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METHOD OF REMOVING WEAKLY ACIDIC ORGANIC COMPOUNDS FROM PETROLEUM OILS

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This invention pertains to a process of removing weakly acidic organic substances from hydrophobe organic liquid mixtures and to a reagent useful in connection therewith. The process is more particularly concerned with the removal of weakly acidic organic sulfur compounds such as mercaptans or thio-alcohols from petroleum oils and to the sweetening of sour petroleum distillates.

It is common practice in the petroleum industry to remove weakly acidic sulfur compounds such as mercaptans from petroleum oils, particularly the lower boiling distillates such as gasoline, kerosene and furnace distillates, or to convert mercaptans into less objectionable compounds. The principal reasons for eliminating mercaptans from petroleum distillate is to effect an improvement in the odor and a reduction of the sulfur content of the distillate. The offensive odor imparted to petroleum distillates by relatively small quantities of mercaptans is a distinct detriment to the marketability of the gasoline. It has also more recently been established that the presence of organic sulfur compounds in motor fuels materially detracts from the antiknock quality of the fuels. This is particularly true when the motor fuels contain an antiknock agent such as tetraethyl lead, the amount of such agent required to produce a given antiknock rating in a motor fuel being substantially higher in those fuels of higher organic sulfur content.

By far the most widely used method heretofore for eliminating the offensive odor in sour or mercaptan bearing distillates has been to treat the distillates with a sodium plumbite or "doctor" solution. Although this method of treatment is satisfactory insofar as improvement of odor is concerned, it is open to several serious objections. In the first place, it is very difficult to control the amount of free sulfur used with the sodium plumbite solution to complete the doctor sweetening reaction and any excess of free sulfur causes the distillate to be corrosive and degrades the distillate in anti-knock properties. Furthermore, the sodium plumbite treatment does not remove the mercaptans but simply converts them to other organic sulfur compounds which are innocuous insofar as odor is concerned, but which are very detrimental to the anti-knock properties of the gasoline. It is apparent that the degrading influence of the original sulfur on the anti-knock properties has not been eliminated when it is understood that the same amount of sulfur or perhaps more, due to the possibility of an excess of sulfur having been added to complete the sodium plumbite treating operation, is still in solution in the distillate after completion of the treating operation.

Aqueous solutions of sodium hydroxide of various concentrations have also been used to remove weakly acidic organic sulfur compounds from petroleum distillates but are subject to the disadvantage that the weakly acidic sulfur compounds, particularly higher molecular weight alkyl mercaptans such as butyl and amyl mercaptans, are not removed or are only incompletely removed, the treated distillates continuing to possess an offensive odor and to be sour to the doctor test.

When aqueous alkali solution has been used to effect the removal of weakly acidic organic compounds from petroleum oils, the alkalinity of the caustic soda solution is reduced in proportion to the amount of acidic compounds extracted. The original alkalinity of the solution may frequently be substantially restored by steam stripping or boiling the used solution, whereupon the reaction products of the alkali and weakly acidic sulfur compounds hydrolyze to release free alkali and the original acidic organic compound, the weakly acidic organic compound passing overhead as such with steam. An example of such an operation is the steam stripping of aqueous sodium hydroxide solutions which have been used to remove alkyl mercaptans such as ethyl mercaptan, from gasoline. In the presence of water and at temperatures of the order of about 150° F. to 300° F., the hydroxide-mercaptan reaction product hydrolyzes to free sodium hydroxide and ethyl mercaptan, the ethyl mercaptan distilling from the aqueous sodium hydroxide solution. In this manner the restored or regenerated alkali solution may be used repeatedly, the loss of extraction efficiency on each regeneration cycle being relatively small.

It has now been found that alkali solutions containing dissolved thiophenolic compounds in which one or more sulfhydryl groups are attached to ring carbon atoms are particularly effective for removing weakly acidic organic compounds from hydrophobe organic liquids such as petroleum oils. The removal of weakly acidic organic sulfur compounds from petroleum oils may be so completely effected as to render the oils sweet to the doctor test.

It is an object of this invention to remove weakly acidic organic compounds from hydrophobe organic liquids.

It is another object of this invention to pro-

vide a method for the removal of mercaptans from petroleum oils.

It is a still further object of this invention to provide a novel treating reagent for desulfurizing hydrocarbon oils and a method for preparing the same.

Still another object of this invention is to provide a method of rendering sour hydrocarbon distillates sweet to the doctor test.

Other objects and advantages will be apparent from the following description.

In accordance with this invention it has been found that when alkali solutions, particularly aqueous alkali solutions, containing thiophenolic compounds are used for the treatment of hydrophobe organic liquids such as petroleum oils, the alkali reagents containing the thiophenolic compounds are much more effective for the removal of weakly acidic organic compounds than are plain alkali solutions of equivalent free alkali content. For a given free alkali content the extraction efficiency of such solutions increases rapidly as the concentration of thiophenolic compounds increases. While aqueous alkali solutions are preferred, there does not appear to be any reason why alcoholic alkali solutions may not also be used. In order to maintain the extraction efficiency of the treating reagent as high as possible, it is preferable to regenerate the reagent after use by heating and/or steam stripping in order to remove readily hydrolyzable components such as alkali alkyl mercaptides and then, if necessary, adding an additional amount of free alkali to restore the regenerated treating reagent to the desired content of free alkali. The reaction products of caustic alkali with thiophenolic compounds do not readily hydrolyze and, therefore, remain in solution in the form of alkali salts.

Thiophenolic compounds which are satisfactory adjuvants for improving the extraction efficiency of alkali solutions for extracting weakly acidic organic compounds from hydrophobe organic liquids include the broad class of compounds of which thiophenol, o-, m- and p-thiocresol, thionaphthol and thioxylenol are specific examples as well as aromatic compounds in which two or more sulfhydryl groups are attached to ring carbon atoms such as dithiocatechol; also compounds such as poly hydroxy phenols in which one or more but not all of the OH groups are replaced with SH groups such as mono thiocatechol. It is apparent that various individual thiophenolic compounds may be added to alkali solutions, preferably aqueous alkali solutions, or that a mixture of one or more of the various thiophenolic compounds may be used in the same solution. A mixture of different thiophenolic compounds is particularly appropriate if the desired concentration of compound is greater than the solubility of a particular compound which it may be desirable to use. In this case the use of two or more different compounds may permit a greater concentration of total dissolved compounds than if a single compound were used.

Satisfactory treating reagents may be prepared by simply dissolving one or more of the thiophenolic compounds of commerce or soluble metal salts thereof in alkali solution or by extraction of naturally occurring solutions which are substantially insoluble in aqueous alkali solution and which contain thiophenolic compounds. For example, thiophenols may be extracted from certain petroleum oils, such as cracked distillates from Van Zandt crude, with aqueous sodium hydroxide solution, the thiophenols forming soluble sodium salts which are not hydrolyzed under the usual conditions of steam stripping. This property may be utilized to separate any alkyl mercaptan-sodium hydroxide reaction products, which may be present, from the sodium salts of thiophenols as the former are readily hydrolyzed and removed by steam stripping. By using a given sodium hydroxide solution a plurality of times to extract thiophenols from oils containing them and then removing the alkyl mercaptans by boiling or steam stripping and evaporating water from or adding water to the solution as required, any desired concentration of thiophenols, up to a saturated solution, may be obtained. By carefully reducing the pH value of alkali solutions containing thiophenols until such solutions are just slightly acid, the thiophenols may be sprung from the solutions as readily separable oils and recovered as such. Such thiophenols may be used to fortify alkali treating reagents having a low content of thiophenols or may be used to prepare fresh treating reagents. It will be understood that the novel treating solution can be prepared by adding to water or alkali solution thiophenolic compounds or salts thereof and adjusting the alkalinity of the solution before or after addition of the salts by addition of the required amount of alkali.

In a specific example which is offered by way of illustration only, thiophenol, o-thiocresol, m-thiocresol and p-thiocresol were added to separate aqueous sodium hydroxide solutions. After dissolving the aforementioned thiophenols in aqueous alkali solutions, the alkalinity of the solutions was adjusted to 14.6% free alkali content. The concentration of the various thiophenols in the sodium hydroxide solutions was approximately 25% by weight of the solution in each case. The extraction efficiency of these solutions for the removal of mercaptan sulfur from untreated gasoline containing 0.0264% of mercaptan sulfur as compared with that of aqueous sodium hydroxide solution of equivalent sodium hydroxide content was tested. The gasoline was a mixture of cracked and straight run gasoline from Van Zandt and Schuler crude oils. The data obtained are shown in Table I:

Table I

Treating reagent	Mercaptan removed
	Percent
Sodium hydroxide solution	61
Sodium hydroxide solution with thiophenol added	78
Sodium hydroxide solution with o-thiocresol added	77
Sodium hydroxide solution with m-thiocresol added	88
Sodium hydroxide solution with p-thiocresol added	82

Each treatment consisted of the application of 10% by volume of treating reagent to a sample of gasoline and the gasoline and reagent contacted with mechanical agitation for a period of 15 minutes. After separation of the treating reagent and gasoline, the gasoline was washed with two consecutive water washes, each consisting of the application of 10% by volume of water. Fresh samples of treating reagents were used for each separate test. The data in Table I clearly show the superior extracting efficiency of the sodium hydroxide reagent containing thiophenol, o-, m- or p-thiocresol. The gasoline treated with the reagent containing m-thiocresol was subjected to two additional applications of fresh reagent of

the same composition whereupon the gasoline so treated was found to contain 0.0007% mercaptan sulfur and to be sweet to the doctor test. Five successive applications of fresh sodium hydroxide solution containing the same amount of free alkali to a separate sample of the same untreated gasoline reduced the mercaptan sulfur content to only 0.005%. The gasoline thus treated was decidedly sour to the doctor test. The odor of the sample of gasoline which was sweetened with three applications of the m-thiocresol reagent was materially better than that of the gasoline which had been treated with five successive applications of free alkali solutions. This result is in agreement with what might be expected in view of the results of the doctor tests on the treated samples. The gasoline used for illustration in Table I was hydrogen sulfide free and in general it is preferable to remove hydrogen sulfide prior to treatment with sodium hydroxide reagent in order to avoid the accumulation of sodium salts thereof, although the treating reagent is not limited in its application to hydrogen sulfide free oils.

That such results as are shown in Table I are not possible with ordinary phenols is shown in Table II.

Table II

Treating reagent	Mercaptan removed
	Percent
Sodium hydroxide solution	57
Sodium hydroxide solution with 26% phenol added	58
Sodium hydroxide solution with 38.7% phenol added	13

Gasoline, of the same type as used in the examples shown in Table I and containing 0.0252% of mercaptan sulfur, was treated for the same period of time, in the same manner and using the same concentration of free alkali in the treating reagents as in the examples of Table I. It is readily seen from the results indicated in Table II that 26% by weight of phenol (C_6H_5OH) when added to aqueous sodium hydroxide solution, produces substantially no improvement in extraction efficiency for removing mercaptans from gasoline. Increasing the amount of phenol added to 38.7% not only did not improve the extraction efficiency but actually reduced the extraction efficiency. These results emphasize the unusual results obtained in treating mercaptan bearing gasoline with sodium hydroxide solution to which thiophenolic compounds have been added.

While sodium hydroxide has been used in the specific examples given, solutions of various alkalis may be used. Other alkali metal hydroxides such as potassium hydroxide or mixtures of various alkali metal hydroxides are entirely satisfactory. The concentration of free alkali in the alkali solution may vary within rather wide limits although in general it is preferable to use solutions containing between approximately 10% and 40% by weight of caustic alkali. The amount of thiophenolic compounds present in the treating reagent is preferably above 5% by weight and best results have been obtained when the concentration of thiophenolic compounds is not less than approximately 15% by weight of the caustic alkali solution. The upper limit of concentration is determined by the solubility of the particular compound or mixture of compounds in the particular caustic alkali solution that is used. In general not over 90% saturation of the caustic alkali solution with thiophenolic compounds is preferred. Since it has been determined that the extraction efficiency decreases with increasing temperature, the extraction temperature is preferably maintained below approximately 120° F. Extraction temperatures below approximately 35° F. can be employed but are not preferred as such temperatures may be unsatisfactory due to possible precipitation from the treating reagent of dissolved thiophenolic compounds. The speed with which the treating reagent separates from the organic liquid being treated is ordinarily less at lower temperatures and, for this reason also, temperatures below approximately 35° F. may not be desirable.

The extraction of the weakly acidic organic compounds from organic liquids may be carried out in any one of a number of ways. Simple batch agitation may suffice or a more thorough extraction may be obtained in a multi-stage countercurrent extraction system. The amount of treating reagent used for the extraction operation is ordinarily above approximately 2% by volume of the liquid or oil treated and generally ranges from approximately 5% to 20% by volume although greater and lesser amounts may be used. Alkali treating reagent prepared in accordance with this invention, that is, alkali solution containing dissolved thiophenolic compounds or soluble metal salts thereof may simply be repeatedly used to extract weakly acidic material from organic liquids until the free alkali content of the treating reagent is below that at which satisfactory extraction efficiency is obtained or until the concentration of extracted materials is above that at which satisfactory extraction efficiency is obtained, and the solution then regenerated; or the free alkali content of such treating reagent may be restored periodically or after each treat by regenerating the used solution by heating and/or steam stripping then, if necessary, adding sufficient fresh caustic to raise the alkalinity to the desired concentration. In a multiple step counter-current treatment of oil with reagent, it is preferable to regenerate the reagent and restore its alkalinity after each cycle through the entire series of treating steps.

The process herein disclosed is applicable not only to cracked and straight run gasoline, but to other essentially water insoluble, neutral or basic organic liquids as well as other petroleum fractions such as kerosene, furnace distillate, crude oil and residual petroleum oil.

Throughout this specification and in the appended claims the words "thiophenolic compounds" are used to indicate generally one or more compounds of that class of aromatic compounds in which one or more sulfhydryl groups are attached to aromatic ring carbon atoms. The term "thiophenols" is used to indicate one or more compounds of that class of aromatic compounds in which one or more sulfhydryl groups are attached to aromatic ring carbon atoms in a single benzene ring. Whenever the term "thiophenol" is used, unless otherwise indicated, it refers to a specific chemical compound, namely, phenyl mercaptan, C_6H_5SH.

We claim:

1. A step in the process of removing weakly acidic organic compounds contained in water insoluble organic liquid which is otherwise neutral or basic comprising contacting said liquid with aqueous alkaline solution to which has been added a substantial quantity of thiophenolic compounds.

2. Method in accordance with claim 1 where the added compounds are thiophenols.

3. Method in accordance with claim 1 where the aqueous alkaline solution contains between approximately 10% and 40% free alkali metal hydroxide and the added thiophenolic compounds consist of not less than approximately 5% of thiophenols.

4. Method in accordance with claim 1 where the weakly acidic organic compounds are alkyl mercaptans.

5. Method in accordance with claim 1 where the added compound is thiophenol.

6. Method in accordance with claim 1 where the added compound is o-thiocresol.

7. Method in accordance with claim 1 where the added compound is m-thiocresol.

8. Method in accordance with claim 1 where the added compound is p-thiocresol.

9. A step in the process of sweetening hydrocarbon distillates containing mercaptan sulfur compounds comprising contacting said distillates with aqueous alkali metal hydroxide solution to which has been added not less than approximately 15% of a mixture of thiophenols.

10. Method in accordance with claim 9 where the added compounds include thiocresol.

11. Method of preparing a treating reagent useful in desulfurizing hydrocarbon oils comprising adding a substantial quantity of thiophenolic compounds to aqueous alkali metal hydroxide solution.

12. Method in accordance with claim 11 where the added compounds are not less than approximately 15% of thiophenols.

13. Method in accordance with claim 11 where the added compound is thiophenol.

14. Method in accordance with claim 11 where the added compound is thiocresol.

15. A step in the process of removing mercaptans from petroleum oils comprising contacting said oils with alkali metal hydroxide solution to which has been added a substantial quantity of thiophenolic compounds.

16. A step in the process of removing weakly acidic organic compounds contained in water insoluble organic liquid which is otherwise neutral or basic comprising contacting said liquid with aqueous alkali metal hydroxide solution containing thiophenolic compounds resulting from the reaction of alkali metal hydroxide and thiophenols in sufficient quantity to materially enhance the ability of said solution to remove said acidic compounds from said liquid.

17. The step in accordance with claim 1 in which the quantity of said thiophenolic compounds in said solution is not less than about 15% by weight calculated as thiophenols.

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