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(54) Method of decreasing acidity of crude oils and fractions

(57) Acidic crude oils and fractions thereof have their acidity decreased by treatment with one or more oxides of manganese.

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Description

FIELD OF THE INVENTION

[0001] The present invention relates to a process for decreasing the acidity and corrosivity of crudes and crude fractions containing petroleum acids.

BACKGROUND OF THE INVENTION

[0002] Many petroleum crudes with high organic acid content, such as whole crude oils containing naphthenic acids, are corrosive to the equipment used to extract, transport and process the crude, such as pipestills and transfer lines.

[0003] Efforts to minimize naphthenic acid corrosion have included a number of approaches. Examples of such technologies include use of oil soluble reaction products of an alkynediol and a polyalkene polyamine (U.S. Patent 4,647,366), and treatment of a liquid hydrocarbon with a dilute aqueous alkaline solution, specifically, dilute aqueous NaOH or KOH (U.S. Patent 4,199,440). U.S. Patent 4,199,440 notes, however, that the use of aqueous NaOH or KOH solutions that contain higher concentrations of the base form emulsions with the oil, necessitating use of only dilute aqueous base solutions. U.S. Patent 4,300,995 discloses the treatment of carbonous materials particularly coal and its products such as heavy oils, vacuum gas oil, and petroleum residua, having acidic functionalities, with a quaternary base such as tetramethylammonium hydroxide in a liquid (alcohol or water). Additional processes using bases such aqueous alkali hydroxide solutions include those disclosed in Kalichevsky and Kobe, Petroleum Refining With Chemicals, (1956) Ch. 4, and U.S. Patent 3,806,437; 3,847,774; 4,033,860; 4,199,440 and 5,011,579; German Patents 2,001,054 and 2,511,182; Canadian Patent 1,067,096; Japanese Patent 59-179588; Romanian Patent 104,758 and Chinese Patent 1,071,189. Publications WO 97/08270, WO 97/08271 and WO 97/08275 published March 6, 1997, collectively disclose treatment with overbased detergents and Group IA and IIA oxides and hydroxides to decrease acidity and/or corrosion. Certain treatments have been practiced on mineral oil distillates and hydrocarbon oils (e.g., with lime, molten NaOH or KOH, certain highly porous calcined salts of carboxylic acids suspended on carrier media). Whole crude oils were not treated.

[0004] U.S. Patents 2,795,532 and 2,770,580 (Honeycutt) disclose processes in which "heavy mineral oil fractions" and "petroleum vapors", respectively are treated, by contacting "flashed vapors" with "liquid alkaline material" containing, inter alia, alkali metal hydroxides and "liquid oil" using mixture of molten NaOH and KOH as the preferred treating agent, with "other alkaline materials, e.g., lime, also employed in minor amounts." The treatment of whole crudes or fractions boiling at 1050 plus °F (565^{+}°C) is not disclosed; only vapors and condensed vapors of the 1050 minus °F (565^{-}°C) fractions, that is, fractions that are vaporizable at the conditions disclosed in '532 are treated. Since naphthenic acids are distributed through all crude fractions (many of which are not vaporizable) and since crudes differ widely in naphthenic acid content the '532 patent does not provide an expectation that one would be able to successfully treat a broad slate of crudes of a variety of boiling points or to use bases other than NaOH and KOH.

[0005] U.S. 2,068,979 discloses a method for preventing corrosion in a petroleum still by adding calcium naphthenate to petroleum to react with and scavenge strong free acids such as hydrochloric and sulfuric acids to prevent corrosion in distillation units. The patent makes no claims with respect to naphthenic acids, which would have been formed when the strong acids were converted to salts. Patents have disclosed, inter alia, the addition or formation of calcium carbonate (Cheng et al, U.S. 4,164,472) or magnesium oxide (Cheng et al, US 4,163,728 and 4,179,383, and 4,226,739) dispersions as corrosion inhibitors in fuel products and lubricating oil products, but not in whole or topped crude oil. Similarly, Mustafaev et al (Sb. Tr., Azerb. Inst. Neft. Khim. (1971) 64-6) reported on the improved detergency and anticorrosive properties of calcium, barium, and zinc hydroxide additives in lubricating oils. Calcium hydroxide (Kessick, Canadian Patent 1,249,760) has been used to aid in separation of water from heavy crude oil wastes.

[0006] Finally, acetone is synthesized commercially by heating calcium acetate at appropriate conditions (see, e.g., Kirk-Othmer, Encyclopedia of Chemical Technology, First Edition, Vol. 1, page 89).

[0007] There is a continuing need to develop methods for reducing the acidity and corrosivity of whole crudes and fractions thereof, particularly residua and other 650^{+}°F (343^{+}°C) fractions. Applicants' invention addresses these needs.

SUMMARY OF THE INVENTION

[0008] The present invention provides for a method for decreasing the acidity and corrosivity of an acid-containing, corrosive crude by contacting a starting acid-containing, corrosive crude oil with an effective amount of at least one oxide of manganese to produce a treated crude oil having a decreased acidity and corrosivity. The treated crude contains naphthenate and ketone derivatives of the naphthenic acids. Water may be present in the crude or added or may be absent.

[0009] The present invention may suitably comprise, consist or consist essentially of the elements disclosed and may be practiced in the absence of an element not disclosed.

DETAILED DESCRIPTION OF THE INVENTION

[0010] Some whole crude oils contain organic acids such as carboxylic acids that contribute to corrosion or fouling of refinery equipment. These organic acids generally fall within the category of naphthenic and other organic acids. Naphthenic acid is a generic term used to identify a mixture of organic acids present in petroleum stocks. Naphthenic acids can cause corrosion at temperatures ranging from about 65°C (150°F) to 420°C (790°F). Naphthenic acids are distributed through a wide range of boiling points (i.e., fractions) in acid containing crudes. The present invention provides a method for broadly treating such acids, and most desirably from heavier (higher boiling point) and liquid fractions in which these acids are often concentrated. The naphthenic acids to be removed may be present either alone or in combination with other organic acids, such as phenols.

[0011] Whole crude oils are very complex mixtures in which a large number of competing reactions may occur. Thus, the potential for successful application of a particular treatment or process is not necessarily predictable from the success of other treatments or processes. Unexpectedly, the acid neutralization reactions described in the present invention occur although the acid is dilute in comparison to the large excess of crude and other reactive species typically present.

[0012] The process of the present invention has utility in processes in which inhibiting or controlling liquid phase corrosion, e.g., of metal surfaces, is desired. More generally, the present invention may be used in applications in which a reduction in the acidity, typically, as evidenced by a decrease in the neutralization number of the acidic crude or a decrease in intensity of the carboxyl band in the infrared spectrum at about 1708 cm^{-1} of the treated (neutralized) crude, would be beneficial and in which oil-aqueous emulsion formation and large solvent volumes are not desirable. Appearance of a band at 1600 cm^{-1} indicates the formation of carboxylate groups and at 1715 cm^{-1} of keto groups from the carboxylic acid groups. Thus, the treated crude contains naphthenate and, preferably ketone derivatives of the organic acids. The present invention also provides a method for controlling emulsion formation in acid crudes, by treating a major contributing component of such emulsions, naphthenic and similar organic acids, and by reducing the attendant handling and processing problems.

[0013] The concentration of acid in the crude oil is typically expressed as an acid neutralization number or total acid number (TAN), which is the number of milligrams of KOH required to neutralize the acidity of one gram of oil. It may be determined according to ASTM D-664. Typically, the decrease in acid content may be determined by a decrease in the neutralization number or in the intensity of the carboxyl band in the infrared spectrum at about 1708 cm^{-1}. Appearance of a band at 1600 cm^{-1} indicates the formation of a carboxylate salt and at 1715 cm^{-1} indicates formation of a keto group from the carboxylic acid groups. Crude oils with total acid numbers of about 1.0 mg KOH/g and lower are considered to be of moderate to low corrosivity (crudes with a total acid number of 0.2 or less generally are considered to be of low corrosivity). Crudes with total acid numbers greater than 1.5 are considered corrosive. The IR analysis is particularly useful in cases in which a decrease in neutralization number is not evident upon treatment with the base as has been found to occur upon treatment with bases weaker than KOH.

[0014] The crudes that may be used are any naphthenic acid-containing crude oils that are liquid or liquefiable at the temperatures at which the present invention is carried out. Typically the crudes have TAN of 0.2 to 10 mg KOH/g. As used herein the term whole crudes means unrefined, undistilled crudes.

[0015] The contacting is typically carried out at a temperature between 100°C and 350°C. Typically, this range is from 120 to 300°C, with narrower ranges suitably from about 150°C to 300°C, preferably 200°C to 300°C.

[0016] Corrosive, acidic crudes, i.e., those containing naphthenic acids alone or in combination with other organic acids such as phenols may be treated according to the present invention.

[0017] The acidic crudes are preferably whole crudes. However, acidic fractions of whole crudes such as topped crudes and other high boiling point fractions also may be treated. Thus, for example, 500°F (260°C) fractions, 650^{+}°F (343^{+}°C) fractions, vacuum gas oils, and most desirably 1050^{+}°F (565^{+}°C) fractions and topped crudes may be treated.

[0018] In the present invention the crude is contacted with an effective amount of at least one oxide of manganese at a temperature sufficient to produce a treated crude having a decreased acidity. The oxides include MnO, Mn_2O_3 and Mn_3O_4. The treatment may be carried out in the presence or absence of water as effective. When present water may be added or naturally occurring.

[0019] Reaction times depend on the temperature and nature of the crude to be treated, its acid content, but typically may be carried out for from less than about 1 hour to about 20 hours to produce a product having a decrease in corrosivity and acid content. The treated crude contains naphthenate salts of the corresponding oxide used in the treatment and more desirably contains ketone derivatives of the naphthenic acids.

[0020] The material is added as a solid, which also may include a solid-in-liquid slurry, solid-in-water or solid-in-organic liquid slurry or aqueous suspension. The material is added to the acid containing crude in a molar ratio effective to produce a neutralized or partially neutralized (i.e., non-corrosive) crude oil; neutralization may be in whole or partial as desired. Typically ratios of oxide to total acid of from 0.01:1 moles up to 5:1, preferably 0.25:1 to 2:1 may be used.

[0021] The formation of a crude oil-aqueous (i.e., either water-in-oil or oil-in-water) emulsion tends to interfere with the efficient separation of the crude oil and water phases and thus with recovery of the treated crude oil. Emulsion formation is undesirable and a particular problem that is encountered during treatment of naphthenic acid-containing crudes with aqueous bases. The processes of the present invention can be carried out in the essential absence of emulsion formation. Thus, an additional benefit of the treatment is the absence or substantial absence of emulsion formation.

[0022] The oxides may be purchased commercially or synthesized using known procedures. In solid form, they may be in the form of a powder or a composite, sized particle or supported on a refractory (ceramic) matrix. Certain of the solids typically occur as crystals of the hydrate.

[0023] The present invention may be demonstrated with reference to the following non-limiting examples.

Example 1

[0024] The reaction apparatus was an autoclave with a capacity of 250 ml.

[0025] 100 g of Bolobo 2/4 crude, having a total acid number of 7.4 mg KOH/g, determined by infrared spectroscopy, were put into the autoclave. 0.53 g of manganous oxide were added, then the autoclave was closed, heated to 300°C and held with stirring for 24 hours. After cooling, the oil was examined by infrared spectroscopy. A band at about 1600 cm^{-1}, partly superimposed on a band already present in untreated Bolobo 2/4, indicated formation of a carboxylate, presumably manganous naphthenate. An intense band at 1708 cm^{-1} present in untreated Bolobo 2/4 and attributed to carboxyl groups, was not present in the treated sample. A weak band at about 1715 cm^{-1}, present in the treated sample, did not change when the sample was treated with triethylamine, indicating presence of a keto group rather than a carboxyl group.

Example 2

[0026] Experiment 1 was repeated without manganous oxide.

[0027] Examination of the reaction product by infrared spectroscopy showed that the band at 1708 cm^{-1}, attributed to carboxyl groups, was slightly lower than in untreated Bolobo 2/4. Addition of triethylamine completely eliminated the band at 1708 cm^{-1}, showing that it was due to unchanged carboxyl groups.

Example 3

[0028] Experiment 1 was repeated, reducing the reaction time at 300°C from 24 to 6 hours. The infrared spectrum of the product was similar to that of Example 1. The intense band at 1708 cm^{-1} present in untreated Bolobo had nearly disappeared. A much smaller band present in the treated sample at about 1715 cm^{-1} did not change after addition of triethylamine, indicating presence of keto groups rather than carboxyl groups.

[0029] A band at about 1600 cm^{-1}, partly superimposed on a band present in untreated Bolobo 2/4, indicated formation of a carboxylate, presumably manganous naphthenate.

Example 4

[0030] The treated oil from Example 1 was distilled to 1050°F. The distillate was found to have less than 0.08 ppm of manganese. The remaining 36 gms of resid, containing all the manganese oxide, was used to treat another 100 g batch of Bolobo 2/4 crude. As in Example 1, the reaction was carried out in a closed 300 ml autoclave for 24 hours at 300°C. After cooling, the oil was examined by infrared spectroscopy. A band at about 1600 cm^{-1}, partly superimposed on a band that was already present in the spectrum of untreated Bolobo 2/4, indicated the formation of carboxylate, presumably manganous naphthenate.

[0031] A band at 1715 cm^{-1}, due to carboxyl groups, was considerably less intense than in untreated Bolobo 2/4. Treatment of the sample with triethylamine eliminated the peak at 1715 cm^{-1} only in part, indicating presence of keto groups.

Example 5

[0032] The reaction apparatus was the same autoclave described in Example 1. 100 g of Gryphon crude, having an acid number of 4.2 mg KOH/g, and 296 mg of Mn_2O_3 were put into the autoclave and heated at 300°C for 24 hours. After cooling, a sample was centrifuged to separate the solids, then the oil was examined by infrared. A peak at 1715 cm^{-1} was about 20% as intense as the 1708 cm^{-1} peak present in untreated Gryphon and due to carboxyl groups. Treatment of the sample with triethylamine did not cause any change in the 1715 cm^{-1} peak, indicating that it was due to keto groups rather than to residual carboxyl groups.

Example 6

[0033] The reaction apparatus was as described in Example 1, except that a non-chilled condenser was attached to the autoclave thus allowing air to enter the reactor and some light ends of the oil to escape. 100 g of Gryphon crude, having an acid number of 4.2 mg KOH/g, and 296 mg of Mn_2O_3 were put into the autoclave and heated at 300°C for 24 hours. After cooling, a sample was centrifuged to separate the solids, then the oil was examined by infrared spectroscopy. A peak at 1715 cm^{-1} was about 20% as intense as the starting oil carboxyl groups at 1708 cm^{-1}. The peak at 1715 cm^{-1} is attributed to keto groups.

Claims

1. A method for decreasing the acidity of an acidic crude oil or an acidic crude oil fraction comprising:

   contacting the acidic crude oil or fraction with an amount of at least one oxide of manganese effective to decrease the acidity thereof.

2. The method of claim 1, wherein the oxide of manganese is selected from one or more of MnO, Mn_2O_3 and Mn_3O_4.

3. The method of claim 1 or claim 2, wherein the oxide of manganese employed is from 0.01 to 5 moles based on acid content of the starting crude oil or fraction.

4. The method of claim 3, wherein the said amount of oxide of manganese employed is from 0.25 to 2 moles.

5. The method of any preceding claim, wherein the oxide of manganese is employed as a solid or solid-in-liquid slurry.

6. The method of any preceding claim, wherein the starting crude oil is selected from crude fractions having a boiling point of 650^{+}°F (343^{+}°C), preferably 1050^{+}°F (565^{+}°C).

7. The method of any preceding claim, wherein the starting crude oil or fraction has a neutralization number of from 0.2 to 10 mg KOH/g.

8. The method of any preceding claim, wherein the contacting is carried out in the range 100 to 350°C.

9. The use of at least one oxide of manganese as an acidity-decreasing agent in the treatment of an acidic crude oil or an acidic crude oil fraction.