the use of alpha-hydroxy carboxylic acid (particularly glycolic acid) for the removal of calcium and amines.

The method of Reynolds, while likely successful at the extraction of low levels of calcium (<30 ppm), has two significant drawbacks which make it impractical for use with the high calcium crudes. One is that since the extraction process is stoichiometric, at the high levels of citric acid needed in the wash water, its pH drops significantly (to below 3) and causes a corrosion issue in the wash water circuit. This can be alleviated by the use of corrosion inhibitors.

A second concern is that the concentration of the resultant calcium citrate has a solubility limitation of approximately 1000 ppm at room temperature, and pH of 6-8 with solubility inversely correlated with temperature. Thus, one can see that deposition of calcium citrate is an issue at typical desalter temperatures (250°F-300°F) and concentrations encountered when extracting higher levels of calcium with the typical 5% wash water rate. In fact, both of these concerns were verified through field experience with citric acid at a refinery processing significant levels of a high calcium crude. Deposition in the brine heat exchanger and transfer piping was one of the problems that was experienced.

SUMMARY ~~OF THE INVENTION~~

The ~~invention~~disclosure pertains to a combination of treatment chemistries to overcome the deficiencies of the Reynolds patent. In one ~~aspect~~embodiment, the ~~invention~~disclosure pertains to the use of a sequestrant to effect sequestration of the calcium from the hydrocarbonaceous medium to the water phase of the W/O emulsion combined with contact of the water phase by a specifically formulated deposited control polymer to thereby inhibit the formation of calcium based scales and deposits in the water phase and along refinery system surfaces in contact with the water phase. Examples of such surfaces include drains, drain lines, desalter vessels, mix valves, static mixers, and heat exchangers that are in contact with the brine (i.e., water phase).

In a more specific ~~aspect~~embodiment of the ~~invention~~disclosure, citric acid or its salts are used as the sequestrant, and the sequestered calcium containing complex is calcium citrate. The deposit control polymer inhibits calcium citrate scale formation in the water phase and along surfaces that contact the water phase. While calcium citrate scale control is important, the treatment should also not adversely affect desalter operation (longer water drop rates, etc.).

In a first aspect, there is provided a method for reducing calcium deposit formation along surfaces in contact with a water phase formed as a result of resolution of an emulsion from crude oil fed to a petroleum refinery desalter, wherein said crude oil has a high calcium content of 30 ppm calcium and greater, said method comprising:

a) contacting said crude oil with citric acid sequestrant and wash water thereby forming sequestered calcium citrate complexes in said water phase of said emulsion; and

b) contacting said water phase with from about 1 to 300 ppm of a deposit control polymer to inhibit the formation of calcium based scales and deposits along said surfaces, wherein said deposit control polymer is AA/AHPSE, AA/APES, AA/APES/AHPSE, or AA/MA/APES.

In a second aspect, there is provided a method for reducing calcium deposit formation along surfaces in contact with a water phase formed as a result of resolution of an emulsion from a crude oil fed to a petroleum refinery desalter, wherein said crude oil has a high calcium content of 30 ppm calcium and greater, said method comprising:

a) contacting said crude oil with citric acid sequestrant and wash water thereby forming sequestered calcium citrate complexes in said water phase of said emulsion; and

b) contacting said water phase with from about 1 to 300 ppm of a deposit control polymer to inhibit the formation of calcium based scales and deposits along said surfaces, wherein said deposit control polymer is AA/AMPS.

DETAILED DESCRIPTION OF EXEMPLARY EMBODIMENTS

Although the present invention is primarily described in conjunction with its use in a conventional desalter operation, the artisan will appreciate that other extraction techniques will also benefit from the invention. One example is countercurrent extraction, wherein an aqueous phase is brought into contact with an oppositely flowing hydrocarbonaceous medium.

Further, although the invention is particularly advantageous in removing calcium from crude oil, the phrase "liquid hydrocarbonaceous medium" should be construed to include other media such as bitumens, atmospheric or vacuum residia or solvent deasphalted oils derived from crudes and residua that are hydroprocessed or cracked into useable products such as gas oils, gasolines, diesel fuel, and shale oil, liquefied coal, beneficiated tar sand, etc. Also, emulsions including such hydrocarbonaceous media or any hydrocarbonaceous product are included within the ambit of this phrase.

High calcium containing crudes are, as used herein, crudes containing greater than about 30 ppm calcium therein relative to one million parts of the crude or other liquid hydrocarbonaceous media. The invention will be particularly beneficial to those crudes having greater than about 100 ppm calcium and higher.

Also, the phrase "sequestered calcium containing complex" as used throughout the specification and claims covers a host of chelated, complexed, or sequestered complexes or ligands, or other species including ionic or covalent compounds in which calcium is extracted from the oil phase and, at least in part, partitions to the

CLAIMS

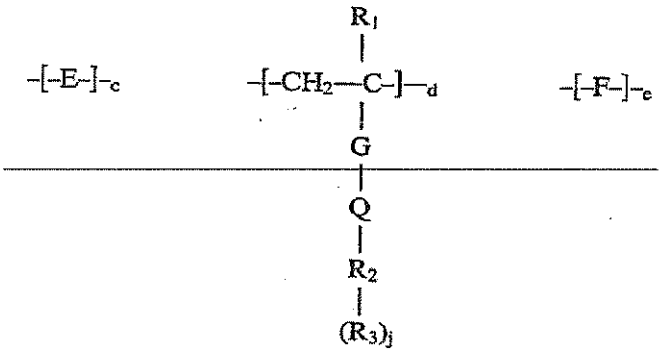
1. A mMethod for reducing calcium ~~content in a liquid hydrocarbonaceous medium~~deposit formation along surfaces in contact with a water phase formed as a result of resolution of an emulsion from crude oil fed to a petroleum refinery desalter, wherein said crude oil has a high calcium content of 30 ppm calcium and greater, said method comprising:

a.) contacting said ~~liquid hydrocarbonaceous medium~~crude oil with ~~a metal sequestering agent~~citric acid sequestrant and wash water thereby forming ~~to form a~~ sequestered calcium citrate~~containing~~ complexes in said water phase of said emulsion;

~~b. contacting said liquid hydrocarbonaceous medium with an aqueous medium to form an emulsion whereby upon resolution of said emulsion at least a portion of said sequestered calcium containing complex remains in said aqueous medium;~~ and

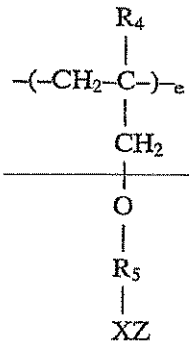
c.b) contacting said ~~aqueous medium with a water soluble or water dispersible polymer having the formula I~~phase with from about 1 to 300 ppm of a deposit control polymer to inhibit the~~calcium deposit~~ formation of calcium based scales and deposits~~therein or~~ along said surfaces ~~in contact with said aqueous medium~~, wherein said deposit control polymer is~~has the formula:~~ AA/AHPSE, AA/APES, AA/APES/AHPSE, or AA/MA/APES.

~~(I)~~



~~wherein E is the repeat unit remaining after polymerization of an ethylenically unsaturated compound; R_1 is H or lower (C_1-C_6) alkyl; G is lower (C_1-C_6) alkyl or carbonyl; Q is O or NH; R_2 is lower (C_1-C_6) alkyl; hydroxy lower (C_1-C_6) alkyl, lower (C_1-C_6) alkyl sulfonic acid -(Et-O)$_n$-(iPr-O)$_n$- or -(Pr-O-)$_n$- wherein n ranges from about 1 to 100 alkyl, and R_3 is H or XZ wherein X is an anionic radical selected from the group consisting of SO_3, PO_3 or COO; Z is H or hydrogens or any other water soluble cationic moiety which counterbalances the valence of the anionic radical X; F, when present, is a repeat unit having the Formula II:~~

~~(II)~~



~~wherein X and Z are the same as in Formula I; R_4 is H or $(C_1$-$C_6)$ lower alkyl, R_5 is a hydroxy substituted alkyl or alkylene having from 1 to 6 atoms, and XZ may or may not be present; e and d are positive integers, e is a non-negative integer, and j is 0 or 1.~~

~~2. Method as recited in claim 1 wherein from about 1 to 300 ppm of said polymer (I) is brought into contact with said aqueous medium, based on one million parts of said aqueous medium.~~

~~3. Method a recited in claim 2 wherein from about 1 to 100 ppm of said polymer (I) is brought into contact with said aqueous medium.~~

4<u>2</u>. Method as recited in claim ~~3~~<u>1</u> wherein said ~~liquid hydrocarbonaceous medium~~<u>crude oil</u> ~~has a calcium content of greater than about 30~~<u>comprises about 100</u> ppm calcium ~~based upon one million parts of said liquid hydrocarbonaceous medium~~<u>and greater</u>.

~~5. Method as recited in claim 4 wherein said liquid hydrocarbonaceous medium is crude oil.~~

~~6. Method as recited in claim 5 wherein said metal sequestering agent is citric acid or salt thereof and wherein said sequestered calcium containing complex is calcium citrate.~~

~~7. Method as recited in claim 6 wherein said polymer I is a member or members selected from the group consisting of~~

~~1) AA/AHPSE;~~

~~2) AA/APES;~~

~~3) AA/AMPS;~~

~~4) AA/APES/AHPSE;~~

~~5) AA/MA/APES;~~

~~6) AA/AMPS/APES~~

~~8. Method as recited in claim 7 wherein said polymer I is~~

~~1) AA/AHPSE;~~

~~2) AA/APES; or~~

~~3) AA/AMPS~~

~~9~~3. Method as recited in claim ~~8~~1 wherein said deposit control polymer ~~I~~ is AA/AHPSE.

~~10~~4. Method as recited in claim ~~8~~1 wherein said deposit control polymer ~~I~~ is AA/APES.

~~11. Method as recited in claim 8 wherein said polymer I is AA/AMPS.~~

~~12. Method as recited in claim 8 further comprising contacting said emulsion with an emulsion breaker.~~

~~13. Method as recited in claim 12 further comprising adding a corrosion inhibitor to said liquid hydrocarbonaceous medium or to said aqueous medium.~~

~~14. Method as recited in claim 8 wherein said emulsion is heated to a temperature of about 100°F-300°F.~~

~~15. Method as recited in claim 14 wherein said resolution of said emulsion is performed in a desalter apparatus.~~

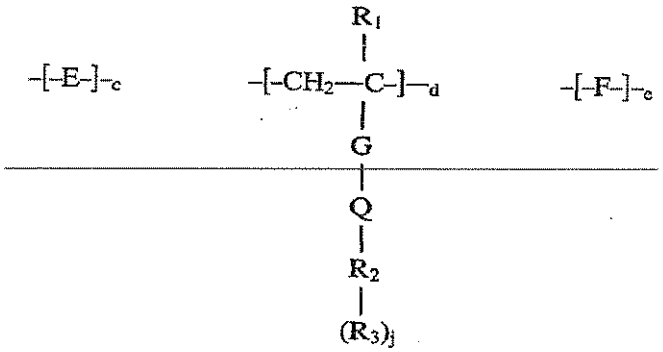
~~16. Method as recited in claim 15 wherein n in Formula I is from 1 to 20 and X in Formula I is selected from Na, K, Ca, and NH_4.~~

~~1~~5. A method for reducing calcium deposit~~ion~~ formation along surfaces in contact with a water phase formed as a result of resolution of an emulsion from a crude oil fed to~~in~~ a petroleum refinery desalter, ~~of the type~~ wherein said crude oil ~~containing~~has a high calcium content of 30 ppm calcium and greater, said method comprising~~therein is contacted with a sequestrant and a water wash to form said emulsion having a sequestered calcium complex in said emulsion, wherein at least a portion of said sequestered calcium complex partitions to said water phase upon said resolution, said method comprising contacting said sequestered calcium complex with a water soluble or water dispersible polymer having the Formula I~~:

a) contacting said crude oil with citric acid sequestrant and wash water thereby forming sequestered calcium citrate complexes in said water phase of said emulsion; and

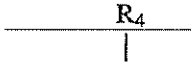
b) contacting said water phase with from about 1 to 300 ppm of a deposit control polymer to inhibit the formation of calcium based scales and deposits along said surfaces, wherein said deposit control polymer is AA/AMPS.

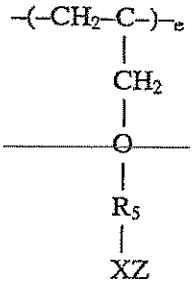
~~(I)~~



~~wherein E is the repeat unit remaining after polymerization of an ethylenically unsaturated compound; R_1 is H or lower (C_1-C_6) alkyl; G is lower (C_1-C_6) alkyl or carbonyl; Q is O or NH; R_2 is lower (C_1-C_6) alkyl; hydroxy lower (C_1-C_6) alkyl, lower (C_1-C_6) alkyl sulfonic acid; $(Et\text{-}O)_n$ $(iPr\text{-}O)_n$ or $(Pr\text{-}O)_n$ wherein n ranges from about 1 to 100, and R_3 is H or XZ wherein X is an anionic radical selected from the group consisting of SO_3, PO_3 or COO; Z is H or hydrogens or any other water soluble cationic moiety which counterbalances the valence of the anionic radical X; F, when present, is a repeat unit having the Formula II:~~

~~(II)~~





~~wherein X and Z are the same as in Formula I. R_4 is H or (C_1-C_6) lower alkyl, R_5 is a hydroxy substituted alkyl or alkylene having from 1 to 6 atoms, and XZ may or may not be present; e and d are positive integers, e is a non-negative integer, and j is 0 or 1.~~

~~18~~6. Method as recited in claim ~~17~~5 wherein said crude oil comprises about 100 ppm calcium and greater.

~~19. Method is recited in claim 18 wherein said sequestrant is citric acid and wherein said sequestered calcium complex is calcium citrate, and wherein about 1 to 300 ppm of said polymer I is added to said water phase based on one million parts of said water phase, said polymer comprising a member or members selected from the group consisting of~~

~~1) AA/AHPSE~~

~~2) AA/APES~~

~~3) AA/AMPS~~

~~4) AA/APES/AHPSE~~

~~5) AA/MA/APES~~

~~6) AA/AMPS/APES~~

~~20. Method as recited in claim 19 wherein said polymer I is~~

~~1) AA/AHPSE;~~

~~2) AA/APES; or~~

~~3) AA/AMPS.~~

~~21. Method as recited in claim 1 wherein said liquid hydrocarbonaceous medium is crude oil produced at an oil production site and wherein said steps (a) through (c) are performed proximate said site.~~