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OXIDATION OF MERCAPTANS

Peter Urban, Jr., Chicago, Ill., assignor to Universal Oil Products Company, Chicago, Ill., a corporation of Delaware

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This invention relates to the oxidation of mercaptans and more particularly to effecting this reaction in the presence of a particular class of compounds.

As is well-known, mercaptans are contained in various hydrocarbon fractions, including liquid fractions such as gasoline, kerosene, gas oil, diesel oil, heater oil, range oil, etc., as well as being contained in normally gaseous hydrocarbon fractions. The presence of mercaptans is objectionable in these fractions for a number of reasons, including undesirable odor, corrosiveness, etc.

In one embodiment the present invention relates to a method of oxidizing a mercaptan to a disulfide which comprises reacting the mercaptan with an oxidizing agent in the presence of an organo-metallic compound.

In a specific embodiment the present invention relates to a method of oxidizing a mercaptan contained in gasoline which comprises reacting said mercaptan with oxygen in the presence of a basic reagent and an organo-metallic compound.

As hereinbefore set forth the mercaptans generally will be contained in a hydrocarbon fraction and usually will be present in a small concentration. When the original mercaptan content of the hydrocarbon fraction is substantial, it generally is preferred to treat the hydrocarbon fraction by means of a suitable alkaline material, including sodium hydroxide, potassium hydroxide, etc., with or without a solutizer, including phenols, cresols, xlenols, isobutyric acid and salts thereof, alcohols and particularly methanol, etc., in order to remove a major proportion of the mercaptans. However, it generally is difficult to remove the final traces of mercaptans, and the present invention is of particular advantage to convert the remaining mercaptans into disulfides and thereby to produce a sweet hydrocarbon fraction.

Air or other suitable source of oxygen is present in order to effect oxidation of the mercaptans to disulfides. In some cases air dissolved or entrained in the hydrocarbon fraction will be sufficient to effect the desired oxidation. In other cases it may be preferred to introduce air from an extraneous source, particularly when the distillate is stored in tanks having floating roofs which serve to exclude air. While air is preferred, it is understood that other suitable oxidizing agents may be employed including oxygen, ozone, hydrogen peroxide, etc.

The oxidation of mercaptans is generally facilitated by the presence of a basic reagent and, in a preferred embodiment of the invention, the oxidation is effected in the presence of a basic reagent. Any suitable basic reagent may be employed. The basic reagent may be inorganic and include sodium hydroxide, potassium hydroxide, etc., or these reagents containing a solutizer as hereinbefore set forth. In some cases the pretreatment of the hydrocarbon fraction with the basic reagent will leave a small amount of basic reagent entrained in the gasoline, and the small amount may be sufficient for the present purpose. In addition to or in the place of the inorganic basic reagents, suitable organic basic reagents may be employed including, for example, heterocyclic

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nitrogen compounds such as pyridine, piperidine, picoline, lutidine, quinoline, pyrrole, pyrazole, indol, carbazole, acridine, etc., quaternary ammonium compounds including tetraalkyl ammonium compounds, and particularly tetrabutyl ammonium hydroxide, tetraamyl ammonium hydroxide, etc., tetrapropyl ammonium methoxide, tetrabutyl ammonium methoxide, tetraamyl ammonium methoxide, etc., tetraethyl ammonium ethoxide, tetrapropyl ammonium ethoxide, tetramethyl ammonium propoxide, tetraethyl ammonium propoxide, tetrapropyl ammonium propoxide, etc., and similar tetra-substituted ammonium pentoxides, hexoxides, heptoxides, octoxides, etc., as well as benzyl trialkyl ammonium hydroxides and alkyl oxides, etc. Other organic basic compounds include the aliphatic amines such as propyl amine, butyl amine, amyl amine, etc., dimethyl amine, diethyl amine, dipropyl amine, etc., trimethyl amine, triethyl amine, tripropyl amine, etc., trimethylene diamine, tetramethylene diamine, ethylene diamine, diethylene triamine, triethylene tetramine, tetraethylene pentamine, etc. It is understood that mixtures of the inorganic basic reagents, mixtures of the organic basic compound, and/or mixtures of the organic basic reagent or reagents and mixtures of the organic basic compound or compounds may be employed.

It generally is preferable to also utilize a phenylene diamine compound and particularly an N,N'-dialkyl-p-phenylene diamine which has been found to facilitate oxidation of mercaptans to disulfides. Of the phenylene diamines, N,N'-di-secondary-butyl-p-phenylene diamine is preferred. 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 generally will be used in a concentration of from about 0.0001% to about 0.5% by weight of the hydrocarbon fraction and preferably of from about 0.0005% to about 0.05% by weight.

In accordance with the present invention, oxidation of mercaptans to disulfides is effected in the presence of an organo-metallic compound. The organo-metallic compound may comprise any suitable hydrocarbon soluble organo-metallic compound. Preferred metals comprise cobalt, chromium, copper, iron, manganese, nickel and vanadium. These metals may be utilized as salts of high molecular weight organic acids including the palmitates, stearates, oleates, naphthenates, etc.

In another embodiment the organo-metallic compound may comprise a chelated compound, including the metal chelates of the condensation product of an orthohydroxyaromatic compound with a suitable nitrogen compound. The ortho-hydroxyaromatic aldehyde may be substituted with alkyl, nitrogen, sulfur, oxygen, halogen, alkyl groups containing nitrogen, sulfur or oxygen, or mixtures of these groups. Particularly preferred chelated compounds include salicylalalalkyl diamines as disalicylal-diamino-ethane, disalicylal-diamino-propane, disalicylal-diamino-butane, disalicylal-diamino-pentane, disalicylal-dipropylene diamine, etc. Other satisfactory chelated compounds include metal chelates of the condensation product of salicylaldehyde with an o-aminophenol. Still other satisfactory compounds comprise ortho-hydroxyaromatic oxines, including salicylaloxine, etc., the tetrametal salts of ethylene diamine tetraacetic acid and similar compounds.

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In some cases the use of the metal in a form other than the chelated form as, for example, the metal oleate, naphthenate, etc., may be objectionable as regards to certain other properties of the hydrocarbon fraction. In another embodiment of the invention, metal added in such other manner may be rendered unobjectionable by commingling a chelating compound with the hydrocarbon fraction after the oxidation of the mercaptans has progressed to the desired extent. The chelating compound may be one or more of those hereinbefore set forth prior to actual chelating with the metal, or any other suitable compound may be used for this purpose. In still another embodiment, the hydrocarbon fraction after oxidation of the mercaptans but containing metals not chelated may be treated in any suitable manner to remove the metals such as, for example, by passing the hydrocarbon fraction through a bed of suitable solid adsorbent including clay, alumina, etc., or by extracting with a suitable liquid which will selectively remove the metal.

The amount of organo-metallic compounds to be employed will vary with the concentration of mercaptans in the hydrocarbon fraction being treated. It is believed that the organo-metallic compounds act in a catalytic manner to catalyze the oxidation reaction and, therefore, will be required only in small amounts. It has been found that, with certain hydrocarbon fractions, the use of the organo-metallic compound in a concentration of one milligram per liter of gasoline is satisfactory. Generally an excess of organo-metallic compound will be utilized in order to insure complete effect thereof. However, too large an excess of organo-metallic compound preferably is not employed because of possible objections for other reasons, as hereinbefore set forth, and, therefore, the organo-metallic compound generally will be used in a concentration of from about 0.000001% to about 0.1% by weight and, in some cases, higher concentrations may be employed.

Oxidation of the mercaptans may be effected in any suitable manner. The exact method of oxidation will depend upon the particular fraction being treated. When treating a liquid fraction, the liquid fraction may be introduced into a suitable vessel, to which the organo-metallic compound has been added either prior to, concurrent with or after passing the fraction into the vessel. When employed, the basic reagent, which may be inorganic and/or organic, is introduced into the vessel either before, concurrent with or after the introduction of the hydrocarbon fraction. Similarly, air may be introduced concurrently with, prior to or after introduction of the hydrocarbon fraction. In one method, the mixture in the vessel may be stirred in any suitable manner in order to obtain intimate mixing of the components of the mixture. In one method this mixing may be obtained by suitable rotating blades, or the mixture may be continuously pumped out and back into the vessel. In still another method, the air or other oxygen-containing gas may be introduced in a manner to effect intimate mixing of the hydrocarbon and organo-metallic compound. In some cases, the vessel may contain baffles, perforated decks, etc. in order to insure thorough mixing.

Batch type mixing is preferred, although it is understood that a continuous process may be employed. The time of mixing again will vary with the mercaptan content of the particular hydrocarbon fraction being treated and may range from 10 minutes or lower to 10 days or more. However, as hereinbefore set forth, the presence of the organo-metallic compound will facilitate the oxidation of the mercaptans, and the time required to effect the oxidation will be less than that necessary in the absence of the organo-metallic compound.

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.

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Example I

Mid-Continent thermally cracked gasoline was sweetened by treatment with caustic-methanol in order to reduce the mercaptan content to substantially zero. It was believed that more satisfactory control of the mercaptan content of the gasoline could be obtained by completely sweetening the gasoline and then adding mercaptan in a predetermined concentration. Thus to the sweetened gasoline, 0.02% by weight of normal butyl mercaptan was added. After two days in storage at room temperature in the presence of air, 89.2% of the mercaptan remained in the gasoline.

In a similar test in which N,N'-di-secondary-butyl-p-phenylene diamine was added in a concentration of 0.0125% by weight, the remaining mercaptans after two days in storage was 78.7%. Thus, it will be noted that the addition of this compound had a slight beneficial effect in the oxidation of the mercaptans.

In still another similar test, to another sample of the gasoline containing 0.02% by weight of normal butyl mercaptan, 0.0125% by weight of N,N'-di-secondary-butyl-p-phenylene diamine and 0.025% by weight of piperidine were added. After two days in storage, this sample contained 5.8% of mercaptans remaining. It will be noted that the addition of both the N,N'-di-secondary-butyl-p-phenylene diamine and piperidine served to considerably reduce the mercaptan content but that the percent of mercaptans still remaining is higher than desired.

To another sample of the gasoline containing 0.02% by weight of the butyl mercaptan, 0.0108% by weight of piperidine, manganese naphthenate in a concentration of 1 milligram of metal per liter of gasoline, and 0.0125% by weight of N,N'-di-secondary-butyl-p-phenylene diamine was added. After two days in storage, the mercaptan content of the gasoline was zero.

Example II

To another sample of the gasoline containing 0.02% by weight of normal butyl mercaptan described in Example I, cobalt in the form of cobalt naphthenate was added in a concentration of 1 milligram of metal per liter of gasoline, along with the same amount of piperidine and N,N'-di-secondary-butyl-p-phenylene diamine as described in Example I. After two days in storage the content was reduced to 0.0002% by weight.

Example III

To another sample of the gasoline containing butyl-mercaptan, piperidine and N,N'-di-secondary-butyl-p-phenylene diamine as described in Example II, cobalt naphthenate and disalicyl propylene diamine were added in a concentration of 1 milligram of metal per liter of gasoline. After two days in storage the mercaptan content of gasoline was reduced to zero.

As hereinbefore set forth, in the case of gasoline, another important factor is the peroxide number which is considered as a measure of the tendency of the gasoline to form gum in storage. As is well known, gum formation in gasoline is objectionable, and, therefore, it is preferred that the oxidation of the mercaptans is not accompanied by excessive increase in peroxide number.

The use of both the cobalt metal and disalicyl propylene diamine, thereby forming a metal chelate, resulted in the mercaptan content being reduced to substantially zero and a peroxide number of only 2.3. On the other hand the use of the cobalt naphthenate alone, while reducing the mercaptan content of the gasoline to a very low value, resulted in a peroxide number of 5.6. Therefore, when treating gasoline, the use of the chelated metal compound is preferred.

Example IV

The organo-metallic compound used in this example comprised iron oleate. When added to another sample of the gasoline, described in the previous examples, contain-

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ing butyl mercaptan, piperidine and N,N'-di-secondary-butyl-p-phenylene diamine, the addition of iron oleate in a concentration of 1 milligram of metal per liter of gasoline reduced the mercaptan content to 0.00029% by weight.

Example V

The organo-metallic compound used in this example was copper naphthenate. When added to another sample of the gasoline, described in the previous examples, containing the butyl mercaptan, piperidine and N,N'-di-secondary-butyl-p-phenylene diamine, the mercaptan content of the gasoline was reduced to substantially zero.

Example VI

The gasoline used in this example was a Mid-Continent thermally cracked gasoline which had been caustic treated to reduce the mercaptan content to substantially zero. 0.01% by weight of mercaptan as normal butyl mercaptan, 0.01% by weight of N,N'-di-secondary-butyl-p-phenylene diamine and 0.0001 gram of the cobalt chelate of disalicylal propylene diamine per 400 grams of gasoline were added. After 19 hours in storage, the mercaptan content was reduced to zero and the peroxide number was only 0.015.

I claim as my invention:

1. A method of oxidizing a mercaptan which comprises reacting the mercaptan with an oxidizing agent in the presence of a metal chelate and a phenylene diamine.

2. A method of oxidizing a mercaptan to a disulfide which comprises reacting the mercaptan with oxygen in the presence of a metal chelate and a phenylene diamine.

3. The process of claim 2 further characterized in that the metal of said chelate is selected from the group consisting of cobalt, iron, manganese, copper, nickel, vanadium and chromium.

4. The process of claim 3 further characterized in that said metal is manganese.

5. The process of claim 3 further characterized in that said metal is copper.

6. The process of claim 3 further characterized in that said metal is cobalt.

7. The process of claim 2 further characterized in that the metal compound is a chelate of a disalicylal polyamine alkane.

8. The process of claim 7 wherein said disalicylal polyamine alkane comprises disalicylal diamino propane.

9. A method of oxidizing a mercaptan contained in a hydrocarbon fraction which comprises reacting said mercaptan with oxygen in the presence of a metal chelate and a phenylene diamine.

10. A method of oxidizing a mercaptan contained in gasoline which comprises reacting said mercaptan with

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air in the presence of a basic reagent, a metal chelate and a phenylene diamine.

11. The process of oxidizing a mercaptan contained in gasoline which comprises reacting said mercaptan with air in the presence of a basic reagent, a phenylene diamine and a chelate of a disalicylal polyamine alkane and a metal selected from the group consisting of cobalt, iron, manganese, copper, nickel, vanadium and chromium.

12. The process of claim 11 further characterized in that said basic reagent comprises caustic.

13. A method of oxidizing a mercaptan contained in gasoline which comprises reacting said mercaptan with air in the presence of caustic, a phenylene diamine and a cobalt chelate of disalicylal diamino propane.

14. A method of oxidizing a mercaptan contained in gasoline which comprises reacting said mercaptan with air in the presence of caustic, a phenylene diamine and a manganese chelate of disalicylal diamino propane.

15. A method of oxidizing a mercaptan contained in gasoline which comprises reacting said mercaptan with air in the presence of caustic, a phenylene diamine and a copper chelate of disalicylal diamino propane.

16. A process which comprises treating a hydrocarbon fraction containing mercaptans with a basic reagent to remove a substantial portion of the mercaptans, and thereafter treating the gasoline with oxygen in the presence of a metal chelate and a phenylene diamine.

17. A process which comprises treating gasoline containing mercaptans with a caustic solution to remove a substantial proportion of the mercaptans, and thereafter treating the gasoline with air in the presence of a metal chelate of disalicylal diamino propane, caustic and an N,N'-dialkyl-p-phenylene diamine.

18. The process of claim 17 further characterized in that said N,N'-dialkyl-p-phenylene diamine comprises N,N'-di-secondary-butyl-p-phenylene diamine.

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