.

One method of sweetening a sour hydrocarbon distillate and particularly cracked gasoline entails the use of a phenylene diamine compound. Because the phenylene diamine compound also serves as an oxidation inhibitor, this process is referred to as "inhibitor sweetening."

In one embodiment, the present invention is directed to a novel method of sweetening sour hydrocarbon distillates. In another embodiment, the present invention comprises an improvement in the inhibitor sweetening process using the phenylene diamine compound.

When employed in conjunction with the inhibitor sweetening, the present process offers the improvement of effecting sweetening of the sour hydrocarbon distillate in a shorter period of time. This accelerated sweetening is important to the refiner in many cases because, due to the shortage of storage capacity or in order to comply with shipping schedules or for other reasons, it is often necessary to transport or use the distillate promptly, and the refiner cannot afford to wait until sufficient time has elapsed for the distillate to become sweet.

In one embodiment the present invention relates to the method of sweetening a sour hydrocarbon distillate which comprises contacting said distillate in the presence of air with a hydrocarbon soluble organic basic compound free from the phenylene diamine configuration.

In a specific embodiment the present invention relates to the process of sweetening sour cracked gasoline which comprises contacting said gasoline in the presence of air with an organic basic compound selected from aliphatic polyamines, heterocyclic nitrogen compounds and quaternary ammonium compounds.

In still another specific embodiment the present invention relates to the method of sweetening sour cracked gasoline which comprises contacting said gasoline in the presence of air with N,N'-di-secondary-butyl-p-phenylene diamine and an organic basic compound selected from the group hereinbefore set forth.

The organic basic compound for use in accordance with the present invention is free from the phenylene diamine configuration. It has been found that these organic basic compounds will serve to effect inhibitor sweetening of sour hydrocarbon distillates in the presence of air. As hereinbefore set forth, in another embodiment, the organic basic compound free from the phenylene diamine configuration may be used in conjunction with the phenylene diamine compound, and the use of these two compounds will serve to produce improved results over the use of the phenylene diamine compound alone.

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Any suitable organic basic compound which is soluble in the hydrocarbon distillate may be used in accordance with the present invention. A preferred type of compound comprises heterocyclic nitrogen compounds including pyridine, piperidine, picoline, lutidine, quinoline, isoquinoline, pyrrole, pyrazole, indole, carbazole, acridine, etc. Another preferred type of compound comprises the quaternary ammonium compounds including tetrabutyl ammonium hydroxide, tetramyl ammonium hydroxide, tetrahexyl ammonium hydroxide, tetraheptyl ammonium hydroxide, tetraoctyl ammonium hydroxide, tetrapropyl ammonium methoxide, tetrabutyl ammonium methoxide, tetramyl ammonium methoxide, tetrahexyl ammonium methoxide, tetraheptyl ammonium methoxide, tetraoctyl ammonium methoxide, tetraethyl ammonium ethoxide, tetrapropyl ammonium ethoxide, tetrabutyl ammonium ethoxide, tetramyl ammonium ethoxide, tetrahexyl ammonium ethoxide, tetraheptyl ammonium ethoxide, tetraoctyl ammonium ethoxide, tetramethyl ammonium propoxide, tetraethyl ammonium propoxide, tetrapropyl ammonium propoxide, tetrabutyl ammonium propoxide, tetramyl ammonium propoxide, tetrahexyl ammonium propoxide, tetraheptyl ammonium propoxide, tetraoctyl ammonium propoxide and similarly substituted tetraalkyl ammonium butoxides, pentoxides, hexoxides, heptoxides, octoxides, etc., as well as benzyl trialkyl ammonium hydroxides and alkoxides, particularly benzyl trimethyl ammonium propoxide, benzyl trimethyl ammonium butoxide, benzyl triethyl ammonium butoxides, benzyl tributyl ammonium butoxide, etc. Another suitable class of organic basic compounds includes the aliphatic amines such as propylamine, butylamine, amylamine, hexylamine, heptylamine, octylamine, dimethylamine, diethylamine, dipropylamine, dibutylamine, diamylamine, dihexylamine, diheptylamine, dioctylamine, trimethylamine, triethylamine, tripropylamine, tributylamine, triamylamine, trihexylamine, triheptylamine, trioctylamine, trimethylene diamine, tetramethylene diamine, ethylene diamine, diethylene triamine, triethylene tetramine, tetraethylene pentamine, etc.

It is understood that the various organic basic compounds which may be used in accordance with

the present invention are not necessarily equivalent. Furthermore, the particular compound selected must be soluble in the amounts to be used in the particular hydrocarbon distillate treated. It is believed that these organic basic compounds function catalytically to accelerate the conversion of mercaptans to products containing disulfides and, therefore, will be effective in low concentrations. The concentration of organic basic compound will be from about 0.0001% to 1% or more and preferably from about 0.001% to about 1% by weight of the hydrocarbon distillate.

Because the inhibitor sweetening reaction comprises the conversion of mercaptans to disulfides, presumably through an oxidation reaction, it is also essential that air be present in the reaction. The amount of air should be sufficient to effect the desired oxidation. In most cases air dissolved or entrained in the hydrocarbon distillate will be sufficient to effect the desired oxidation. In other cases it may be necessary to introduce air from an extraneous source, particularly when the distillate is stored in tanks having floating roofs which serve to exclude air. It is understood that oxygen or other oxygen-containing gases may be used in place of air.

As hereinbefore set forth, the organic basic compound may be used in conjunction with the phenylene diamine compound. The preferred phenylene diamine compound comprises N,N'-di-secondary-butyl-p-phenylene diamine. Other suitable phenylene diamine compounds include N,N'-di-isopropyl-p-phenylene diamine, N,N'-di-secondary-amyl p-phenylene diamine, N-isopropyl - N' secondary - butyl - p - phenylene diamine, N - isopropyl - N' - secondary - amyl - p - phenylene diamine, N - secondary - butyl - N' - secondary - amyl - p - phenylene diamine, etc. It is understood that other substituted phenylene diamines in which one or more alkyl radicals are substituted for the amino hydrogens or are attached to the phenyl rings, these alkyl radicals being the same or different, are comprised within the scope of the present invention but not necessarily with equivalent results. The phenylene diamine compound may be utilized in a concentration of from about 0.0001% to about 0.5% by weight of the hydrocarbon distillate and preferably of from about 0.0005% to about 0.05% by weight.

The use of the organic basic compound of the present invention in combination with the phenylene diamine compound offers numerous advantages over the use of the phenylene diamine compound alone. In the first place, the amount of phenylene diamine compound to be employed may be less than that required in the absence of other organic basic compound. In the second place, the use of these two types of compounds may exert a peculiar effect on the inhibitor sweetening reaction which is not obtained through the use of the phenylene diamine compound alone, and this may serve to effect inhibitor sweetening of some hydrocarbon distillates which do not respond to the use of phenylene diamine compound alone. Furthermore, the use of the mixture of compounds may serve to effect sweetening within a shorter time than otherwise obtained through the use of the phenylene diamine compound alone.

The process of the present invention may be effected in any suitable manner whereby the hydrocarbon distillate is intimately contacted with the organic basic compound. In a preferred method the organic basic compound is commingled with the hydrocarbon stream and the resultant mixture is passed through suitable mixing devices such as duriron mixers, orifice mixers, etc. The resultant mixture is then introduced into a storage tank which may contain suitable stirring means such as mixing paddles, etc., to effect further mixing of the components therein. If sufficient air is not contained in the hydrocarbon distillate, air may be introduced directly into the storage tank or it may be supplied to the stream of hydrocarbon distillate before or after mixing within the organic basic compound. When employed, the phenylene diamine compound may be introduced into the hydrocarbon before it is mixed with the organic basic compound or it may be introduced after such mixing.

The sweetening of the present invention is readily effected at atmospheric temperature which generally ranges from about 50° to about 90° F. However, in some cases, it may be desirable to utilize temperatures which may range up to 125° or more.

While this process is particularly applicable for the treatment of cracked gasoline, it is understood that with suitable modifications the process may be utilized for the treatment of straight run gasoline and cracked or straight run higher broiling hydrocarbon distillates, including kerosene, diesel fuel, gas oil, etc.

The following examples are introduced to illustrate further the novelty and utility of the present invention but not with the intention of unduly limiting the same.

Example I

A Pennsylvania thermally cracked gasoline containing about 0.025% by weight of mercaptan sulfur after 6 days in storage at 75° F. had a mercaptan sulfur content of 0.015%.

0.03% by weight of benzyl trimethyl ammonium butoxide was dissolved in another sample of the gasoline and, after 6 days in storage at 75° F., the mercaptan sulfur content was 0.0014%.

When 0.03% by weight of benzyl trimethyl ammonium hydroxide and 0.01% by weight of N,N' - di - secondary - butyl - p - phenylene diamine were added to another sample of the gasoline, the gasoline became sweet within 3 days in storage.

Example II

The hydrocarbon distillate used in this example was a polymer gasoline containing 0.025% by weight of mercaptan sulfur. After storage for 6 days at 75° F., the mercaptan sulfur content was 0.023% by weight.

Upon the addition of 0.03% by weight of benzyl trimethyl ammonium hydroxide to another sample of the gasoline, the mercaptan sulfur content was reduced to 0.003% after 4 days in storage at 75° F. and was sweet after 5 days in storage.

Example III

A thermally cracked gasoline having a mercaptan content of 0.007% by weight may be treated with 0.05% by weight of piperidine at a temperature of 100° F.

Example IV

Cracked light gas oil having a mercaptan content of about 0.006% by weight may be sweetened by treatment with 0.15% by weight of pyridine at a temperature of 90° F.

Example V

Cracked gasoline having a mercaptan sulfur content of 0.008% by weight may be treated with 0.04% by weight of piperidine and 0.002% by weight of N,N'-di-secondary-butyl-p-phenylene diamine at a temperature of 80° F.

I claim as my invention:

1. The method of sweetening a sour hydrocarbon distillate which comprises contacting said distillate in the presence of air with a phenylene diamine sweetening agent and a hydrocarbon soluble organic base compound selected from the group consisting of aliphatic polyamines, heterocyclic nitrogen compounds and quaternary ammonium compounds.

2. The method of sweetening a sour cracked hydrocarbon distillate which comprises contacting said distillate in the presence of air with a phenylene diamine sweetening agent and a hydrocarbon soluble aliphatic amine and maintaining said distillate in storage until it becomes substantially sweet.

3. The method of sweetening a sour hydrocarbon distillate which comprises contacting said distillate in the presence of air with a phenylene diamine sweetening agent and a hydrocarbon soluble heterocyclic nitrogen compound and maintaining said distillate in storage until it becomes substantially sweet.

4. The method of sweetening a sour hydrocarbon distillate which comprises contacting said distillate in the presence of air with a phenylene diamine sweetening agent and a hydrocarbon soluble quaternary ammonium compound.

5. The method of sweetening sour cracked gasoline which comprises contacting said gasoline in the presence of air with a phenylene diamine sweetening agent and a hydrocarbon soluble organic basic compound selected from the group consisting of aliphatic polyamines, heterocyclic nitrogen compounds and quaternary ammonium compounds at a temperature of from about 50° to about 125° F.

6. The method of sweetening sour cracked gasoline which comprises commingling a phenylene diamine sweetening agent and from about 0.001% to about 1% by weight of a hydrocarbon soluble aliphatic amine with said gasoline, and maintaining the resultant mixture in storage at a temperature of from 50° to about 125° F. until the gasoline is substantially sweet.

7. The method of sweetening sour cracked gasoline which comprises commingling a phenylene diamine sweetening agent and from about 0.001% to about 1% by weight of diethylene triamine with said gasoline, and maintaining the resultant mixture in storage at a temperature of from 50° to about 125° F. until the gasoline is substantially sweet.

8. The method of sweetening sour cracked gasoline which comprises commingling a phenylene diamine sweetening agent and from about 0.001% to about 1% by weight of a hydrocarbon soluble heterocyclic nitrogen compound with said gasoline, and maintaining the resultant mixture in storage at a temperature of from 50° to about 125° F. until the gasoline is substantially sweet.

9. The method of sweetening sour cracked gasoline which comprises commingling a phenylene diamine sweetening agent and from about 0.001% to about 1% by weight of piperidine with said gasoline, and maintaining the resultant mixture in storage at a temperature of from 50° to about 125° F. until the gasoline is substantially sweet.

10. The process of claim 9 further characterized in that from about 0.0001% to about 0.5% by weight of N,N'-di-secondary-butyl-p-phenylene diamine is added to the gasoline as said sweetening agent.

11. The method of sweetening sour cracked gasoline which comprises commingling a phenylene diamine sweetening agent and from about 0.001% to about 1% by weight of pyridine with said gasoline, and maintaining the resultant mixture in storage at a temperature of from 50° to about 125° F. until the gasoline is substantially sweet.

12. The process of claim 11 further characterized in that from about 0.0001% to about 0.5% by weight of N,N'-di-secondary-butyl-p-phenylene diamine is added to the gasoline as said sweetening agent.

13. The method of sweetening sour cracked gasoline which comprises commingling a phenylene diamine sweeting agent and from about 0.001% to about 1% by weight of a hydrocarbon soluble quaternary ammonium compound with said gasoline, and maintaining the resultant mixture at a temperature of from 50° to about 125° F. until the gasoline is substantially sweet.

14. The method of sweetening sour cracked gasoline which comprises commingling a phenylene diamine sweetening agent and from about 0.001% to about 1% by weight of benzyl trimethyl ammonium butoxide with said gasoline, and maintaining the resultant mixture at a temperature of from 50° to about 125° F. until the gasoline is substantially sweet.

15. The process of claim 14 further characterized in that from about 0.0001% to about 0.5% by weight of N,N'-di-secondary-butyl-p-phenylene diamine is added to the gasoline as said sweetening agent.

16. The method of sweetening sour cracked gasoline which comprises commingling a phenylene diamine sweetening agent and from about 0.001% to about 1% by weight of benzyl trimethyl ammonium pentoxide with said gasoline, and maintaining the resultant mixture at a temperature of from 50° to about 125° F. until the gasoline is substantially sweet.

ROBERT H. ROSENWALD.

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