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METHOD OF REMOVING FROM HIGH-BOILING TAR ACIDS, BODIES WHICH IMPART COLOR TO WATER-WHITE HYDROCARBON LIQUIDS

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This invention relates to a method and reagent for removing weakly acidic bodies from water-immiscible organic fluids and is more particularly concerned with a method and reagent for removing mercaptans from petroleum oils.

In Patent No. 2,316,966 there is disclosed and claimed a method for removing acidic bodies from water-immiscible fluids by contacting such fluids with aqueous alkali solutions containing the reaction product of an alkali and high-boiling tar acids. We have found that high-boiling acids may cause difficulties when used in the extraction of mercaptans from gasoline and other petroleum distillates. These tar acids contain substances which impart to the gasoline or other oil which is treated therewith, objectionable color and cloudiness. Moreover, in certain instances, alkali solutions containing these tar acids become very viscous and even solidify at temperatures of 40° F. or lower, with the result that emulsion difficulties are encountered during use of such solutions. Gasoline treated with alkali solutions containing high-boiling tar acids may acquire an unpleasant odor. A further difficulty which is sometimes experienced is the interference with the analytical determination of the mercaptan sulfur content of the treated gasoline. Difficulty is experienced in determining the end point during the titration of the gasoline using the silver nitrate-ammonium thiocyanate titration method disclosed in the May 13, 1941 Analytical Edition of "Industrial and Engineering Chemistry," volume 13, page 298, in an article by Bell and Agruss entitled "Analytical procedure for mixtures of organic sulphur compounds."

We have discovered that all of the foregoing difficulties can be eliminated if aqueous alkali solutions of the high-boiling tar acids are blown with air or other free-oxygen containing gas for a sufficient period of time to convert the color-imparting bodies contained therein to products which are readily extractable therefrom by means of low-boiling hydrocarbons and then washing the blown solution with sufficient low-boiling hydrocarbons to remove the objectionable bodies therefrom.

An object of the invention is to provide an improved method for removing weakly acidic bodies from otherwise neutral organic water-immiscible fluids.

Another object of the invention is to provide a method for removing from high-boiling tar acids, constituents which are objectionable when tar acids are used as solubility promoters in alkali solutions to remove weakly acidic bodies such as mercaptans from hydrocarbon or other substantially neutral water-immiscible fluids.

A still further object of the invention is to provide an improved solubility promoter for use in extracting weakly acidic bodies from organic water-immiscible fluids.

Other objects of the invention will appear from the following description.

In the low-temperature, by-product, destructive distillation of coal, there is ordinarily contained a dark liquid called coal tar which upon distillation produces oils of different boiling ranges and a residual pitch. It is common practice in the coal-tar industry to distill coal-tar into several fractions; one being light oil, boiling up to about 200° C., another known as middle oil boiling from about 200 to 250° C., a third fraction known as heavy oil boiling from about 250 to 300° C., and a fourth fraction known as anthracene oil boiling from about 300 to 350° C. It is common practice to treat fractions with aqueous solutions to remove therefrom the acidic substances contained therein. The resulting aqueous alkali solution is neutralized with acid to recover the acidic substances extracted from the various oil fractions. The acidic substances are then fractionated to obtain various phenols, such as, phenol, cresols and one or more xylenols. In the fractionation, the separation is made between those constituents boiling below and above approximately 220° C. The residual liquid from the fractionation of the tar acids is the material herein referred to as "high-boiling tar acids" and shows the following distillation analysis:

	° C.
Initial boiling point	100
5% off	220
10% off	229
20% off	247
30% off	261
40% off	270
50% off	280
60% off	296
70% off	312
80% off	326
90% off	350
95% off	375
Dry point	400

A solution was prepared, using high-boiling tar acids made in the manner just set forth and obtained from the Reilly Tar & Chemical Corporation by mixing together 20% dry sodium hydroxide, 20% high-boiling tar acids and 60% of water, by weight. The resulting solution was not entirely homogeneous, but contained liquid or solid

material which had a shiny appearance. 300 cc. of Dubbs cracked gasoline from Texas crude oil was agitated with 7% by volume of the solution and the resulting gasoline was colored yellow-brown. The treating solution continued to impart the yellow-brown color to successive batches of gasoline. In addition, the gasoline was cloudy. An attempt was made to determine the mercaptan sulfur content by the silver nitrate-ammonium thiocyanate titration method, but considerable difficulty was experienced in determining the end point of the titration. Moreover, emulsion difficulties were encountered when an attempt was made to counter-currently contact gasoline with the treating solution in a counter-current contact tower.

A treating solution made as just described was contacted with another portion of the same gasoline in a counter-current treating tower in a ratio of 7.6 volumes of solution to 100 volumes of gasoline. The treated gasoline had a yellow-brown color and a bad odor. The treating solution was then regenerated by first diluting with water and boiling until the solution reached its original volume before dilution. Air was then blown through the solution for a period of approximately six hours while the temperature was maintained at about 160 to 170° F. The resulting solution was then washed with gasoline and again used to extract mercaptans from another sample of the same gasoline, using 7.6 volumes of treating solution to one hundred volumes of gasoline. The gasoline before treatment with the treating solution contained .088% by weight of mercaptan sulfur and .013% by weight of disulfide sulfur. After treatment with the solution, the gasoline contained .005% by weight of mercaptan sulfur and .012% by weight of disulfide sulfur. Not only was the solution extremely effective in removing mercaptans from the gasoline, but it did not cause oxidation of sulfur compounds to disulfide and it did not impart an objectionable odor or color to the gasoline.

In carrying out our invention, we prefer to prepare a treating solution containing alkali metal hydroxide and high-boiling tar acids, heat the solution to approximately 200–250° F. and preferably to approximately the boiling point thereof and blow air or other oxygen containing gas therethrough until the color-producing bodies in the solution are converted to a form where they are readily extractable therefrom with gasoline. When air is used, it will generally require from one to ten hours to complete the blowing. The sufficiency of the air-blowing can be determined by cooling a sample of the blown solution to atmospheric temperature and washing it thoroughly with 20 volumes of gasoline of good color. This washing should remove from the treating solution substantially all of the color-producing bodies if the blowing has been adequate. The washed gasoline is decanted from the treating solution and the treating solution is again mixed with a similar amount of gasoline to see if the gasoline goes off color. If the color of the second batch of gasoline is substantially unaffected, the blowing is sufficient. If the gasoline is discolored, the blowing must be continued.

Although we prefer to carry out the blowing of the treating solution at temperatures approximating the boiling temperature of the solution, the blowing may be conducted at lower temperatures ranging from approximately 150° F. upward. However, at lower temperatures, the length of the blowing required is considerably extended. Higher temperatures than the normal boiling temperature of the solution may be resorted to in the air-blowing operation if the operation is conducted under pressure. It may be necessary to add water to the solution from time to time during or at the end of the blowing operation to compensate for water which escapes with the air.

After it has been determined that the solution has been blown sufficiently, it is contacted with approximately 20 volumes of low-boiling hydrocarbons such as those boiling within the gasoline boiling range or liquid propane, butane or mixtures thereof, in order to extract the objectionable color-producing bodies from the treating solution. The solution is then ready to be used to treat water-immiscible liquids to remove weakly acidic bodies therefrom. The washing liquid can be recovered for further use by distillation and/or filtration through fuller's earth or similar adsorptive clay to remove the color bodies therefrom.

If desired after the blowing of the solution to convert the color-producing bodies into readily extractable constituents, instead of extracting these bodies from the blown solution in a separate step, the solution may be used in a treating operation without previous washing. In such case, the first portion of gasoline or other liquid treated, will extract the objectionable color bodies from the treating solution. This first portion may be segregated and separately treated if desired.

If the objectionable color-producing bodies are not removed from the treating solution or from the high-boiling tar acids, the treating solution continues to impart to the gasoline or other liquids to be treated, an objectionable color and odor for a long period of time; even after repeated regeneration of the treating liquid by means of steam or boiling with water.

Although for purposes of demonstrating the invention we used a solution made by mixing together 20% of sodium hydroxide, 20% of air blown high-boiling tar acids and water, the composition of the solution may vary within wide limits. In order to obtain appreciable removal of mercaptans from hydrocarbon oils the treating solution should contain at least 5% by weight of free alkali metal hydroxide, i. e. alkali metal hydroxide over and above that necessary to react with other constituents of the solution, and at least 5% by weight of high-boiling tar acids, but preferably in excess of 10%. Either sodium or potassium hydroxide or a mixture thereof may be used as the alkali metal hydroxide. Care should be exercised to keep the free alkali hydroxide concentration of the solution below the point at which the solution becomes so viscous as to cause emulsion difficulties during the treating steps. Free sodium hydroxide concentrations up to 20% by weight and free potassium hydroxide concentrations up to 25% by weight are satisfactory. The treated tar acids may be added to the solution as such or in the form of alkali metal salts. The tar acid content of the solution may extend up to the maximum amount which is compatible with the solution and will vary with the alkali concentration of the solution. Other solubility promoters such as phenols, particularly cresols, low boiling fatty acids and naphthenic acids may be used as components of the treating solution.

Treatment of gasoline and other hydrocarbon distillates by means of alkali solutions containing tar acids prepared in accordance with our

invention may take place at ordinary atmospheric temperature and preferably within the range of approximately 40–100° F. The ratio of treating solution to oil undergoing treatment will depend on the nature and amount of acidic bodies contained in the oils, but in general, a ratio of 5 to 20% of treating solution by volume based on the oil undergoing treatment can be used with good results. The treating solution can be regenerated by boiling or by stripping the absorbed acidic constituents therefrom by means of steam at temperatures of approximately 220–250° F.

It is claimed:

1. The method of preparing a treating agent for removing weakly acidic bodies from organic, water-immiscible liquids which comprises preparing a solution of high-boiling tar acids in aqueous alkali, and blowing the solution at elevated temperature with free oxygen-containing gas until the color-imparting bodies contained therein can be readily extracted with liquid-low-boiling hydrocarbons and extracting said color-imparting bodies therefrom by means of low boiling hydrocarbon liquid.

2. The method for preparing a treating agent for removing weakly acidic bodies from organic, water-immiscible liquids which comprises preparing a solution of high-boiling tar acids in aqueous alkali and blowing the solution with air at approximately the boiling temperature of said solution for a period of time ranging from 1 to 10 hours and extracting the resulting solution with liquid low boiling hydrocarbons.

3. The method of removing from high-boiling tar acids, bodies which impart color to water white hydrocarbon liquids comprising blowing said tar acids at elevated temperature, mixed with aqueous alkali metal hydroxide solution, with air until said solution no longer imparts substantial color to successive batches of said hydrocarbon liquids, contacting the blown solution with low boiling hydrocarbon liquid to extract oxidized color-imparting bodies and separating the extract from the said alkali metal hydroxide solution.

4. Method in accordance with claim 3 in which the solution is blown with air at approximately the boiling point of the solution.

5. The method of simultaneously removing color-imparting bodies from an aqueous alkali solution containing high boiling tar acids and removing mercaptans from low boiling-hydrocarbon oils which comprises contacting said oil with an aqueous solution containing free alkali hydroxide and high-boiling tar acids in sufficient amount to enhance the ability of said solution to extract mercaptan from said oil, said solutions having been air blown at temperatures of approximately the boiling point of the solution for a sufficient period of time to oxidize the color-imparting bodies therein to substances which are readily extractable therefrom with low-boiling liquid hydrocarbons.

6. The method of simultaneously removing color-imparting bodies from an aqueous alkali solution containing high boiling tar acids and removing mercaptans from hydrocarbons boiling within the gasoline range which comprises contacting said hydrocarbons with an aqueous solution containing not less than 5% by weight of free alkali metal hydroxide and not less than 10% by weight of high boiling tar acids, said solution having been blown at a temperature above 150° F. under sufficient pressure to keep it in liquid phase with air until the color-producing bodies contained therein can be removed by washing with 20 times its volume of gasoline boiling range hydrocarbons.

7. Method in accordance with claim 6 in which the solution is blown at a temperature of approximately 220–250° F.

8. Method in accordance with claim 3 in which the solution is blown with air at a temperature above 150° F. under sufficient pressure to keep the solution in liquid phase.

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