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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 alkaline earth metal carbonates. Magnesium carbonate is preferred.

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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] 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

[0007] 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 alkaline earth carbonate selected from calcium and magnesium carbonates, preferably magnesium carbonate to produce a treated crude oil having a decreased acidity and corrosivity. Typically, the contacting is carried out in the presence of a corresponding effective amount of water, which may be present in the crude or added.

[0008] 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

[0009] 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 removing such acids, and most desirably from heavier (higher boiling point) and liquid fractions in which these acids are often concentrated. The naphthenic acids may be present either alone or in combination with other organic acids, such as phenols.

[0010] 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 occur although the acid is dilute in comparison to the large excess of crude and other reactive species typically present. And desirably the resulting salts remain oil soluble and tend to concentrate in the residua rather than distributing in lower boiling point side streams.

[0011] 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. The present invention also provides a method for controlling emulsion formation in acidic crudes, by treating a major contributing component of such emulsions, naphthenic and similar organic acids, and by reducing the attendant handling and processing problems.

[0012] 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}. 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 base as has been found to occur upon treatment with bases weaker than KOH.

[0013] 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.

[0014] The contacting is typically carried out at a temperature between ambient temperature and 350°C, with narrower ranges suitably from about 20°C to 300°C, preferably 30°C to 300°C.

[0015] 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.

[0016] 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.

[0017] In the present invention the crude is contacted with an effective amount of an alkaline earth metal carbonate of which magnesium carbonate is the most preferred although calcium carbonate may also be used. 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. The carbonate is added to the acid containing crude in a molar ratio effective to produce a neutralized or partially neutralized crude oil; neutralization may be in whole or partial as desired. Typically ratios of Group IIA metal carbonate to total acid of from 0.05:1 to 10:1, preferably 0.05:1 to 5:1, more preferably 0.25:1 to 1:1 may be used.

[0018] Some crudes themselves contain a sufficient amount of water, others require water addition to the ranges specified herein. The total amount of water is an effective amount of from zero to 7 wt% of the crude, preferably 1 to 5 wt% of the crude.

[0019] 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.

[0020] The carbonates 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 may occur as crystals of the hydrate.

[0021] 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 acid content. The treated crude may contain naphthenate salts of the corresponding carbonate used in the treatment.

[0022] The present invention may be demonstrated with reference to the following non-limiting examples.

Example 1

[0023] The reaction apparatus was an autoclave with a capacity of 250 ml. 100 g of Bolobo 2/4 crude, having a total acid number of 7.4 mg KOH/g, determined by infrared, were put into the autoclave. 0.62 g of magnesium carbonate was added, then the autoclave was closed and heated at 300°C for 7 hours. After cooling, the crude was analyzed by infrared and found to have an acidity corresponding to 1.8 mg KOH/g, i.e., 24% of the original.

Example 2

[0024] An experiment, as in Example 1 was carried out in which $MgCO_3$ was replaced by twice an equivalent amount of $CaCO_3$. Analysis of the treated crude showed residual acidity of 6.2 mg KOH/g, corresponding to 84% of the original. Thus $MgCO_3$ neutralizes 76% of the acid present while $CaCO_3$ only neutralizes 16%.

Example 3

[0025] The reaction apparatus was a glass vessel, equipped with stirrer and reflux condenser, immersed in an oil bath. 100 g of Bolobo 2/4 crude and 0.62 g of $MgCO_3$ were put into the reactor, which was then brought to 180°C and held for 8 hours. After cooling, the crude was examined by infrared and found to have a residual acidity of 4.7 mg KOH/g, corresponding to 63% of the original.

Example 4

[0026] An experiment as in Example 3 was carried out in which $MgCO_3$ was replaced by an equivalent amount of $CaCO_3$. Analysis of the treated crude showed an acidity of 7.1 mg KOH/g, corresponding to 96% of the original.

Example 5

[0027] The reaction apparatus was a glass jar with a magnetic bar.

[0028] 50 g of Gryphon crude, with a total acid number of 4.2 mg KOH/g, determined by infrared spectroscopy, were put into the jar and 3.75 g of calcium carbonate added. The mixture was stirred at room temperature for about 36 hours.

[0029] A small sample was centrifuged and submitted to infrared examination. The peak at 1708 cm^{-1}, due to carboxyl groups, was only marginally smaller than in untreated Gryphon.

Example 6

[0030] 2.5 g of water were added and the treated crude of Example 5 was stirred at room temperature for about 36 hours. A small sample was centrifuged and submitted to infrared examination. The peak at 1708 cm^{-1}, due to carboxyl groups, was about 50% as intense as in untreated Gryphon.

Claims

1. A method of 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 alkaline earth metal carbonate effective to decrease the acidity thereof.

2. The method of claim 1, wherein the amount employed is from 0.05 to 10 moles based on acidic functionality in the starting crude oil or fraction.

3. The method of claim 1 or claim 2, wherein the alkaline earth carbonate is employed as a solid or solid-in-liquid slurry.

4. The method of any preceding claim, wherein the alkaline earth metal carbonate is calcium and/or magnesium carbonate.

5. The method of claim 1, wherein the amount of magnesium and/or calcium carbonate employed is from 0.1 to 5 moles based on acid content of the starting crude oil or fraction.

6. The method of any preceding claim, wherein magnesium carbonate is employed.

7. The method of any preceding claim, wherein a crude oil fraction is treated, having a boiling point of 650^{+}°F (343^{+}°C), preferably 1050^{+}°F (565^{+}°C).

8. 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.

9. The method of any preceding claim, wherein the contacting is carried out in the presence of an effective amount of water.

10. The method of claim 9, wherein the amount of water employed is up to 7 wt% of the starting crude oil or fraction.

11. The method of any preceding claim, wherein the

contacting is carried out in the range 20°C to 350°C.

12. The use of at least one alkaline earth metal carbonate, preferably magnesium carbonate,as an acidity-decreasing agent in the treatment of an acidic crude oil or an acidic crude oil fraction.