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METHOD FOR REMOVING ORGANIC ACIDIC SUBSTANCES FROM HYDROCARBON FLUIDS

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This invention relates to a method and reagent for removing weakly acidic substances from water immiscible liquid and more particularly to method and reagent for removal of mercaptans and other acidic organic sulfur compounds from hydrocarbon oils.

It is common practice in the petroleum refining industry to treat petroleum distillate, particularly cracked distillate, with alkali solutions in order to remove acid organic sulfur compounds such as mercaptans.

It is known that the efficacy of alkaline-reacting solutions in removing mercaptans from hydrocarbon liquids can be materially improved by adding to such solutions various compounds such as alkali salt of the more volatile members of the fatty acid series, for example, sodium or potassium isobutyrate. The use of such salts commonly known as solutizers has proved beneficial but the amount of mercaptans removed with these reagents is not as great as is frequently desired.

It has been found that excellent results may be obtained by the use of aqueous alkali solutions containing a cheap readily available material obtained in the course of low temperature, by-product, destructive distillation of carbonaceous materials such as coal. Such a material is high boiling tar oil or tar acid which has been treated in a particular manner as hereinafter set forth. The term "high boiling tar acid" as herein used refers to the heavy, oily liquid boiling above approximately 230° C. remaining after distillation of lower boiling components from the alkali soluble portion of coal tar light oils and coal tar middle oils. In the commercial destructive distillation of coal there is ordinarily obtained a dark liquid known as coal tar and which upon distillation produces oils of varying boiling ranges and a residual pitch. It is common practice to fractionate the oils obtained from the distillation of coal tar into several fractions known as light oil boiling up to about 200° C., middle oil boiling from about 200 to 250° C., and heavy oil boiling from about 300 to 350° C. In the course of refining these fractions, acidic materials are separated by treatment of the oils with aqueous alkali solution and from which the acidic products may be sprung by acidification. These acidic products are fractionated to obtain phenol and phenolic compounds boiling up to about 230° C. The remaining residual liquid boiling above about 230° C. forms what is known as high boiling coal tar oil or high boiling coal tar acids. The portion of this oil that reacts with aqueous alkali solution has been found unusually effective in increasing the extraction power of aqueous alkali solutions for removing organic acidic compounds from neutral or alkaline water-immiscible liquids.

It is an object of this invention to provide an improved method of removing organic acidic compounds, particularly sulfur compounds, from water-immiscible liquids such as hydrocarbon oils.

It is another object of this invention to provide a composition of matter which is highly usable in enhancing the ability of aqueous alkali solutions for removing organic acidic compounds, especially sulfur compounds, from water-immiscible liquids such as hydrocarbon oils.

When high boiling coal tar oil is treated with aqueous alkali solution a portion usually a predominant amount, of the oil reacts to form products soluble in the aqueous solution. It has been discovered that this portion of the high boiling coal tar oil which reacts with alkali and which is soluble in aqueous alkali solutions possesses superior properties for enhancing the ability of aqueous alkali treating reagents to extract weakly acidic organic compounds, for example, mercaptans from water-immiscible liquid such as hydrocarbon oil. Furthermore, such portions of the high boiling coal tar oil are greatly superior to fractions obtained by similar treatment of coal tar oils boiling below 230° C. and particularly between about 175° C. and 225° C.

As an illustration of my invention, high boiling coal tar acids obtained from the Reilly Tar and Chemical Company and produced by conventional commercial low temperature, by-product destructive distillation of coal was mixed with an equal volume of benzene and treated with a 10% aqueous sodium hydroxide solution. The amount of aqueous solution used was about 5 to 10 times the volume of the tar acids. The dilution of the tar acids with benzene prior to treatment with alkali solution was for the purpose of reducing the viscosity of the tar acids and facilitating the subsequent extraction with the aqueous alkali solution. The aqueous alkali solution containing alkali reaction products of the tar acids could have been used directly for the purpose of extracting mercaptans from petroleum oils, but in order to more accurately determine the amount of the reaction product being used in the various treating operations, the aqueous solution was acidified and the tar acid fraction sprung therefrom. The springing operation was accomplished in the presence of benzene to facilitate separation of the sprung tar acids from the acidified aqueous phase. The benzene was evaporated from the extracted portion of the tar acid and the residual acids thus obtained were added in carefully regulated portions to aqueous sodium hydroxide solutions of known concentration. The resulting aqueous alkali treating reagent was used in the amount of 7% by volume in treating separate samples of the same gasoline. The gasoline was a mixture of straight

run and cracked gasolines. In each case the treating reagent and gasoline were contacted for five minutes with vigorous shaking in a closed container in an atmosphere of nitrogen. The treated gasoline was subsequently separated from the treating reagent and analyses made for mercaptan sulfur content. The results of these tests are shown in Table I. The data are in per cent by weight.

Table I

No.	Wt. per cent composition of treating solution					Per cent RSH sulfur in gaso.		Per cent RSH sulfur removed
	NaOH	High boiling tar acids	Water	Cresols	Naph. acid	Untrt'd.	Trt'd.	
1	20	0	0	None	None	0.0184	0.0110	40.2
2	20	20	60	None	None	0.0200	0.0043	78.5
3	20	25	55	None	None	0.0200	0.0036	82.0
4	20	30	50	None	None	0.0200	0.0031	84.5
5	20	None	55	6.2	18.8	0.0200	0.0046	77.0

It will be seen from the results in Table I that the mercaptan extracting power of 20% aqueous sodium hydroxide solution is greatly increased by incorporating therein from 20 to 30% by weight of the high boiling coal tar acids. As a result of an extensive amount of work, it has been found that aqueous alkali solutions containing cresols and naphthenic acid are very efficient mercaptan extracting reagents for extracting mercaptans from petroleum oils. Reference to Table I, however, shows that 6.2% cresols and 18.8% naphthenic acid in 20% sodium hydroxide solution is not as effective in extracting mercaptans as is 20% aqueous sodium hydroxide solution containing either 20 or 25% of aqueous alkali soluble fraction of high boiling coal tar oil. Although the same large original sample of gasoline was used as a source of gasoline for the various individual treating operations carried out, the work on sample number 1 was conducted at a date appreciably after the work which was done on the other samples and the aging of the gasoline with concomitant oxidation of mercaptans undoubtedly accounts for the difference in the mercaptan sulfur content of the untreated gasoline of sample number 1 and the remaining samples.

Another series of tests were carried out to determine the relative efficacy of the alkali soluble portion of tar acids boiling between 175 and 230° C. as compared to the alkali soluble residual tar acids remaining after the aforementioned fraction had been removed by careful fractionation. Separate samples of another gasoline were treated by the same procedure as described in connection with the samples of Table I. The treating solutions all contained approximately the same proportion by weight of sodium hydroxide. The data obtained are shown in Table II.

Table II

Sample number	Boiling range of tar acids	NaOH	RSH sulfur removed
	°C.	*Per cent*	*Per cent*
1	175–230	20.1	64.1
2	Over 230	20.2	77.5
3		20.0	46.6

Samples 1 and 2 each contained 20% by weight of tar acids. Sample 3 is a straight sodium hydroxide solution. The data clearly show that while either the high boiling or low boiling tar acids enhance the ability of straight aqueous sodium hydroxide solution to remove mercaptans from gasoline, the high boiling tar acids are much more effective than the lower boiling tar acids boiling between 175 and 230° C.

The amount of the aqueous alkali soluble fraction of high boiling coal tar acids which may be used in alkali treating reagent may be varied between rather wide limits, depending upon such factors as temperature, concentration of alkali and the presence of other materials such as mercaptan solubility promoters which enhance the ability of aqueous alkali solution for extracting mercaptans from petroleum oils and which may affect the solubility of the tar oil fraction. In general, however, it is preferred to use not substantially less than 5% by weight of the high boiling tar acid fraction. Larger amounts of the tar acid fraction may be used ranging up to the maximum solubility thereof in the particular alkali treating reagent under consideration. The tar acid fractions may be dissolved in various aqueous alkali solutions although solutions of sodium or potassium hydroxide are preferred. In general, the mercaptan extracting powers of potassium hydroxide solution are greater than those of comparable sodium hydroxide solution but the original cost of the solution is considerably greater. The concentration of alkali in the aqueous treating reagent preferably ranges from approximately 5% by weight up to about 40% by weight although best results have been obtained when the concentration is above approximately 10% by weight. In referring to the concentration of alkali throughout this specification and in the appended claims it is intended that this shall refer to weight per cent of alkali in the reagent solution. The alkali content of the reagent as thus defined may be readily determined in these solutions by titration with standard acid solution to a phenolphthalein end point.

It will be apparent that in preparing treating reagents in accordance with this invention, the desirable high boiling tar acid fraction may be added as such or as the alkali compound thereof since the tar acid forms alkali compounds when dissolved in aqueous alkali solutions.

The specific examples given are only by way of illustration and are not intended to limit the invention to the specific quantities or to the particular materials named. Mixtures of various mercaptan solubility promoters may be used as well as the tar acid fraction alone. Treating solutions in accordance with this invention can be regenerated in the same manner as aqueous alkali solutions, namely, by boiling or by steam stripping and reusing the regenerated solution either with or without adjusting the alkali concentration and with or without further addition of tar acid and/or solutizers.

What is claimed is:

1. In a method for removing organic acidic substances from hydrocarbon fluids the step which comprises contacting said fluids with alkali solution containing a product prepared by separating from high boiling tar acids at least a portion thereof which reacts with aqueous alkali solution.

2. The step in accordance with claim 1 where the said product is present in the solution in an amount of approximately 20% to 30% by weight.

3. In a method for removing weakly acidic organic sulfur compounds from hydrocarbon liquids the step which comprises contacting said

liquids with aqueous reagent containing alkali metal hydroxide and a product prepared by reacting high boiling tar acids with sufficient aqueous alkali metal hydroxide solution to dissolve at least a portion of the tar acids and employing the dissolved portion as the said product.

4. In a method for removing weakly acidic organic sulfur compounds from hydrocarbon liquids the step which comprises contacting said liquids with aqueous reagent containing alkali metal hydroxide and product prepared by reacting high boiling tar acids with sufficient aqueous alkali metal hydroxide solution to dissolve at least a portion of the tar acids, separating and discarding the undissolved portion, acidifying the remaining solution whereby to spring dissolved acids and separating the acids thus obtained as said product.

5. The method for removing mercaptans from hydrocarbon oils which comprises contacting said oils with an aqueous alkali metal hydroxide solution containing at least 5% by weight of alkali and containing the reaction product of alkali metal hydroxide and high boiling tar acids in an amount sufficient to enhance the ability of said alkali metal hydroxide solution to extract acidic bodies from said fluids.

6. Method in accordance with claim 5 in which said solution contains at least 5% by weight of aqueous alkali-soluble, high boiling tar acids in the form of their alkali metal hydroxide reaction products.

7. Method in accordance with claim 5 in which the solution contains from 5 to 40% by weight of alkali and from 5% by weight up to the maximum amount soluble in the solution of aqueous alkali-soluble high boiling tar acids in the form of their alkali metal hydroxide reaction product.

8. The method of removing mercaptans from low-boiling hydrocarbon oils which comprises contacting said oils with an aqueous solution prepared by adding together approximately 20% by weight of sodium hydroxide, approximately 20–30% by weight of aqueous alkali-soluble high boiling tar acids and the balance water.

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