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(54) Title: EMULSION NEUTRALIZATION OF HIGH TOTAL ACID NUMBER (TAN) CRUDE OIL

(57) Abstract: This invention is a method for reducing the total acid number of organic acid containing petroleum oil comprising forming a water-in-oil emulsion comprising an aqueous Group IIA metal hydroxide solution or slurry in a hydrocarbon oil, said water-in-oil emulsion having an aqueous droplet particle size diameter of from 1 to 25 μ , adding the water-in-oil emulsion to the organic acid containing petroleum oil and permitting the mixture to stand for a time sufficient to permit the neutralization of the organic acids in the petroleum oil.



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EMULSION NEUTRALIZATION OF HIGH TOTAL ACID NUMBER (TAN) CRUDE OIL

FIELD OF THE INVENTION

[0001] This invention relates to the neutralization of the organic acids contained in petroleum oils to reduce the acidity and corrosivity of such oils.

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. USP 5,182,013 refers to such recognized approaches as blending of higher naphthenic acid content oils with low naphthenic acid content oils. Additionally, a variety of attempts have been made to address the problem by replacing carbon or low alloy steels by more expensive, highly alloyed stainless steels, using corrosion inhibitors for the metal surfaces of equipment exposed to the acids, or by neutralizing and removing the acids from the oil. Some inhibitor manufacturers have claimed that the use of specific sulfur and phosphorus based organic corrosion inhibitors can be effective in reducing corrosion by naphthenic acids. Examples of such technologies include treatment of metal surfaces with corrosion inhibitors such as polysulfides (USP 5,182,013) or oil soluble reaction products of an alkyne diol and a polyalkene polyamine (USP 4,647,366), and treatment of a liquid hydrocarbon with a dilute aqueous alkaline solution, specifically, dilute aqueous NaOH or KOH (USP 4,199,440). USP 4,199,440 notes, however, that a problem arises with the use of aqueous solutions that contain higher concentrations of aqueous base. These solutions form emulsions with the oil, necessitating use of only dilute aqueous base solutions. USP 4,300,995 discloses the treatment of carbonous materials particularly coal and its

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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 aqueous alkali hydroxide solutions include those disclosed in Kalichevsky and Kobe, Petroleum Refining With Chemicals, (1956) Ch. 4, as well as U.S. Pat. Nos. 2,302,281; 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. 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. Pat. Nos. 2,795,532 and 2,770,580 (Honeycutt) disclose processes in which "heavy mineral oil fractions" and "petroleum vapors", respectively are treated. The '532 patent further discloses that "flashed vapors" are contacted with "liquid alkaline material" containing, inter alia, alkali metal hydroxides and "liquid oil". A mixture solely of NaOH and KOH in molten form is disclosed as the preferred treating agent, however, "other alkaline materials, e.g., lime, can also be employed in minor amounts". Importantly, '532 does not disclose the treatment of whole crudes or fractions boiling at 1050+°F (565+°C). Rather '532 treats only vapors and condensed vapors of the 1050°F (565°C) fractions, that is, fractions that are vaporizable at the conditions disclosed in '532. Petroleum residua and other non-vaporizable (at '532 process conditions) fractions containing naphthenic acids would not be treatable by the process. 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

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would be able to successfully treat a broad slate of crudes of a variety of boiling points.

[0005] In USP 2,068,979, it is disclosed that naphthenates were used to prevent corrosion in a petroleum still. The patent teaches the addition of calcium naphthenate to petroleum to react with and scavenge strong free acids such as hydrochloric and sulfuric acids. This was intended to prevent corrosion in distillation units by those strong acids and makes no claims with respect to naphthenic acids. In fact, naphthenic acids would have been formed when the strong acids were converted to salts. Some prior art involved the addition or formation of calcium carbonate (Cheng et al, USP 4,164,472) or magnesium oxide (Cheng et al, U.S. Pat. Nos. 4,163,728; 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 (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. Amine naphthenates (Wasson et al, USP 2,401,993) and zinc naphthenates (Johnson et al, USP 2,415,353; Rouault, USP 2,430,951; and Zisman et al, USP 2,434,978) were also claimed as anticorrosive additives in various lubricating oil products. Another use of calcium compounds with petroleum includes removal of naphthenic acids from hydrocarbon oils by limestone-on-glass abstraction (Elkin et al, Soviet Union 1,786,060) or by metal oxides related to hydrotalcites (Gillespie et al, USP 5,389,240). Finally, calcium hydroxide (Kessick, Canadian Patent 1,249,760) aids in separation of water from heavy crude oil wastes.

[0006] USP 5,683,626 teaches treatments of acidic crudes with tetraalkylammonium hydroxide and USP 5,643,439 uses trialkylsilanolates. US/13689 and US/13690 (Publications 97/08271 and 97/08275 dated March 6, 1997) teach the use of Group IA and Group IIA oxides and hydroxides to treat whole crudes and crude fractions to decrease naphthenic acid content.

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[0007] USP 3,847,774 teaches treatment of heavy petroleum distillates containing naphthenic acids by employing a caustic solution in the form of a fine droplet dispersion of an aqueous alkali metal hydroxide within an inert or non-reactive carrier hydrocarbon wherein the aqueous droplet size is about 1 to 10 μ . This dispersion is mixed with the heavy distillate in a common conduit by passing through a mixing means for dispersing the aqueous alkali metal hydroxide in carrier hydrocarbon uniformly throughout the heavy petroleum distillate stream containing naphthenic acids and subjecting this mixture immediately after mixing and before any significant phase separation occurs to an electrical field to separate purified heavy hydrocarbon distillate phase from an aqueous mixture of excess alkali metal hydroxide and the alkali metal hydroxide salts of naphthenic acid.

[0008] USP 6,022,494 teaches a process for treating acidic crudes or fractions thereof to reduce or eliminate their acidity and corrosivity by, in one embodiment, the direct addition of metal carboxylates into the crude. The metal carboxylates are prepared by adding an alkaline earth metal hydroxide to a small quantity of the crude to be treated or other hydrocarbon oil to produce a treating crude oil containing alkaline earth metal naphthanate which is then combined into the total quantity of the crude to be treated. In practice when using the treating crude as the metal naphthanate salt source, a naphthanate salt content in the range of 0.025:1 to 1:1 moles of metal based on acid content of the acidic crude to be treated. The acidic crude to be treated and the treating crude oil containing the metal naphthate salts should have comparable boiling points and characteristics. Thus the preferred hydrocarbon oil for the production of the treating crude oil is a small quantity of the same crude oil which is to be neutralized. If a different hydrocarbon oil is used, it must be compatible with the crude oil to be neutralized. The patent goes on to expressly state that the formation of a crude oil-aqueous emulsion (i.e., either water-in-oil or oil-in-

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water) 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.

[0009] It is common practice in petroleum refining to avoid formation of aqueous-oil emulsions. This is because often emulsions may be stabilized and then become very difficult to "break" or separate into oil and aqueous phases. Sometimes extraordinary and costly methods such as high gradient centrifugation, microwaves, etc. are needed to separate such emulsions so they are best avoided.

[0010] For example, in normal desalting operations, wash water is mixed with crude usually through a mixing valve to produce an emulsion which is then sent to the desalter vessel where the wash water coalesces with brine droplets present in the crude. An electrostatic field in the vessel serves to enhance coalescence and the large coalesced droplets settle by gravity and are withdrawn as waste water at the vessel bottom. Desalted crude leaves from the vessel top. Mixing valve pressure drop and hence mixing energy must be carefully controlled to avoid formation of too tight an emulsion which could then become difficult to separate electrostatically. This is especially important for certain crudes which contain naturally occurring surfactants or finely divided solids, both of which can stabilize emulsions. Frequently special desalting chemicals or aids are used to suppress emulsion stability or demulsifiers are added to break the emulsions. USP 6,022,494 states that a benefit of its process is the absence or substantial absence of emulsion formation.

[0011] USP 6,627,069 teaches a process for reducing the naphthenic acid content of crude oils and fractions thereof in the essential absence of oxygen in the presence of an aqueous base selected from Group IA and Group IIA

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hydroxides and ammonium hydroxide and mixtures thereof, a phase transfer agent that is a quaternary ammonium salt in amounts of from 10⁻⁵ to 10⁻¹ at a temperature and pressure effective to produce a treated petroleum feed having a decreased naphthenic acid content and an aqueous phase containing naphthenate salts, phase transfer agent and base. The feed is in the liquid state. On mixing the feed with the aqueous base-phase transfer agent mixture, the oil is in droplet form, the oil droplets being of sufficient size to enable the naphthenic acid containing component to achieve intimate contact with the aqueous phase. Oil droplet having a mean droplet size of about 1 to 100 microns (diameter) would be typical, and 1 to 20 microns are preferable. Contact can be achieved by vigorous mixing of the components of the mixture. Thus it is seen that in this case an oil in water emulsion/mixture is created.

[0012] WO 00/75262 teaches deacidifying crude oil and/or fraction(s) thereof comprising contacting the crude oil and/or fraction(s) thereof with a Group IIA metal hydroxide in the presence of water wherein water is present in a concentration of 0.01 to 100 wt% of the crude oil and/or fraction(s) thereof, introducing a demulsifier to the mixture of crude oil and/or fraction thereof, Group IIA metal hydroxide and water in an amount effective to cause the mixture to separate into an oil rich phase, an aqueous phase and an interface layer disposed between the oil rich phase and the aqueous phase. The crude oil and/or fraction thereof and the Group IIA metal hydroxide may be mixed by stirring or agitation using a mechanical stream an ultrasonic stirrer or by bubbling an inert gas through the reaction mixture.

[0013] It would be beneficial if a process is developed which eliminates the necessity of avoiding emulsion formation.

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SUMMARY OF THE INVENTION

[0014] It has been discovered that acid neutralization can be accomplished in a process that does not avoid emulsion formation and in fact practices emulsion formation and maintenance as part of the process eliminating the need for chemical demulsifiers.

[0015] The present invention is a method for decreasing the acidity and corrosivity of an acid containing corrosive crude comprising, securing an aqueous alkaline earth metal hydroxide solution or slurry, forming a water-in-oil emulsion of the aqueous alkaline earth metal hydroxide solution or slurry in a hydrocarbon carrier oil, preferably a small quantity of the same corrosive crude to be treated, the water-in-oil emulsion having an aqueous phase droplet size of between about 0.5 to 50 μ , preferably between about 1 to 25 μ , more preferably between about 1 to 10 μ , mixing the water-in-oil emulsion with the crude to be treated in a ratio of about 0.2 to 10 volume of emulsion to 100 volumes of crude to be treated, preferably 0.5 to 5 volume of emulsion to 100 volumes of crude or fraction thereof to be treated, holding the crude or fraction thereof to which the water-in-oil emulsion has been added at a temperature sufficient to promote interaction between the alkaline earth metal hydroxide and the naphthenic acid in the crude to be treated, preferably between about 20°C to 150°C, more preferably between about 20°C to 100°C most preferably between about 20°C to 60°C for a time sufficient for the partial or complete neutralization of the naphthenic acids contained in the crude to be treated by conversion of the naphthenic acids into alkaline earth metal naphthenic salts which remain dissolved in the crude oil, e.g., at least about 30 minutes, preferably at least about 1 hour, more preferably at least about 2 hours, still more preferably at least about 4 hours. The treated crude without the addition of a demulsifier can then be passed for further processing using standard techniques in the refinery. It can

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be dewatered and desalted and then passed on for distillation and subsequent standard processing.

DETAILED DESCRIPTION OF THE INVENTION

[0016] 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.

[0017] 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.

[0018] 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.

[0019] The process of the present invention has utility in processes in which inhibiting or controlling or removing oil soluble contaminants present in crude oils or fractions thereof, is desired. The reactive contacting method exploits the very large interfacial area characteristic of the fine water-in-oil emulsion and the

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long time available before the fine aqueous droplets will coalesce and settle. This permits sufficient mass transfer between the two phases and reactions to occur at the interface. Thus the method has application in the removal of acidic compounds from crude oil and/or fractions thereof by use of water-in-oil emulsions of alkaline earth metal hydrocarbons in carrier oil, in the removal of nitrogen compounds from oil by sulfuric acid treatment, in the removal of elemental sulfur and sulfur compounds from pipelined products, e.g., motor gasoline, diesel, crude, etc., using sodium hydroxide. More specifically, 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 an acidic crude or fraction thereof would be beneficial.

[0020] The concentration of acid in the crude oil is typically expressed as an acid neutralization number or acid number, 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 (TAN) of about 1.0 mg KOH/g and lower are considered to be of moderate to low corrosivity (crudes with a TAN 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. Acidic crudes having free carboxyl groups may be effectively treated using the process of the present invention. 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.

[0021] The crudes that may be used are any naphthenic acid-containing crude oils or fractions thereof that are liquid or liquefiable at the temperatures at which the present invention is carried out.

[0022] As used herein, the term whole crudes means unrefined, undistilled crudes.

[0023] As used herein the term stoichiometric amount means a sufficient amount of alkaline earth metal hydroxide on a molar basis to neutralize a mole of acidic functionality in the crude oil. In moles, for Group IIA hydroxides the stoichiometric ratio is 0.5:1 moles of metal to acid functionality. The terms "above", "greater than" or "in excess of" stoichiometric are defined in relation to the foregoing, as is the term "substoichiometric". Substoichiometric ranges from 0.025:1 moles up to a stoichiometric amount, preferably 0.25:1 to less than 0.5:1 (i.e., a stoichiometric amount) for Group IIA. Greater than stoichiometric can range up to 10:1 moles preferably up to 5:1. In the present process, however, preferably a stoichiometric to substoichiometric amount of alkaline earth metal hydroxide as metal to the acid to be treated in the crude is employed. Preferred metals are calcium, magnesium, barium and strontium, with calcium and magnesium preferred, and calcium most preferred.

[0024] Contacting can be at any convenient temperature sufficient to facilitate reaction between the alkaline earth metal hydroxide and the acidic component in the crude or fraction thereof to be treated, typically about 20°C to 150°C, preferably about 20°C to 100°C, more preferably about 20°C to 60°C.

[0025] In the practice of the present invention use is made of one or more alkaline earth metal hydroxides in the form of a solid in water slurry. Insofar as the aqueous slurry is then utilized as a water-in-oil emulsion which has an aqueous droplet size in the range of 0.5 to 50 μ , preferably 1 to 25 μ , more preferably about 1 to 10 μ , it is desirable that the alkaline earth metal hydroxide employed be in the form of a fine powder of a particle size in the range of and preferably smaller than the average aqueous droplet size in the water-in-oil emulsion.

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[0026] The water-in-oil emulsion employed contains about 5 to 45 vol% of aqueous alkaline earth metal hydroxide solution or slurry to hydrocarbon carrier oil continuous phase, preferably 20 to 33 vol% of the aqueous alkaline earth metal hydroxide slurry to the hydrocarbon oil continuous phase. The highest concentration is economically preferable while maintaining a water-in-oil emulsion to permit subsequent blending with a large volume of untreated crude.

[0027] The water-in-oil emulsion is formed by vigorously mixing the aqueous alkaline earth metal hydroxide slurry with the hydrocarbon phase to produce an emulsion wherein the aqueous droplet size is about 0.5 to 50 μ , preferably 1 to 25 μ , more preferably about 1 to 10 μ . This vigorous mixing can be accomplished by use of impellers, paddles, or other mechanical mixing means, sonic mixers, air-jet mixers, static mixers at high velocity, etc. Specifically, high shear high speed rotor-stator mixers are capable of producing the desired aqueous droplet size with low required residence times. Regardless of the technique employed, however, the aqueous droplet size is in the 0.5 to 50 μ , preferably 1 to 25 μ , more preferably 1 to 10 μ range.

[0028] While all emulsions reported in the examples herein were made in the laboratory at room temperature and pressure, any combination of temperature and pressure may be employed so long as droplets of the above recited size are obtained. High shear rotor-stator mixers appear to provide adequate droplet size for the viscosity range of most crudes at ambient temperature, however, for the higher viscosities, using elevated temperature would be advantageous to produce droplets of the above recited size.

[0029] The hydrocarbon oil which is employed in the production of the water-in-oil emulsion can be any hydrocarbon or petroleum oil having a boiling point, viscosity, miscibility, etc., compatible with the crude oil or fraction

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thereof which is to be treated for acid removal. Most preferably it can be the same as the high TAN crude or fraction thereof to be treated.

[0030] The water-in-oil emulsion and the crude oil or fraction thereof which is to be treated are mixed at about 0.2 to 10 vol%, preferably about 1 to 5 vol% emulsion added to the crude oil or fraction thereof to be treated. The amount added depends on the basicity of the emulsion and the acidity of the crude or fraction thereof to be treated.

[0031] In determining the amount of emulsion which is to be combined with the crude or fraction thereof to be treated the alkaline earth metal hydroxide content of the amount of emulsion added can range from substoichiometric to super stoichiometric of the amount of metal needed to neutralize the total acid content of quantity of crude or fraction thereof to be treated. It is most desirable that the alkaline earth metal hydroxide content of the amount of emulsion added not be in excess of the stoichiometric amount of metal needed to neutralize the total acid content of the crude or fraction thereof to be treated. Preferably, an amount of emulsion is used such that the alkaline earth metal hydroxide content is about 0.375 to 0.5 mole of metal per mole of acid to be neutralized. Operation at substoichiometric concentration increases the likelihood of not ensuring the preferred condition that no unreacted alkaline earth metal hydroxide remains in the treated crude oil.

[0032] The mixing of water-in-oil emulsion and crude or fraction thereof to be treated is conducted under conditions to insure a complete and thorough blending of water-in-oil emulsion and the crude or fraction thereof to be treated. This step involves macro-mixing rather than a more intense micro-mixing.

[0033] While a separate mixing of the mixture can be practiced during the standing or holding period, it is preferred that no extraneous mixing be

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employed, the initial blending upon introduction into the holding zone having been found to be sufficient.

[0034] The mixture of the water-in-oil emulsion and the crude or fraction thereof to be treated is permitted to stand for a time sufficient to permit the desired partial or complete neutralization of the oil to be treated. When a substoichiometric amount of alkaline earth metal hydroxide is employed the holding time employed is typically that necessary for the complete consumption of the alkaline earth metal hydroxide. Holding times on the order of at least about 30 minutes, preferably at least about 1 hour, more preferably at least about 2 hours, and still more preferably at least about 4 hours are desirable, the upper limit to be set solely by practicality and storage issues.

[0035] Holding can be accomplished in crude storage tanks at the refinery if the neutralization step is practiced at the refinery or in the storage compartments of oil transport vessels, i.e., tankers, tank truck, barrels, etc., if the process is practiced at the well head or near the production facility. If the crude is to be pipelined over a distance even the holding time experienced in the pipeline during transit by the water-in-oil emulsion plus crude oil or fraction thereof to be treated may be sufficient to insure adequate reaction time and the desired level of neutralization.

[0036] A further advantage of treatment in crude storage tanks or upstream (well head, pipeline, etc.) is that contaminants in the added alkaline earth metal hydroxide, which are inevitably present in commercial grades of such materials, or unreacted alkaline earth metal hydroxides can be effectively removed in the normal desalting operation in the refinery. Modern desalters can efficiently remove undissolved, unreacted particulates into the desalter waste water thereby preventing potential downstream deposition and fouling in process equipment such as heat exchangers, furnaces, tower internals, etc.

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[0037] Intense or extraneous mixing during the standing/holding stage is not needed. Because of the small aqueous droplet size, the aqueous phase remains distributed in the oil continuous phase for a long time. Settling occurs very slowly and the small droplets also provide a very large interfacial surface area for mass transfer and reaction. The acidic species, e.g., naphthenic acids, in the crude or fraction thereof to be treated diffuse through the oil to the surface of the aqueous droplets there contacting the dissolved alkaline earth metal hydroxide. Reaction of the acid and the alkaline earth metal hydroxide is very rapid at this emulsion interface causing neutralization of the acid.

[0038] As previously stated complete neutralization of the acid in the oil can be achieved using a stoichiometric amount of alkaline earth metal hydroxide and a sufficiently long holding or contacting time but it is more desirable to use substoichiometric amounts of alkaline earth metal hydroxide to achieve partial neutralization and consume all of the alkaline earth metal hydroxide in the slurry. Further handling of the mixture is accomplished without the need for the use of any added demulsifier.

EXAMPLES

Example 1

[0039] 1-5 μm droplet size $\text{Ca}(\text{OH})_2$ -slurry-in-crude emulsion was prepared in the lab by mixing 5 gm $\text{Ca}(\text{OH})_2$, 20 cc H_2O and 140 cc Gryphon crude in a beaker with a 19000 rpm batch single stage rotor/stator blender at room temperature.

[0040] Stoichiometric amount of $\text{Ca}(\text{OH})_2$ slurry-in-oil emulsion (29.5 ml) was then blended with (440 ml) Gryphon crude (volumetric ratio of 6.7%) and allowed to sit overnight at room temperature in a 2" d x 10" h graduated cylinder simulating ambient temperature crude storage tank conditions. A similar

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experiment was done with Chad crude at 50°C simulating a heated storage tank at 50°C.

[0041] TAN analysis next morning showed 75% and 76% TAN reduction respectively for two repeated experiments. The calcium analysis of the crude showed 80% TAN neutralization for both, which checks the TAN reduction data.

Example 2

[0042] An emulsion of aqueous calcium hydroxide in Gryphon crude was prepared using a high-speed (19000 rpm) shear mixer at room temperature. A mixing time as short as 20 seconds is very effective in preparing small drop size water-in-oil emulsions giving a water droplet size distribution of 1 to 10 microns with occasional droplets up to 25 microns. A measured amount of this emulsion equivalent to 100% TAN neutralization was dispersed in the crude oil (separately Gryphon and Chad) by moderate hand shaking for less than 15 seconds. The mixture was allowed to stand overnight in a tall vessel (H/W ~ 6) with periodic sampling of the crude mixture. Summarized below is the effective TAN reduction vs. time for both Gryphon and Chad crudes:

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- (a) Gryphon Crude (TAN = 3.14) at 20°C (room temperature) using 1 to 10 μ droplets: 29.5 ml of emulsion added to 440 ml of Gryphon crude (volumetric ratio of 6.7%) to achieve full stoichiometric neutralization.

<u>Settling Time</u>	<u>TAN Neutralized</u>	<u>TAN Neutralized (as Ca content) *</u>
1.5 hours	66.2%	66.2%
4.0 hours	71.7%	73.6%
16 hours	77.1%	79.4%

- (b) Chad Crude (TAN = 4.22) at 50°C (hot water bath) using 1 to 10 μ droplets: 39.7 ml of emulsion added to 440 ml of Chad crude (volumetric ratio of 9.03%) to achieve full stoichiometric neutralization.

<u>Settling Time</u>	<u>TAN Neutralized</u>	<u>TAN Neutralized (as Ca content) **</u>
1.5 hours	54.3%	54.8%
4.0 hours	64.5%	66.1%
8.0 hours	71.8%	70.8%
21 hours	73.5%	76.7%

* Corrected for inherent calcium content of 41 ppm

** Corrected for inherent calcium content of 435 ppm

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CLAIMS:

1. A process for reducing the acidity of an acid containing crude comprising:
 - (a) securing an aqueous alkaline earth metal hydroxide solution or slurry;
 - (b) forming a water-in-oil emulsion of the aqueous alkaline earth metal hydroxide solution or slurry in a hydrocarbon carrier oil, the water-in-oil emulsion having an aqueous phase droplet size of between about 0.5 to 50 μ ;
 - (c) mixing the water-in-oil emulsion with the acid containing crude to be treated in an amount such that the alkaline earth metal hydroxide content of the amount of emulsion added ranges from substoichiometric to in excess of the stoichiometric amount of metal needed to neutralize the total acid content of the quantity of crude or fraction thereof to be treated.
 - (d) holding the mixture at a temperature and for a time sufficient to effect the desired level of neutralization of the crude or fraction thereof to be treated; and
 - (e) passing the treated crude or fraction thereof on for further processing.
2. The process of claim 1 wherein the water-in-oil emulsion has an aqueous phase droplet size of between about 1 to 25 μ .
3. The process of claim 1 wherein the water-in-oil emulsion has an aqueous phase droplet size of between about 1 to 10 μ .
4. The process of claim 1, 2 or 3 wherein the mixture of water-in-oil emulsion and crude or fraction thereof to be treated is held at a temperature between about 20°C to 150°C.

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5. The process of claim 1, 2 or 3 wherein the mixture of water-in-oil emulsion and crude or fraction thereof to be treated is held at a temperature between about 20°C to 100°C.

6. The process of claim 1, 2 or 3 wherein the mixture of water-in-oil emulsion and crude or fraction thereof to be treated is held at a temperature between about 20°C to 60°C.

7. The process of claim 1, 2 or 3 wherein the mixture of water-in-oil emulsion and crude or fraction thereof to be treated is held for at least 2 hours.

8. The process of claim 1, 2 or 3 wherein the aqueous alkaline earth metal hydroxide solution or slurry is prepared by mixing a fine powder of alkaline earth metal hydroxide into water, the fine powder having a particle size in the range of the subsequent average aqueous droplet size in the water-in-oil emulsion.

9. The proviso of claim 1, 2 or 3 wherein the alkaline earth metal hydroxide is calcium hydroxide.

10. The process of claim 1, 2 or 3 wherein the water-in-oil emulsion comprises about 5 to 45 vol% of aqueous alkaline earth metal hydroxide solution or slurry to hydrocarbon carrier oil.

11. The process of claim 1, 2 or 3 wherein the mixing of the water-in-oil emulsion and the crude or fraction thereof to be treated is in a tank.

12. The process of claim 11 wherein the tank is in a tanker.

13. The process of claim 11 wherein the tank is a crude storage tank.

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14. The process of claim 1, 2 or 3 wherein the mixing of the water-in-oil emulsion and the crude or fraction thereof to be treated is in a crude transport pipeline.

15. The process of claim 1, 2 or 3 wherein the amount of water-in-oil emulsion added to the crude or fraction thereof to be treated is such that the alkaline earth metal hydroxide content is about 0.375 to 0.5 mole of metal per mole of acid to be neutralized.

16. The process of claim 1, 2 or 3 wherein the treated crude or fraction thereof is dewatered and desalted.

17. The process of claim 1, 2 or 3 wherein the water-in-oil emulsion and the crude or fraction thereof to be treated is mixed at a ratio of about 0.2 to 10 volumes of emulsion to 100 volumes of crude or fraction thereof to be treated.