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(54) Titre : ADDITIFS PERMETTANT D'ACCROITRE L'ELIMINATION DE METAUX ET AMINES DANS DES
 PROCESSUS DE RAFFINAGE-DESSALEMENT
 (54) Title: ADDITIVES TO ENHANCE METAL AND AMINE REMOVAL IN REFINERY DESALTING PROCESSES

(57) **Abrégé/Abstract:**

It has been discovered that metals and/or amines can be removed or transferred from a hydrocarbon phase to a water phase in an emulsion breaking process by using a composition that contains water-soluble hydroxyacids. Suitable water-soluble hydroxyacids include, but are not necessarily limited to glycolic acid, gluconic acid, C₂-C₄ alpha-hydroxy acids, poly-hydroxy carboxylic acids, thioglycolic acid, chloroacetic acid, polymeric forms of the above hydroxyacids, poly-glycolic esters, glycolate ethers, and ammonium salt and alkali metal salts of these hydroxyacids, and mixtures thereof. The composition may also include at least one mineral acid to reduce the pH of the desalter wash water. A solvent may be optionally included in the composition. The invention permits transfer of metals and/or amines into the aqueous phase with little or no hydrocarbon phase undercarry into the aqueous phase. The composition is particularly useful in treating crude oil emulsions, and in removing calcium and other metals therefrom.

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(54) Title: ADDITIVES TO ENHANCE METAL AND AMINE REMOVAL IN REFINERY DESALTING PROCESSES

(57) Abstract: It has been discovered that metals and/or amines can be removed or transferred from a hydrocarbon phase to a water phase in an emulsion breaking process by using a composition that contains water-soluble hydroxyacids. Suitable water-soluble hydroxyacids include, but are not necessarily limited to glycolic acid, gluconic acid, C₂-C₄ alpha-hydroxy acids, poly-hydroxy carboxylic acids, thioglycolic acid, chloroacetic acid, polymeric forms of the above hydroxyacids, poly-glycolic esters, glycolate ethers, and ammonium salt and alkali metal salts of these hydroxyacids, and mixtures thereof. The composition may also include at least one mineral acid to reduce the pH of the desalter wash water. A solvent may be optionally included in the composition. The invention permits transfer of metals and/or amines into the aqueous phase with little or no hydrocarbon phase undercarry into the aqueous phase. The composition is particularly useful in treating crude oil emulsions, and in removing calcium and other metals therefrom.



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ADDITIVES TO ENHANCE METAL AND AMINE REMOVAL IN REFINERY DESALTING PROCESSES

Field of the Invention

5 The present invention relates to methods and compositions for separating emulsions of hydrocarbons and water, and more particularly relates, in one embodiment, to methods and compositions for transferring metals and/or amines to an aqueous phase in an emulsion breaking process.

Background of the Invention

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In an oil refinery, the desalting of crude oil has been practiced for many years. The crude is usually contaminated from several sources, including, but not necessarily limited to:

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- Brine contamination in the crude oil as a result of the brine associated with the oil in the ground;

- Minerals, clay, silt, and sand from the formation around the oil well bore;

- Metals including calcium, zinc, silicon, nickel, sodium, potassium, etc.;

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- Nitrogen-containing compounds such as amines used to scrub H₂S from refinery gas streams in amine units, or from amines used as neutralizers in crude unit overhead systems, and also from H₂S scavengers used in the oilfield; and

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- Iron sulfides and iron oxides resulting from pipeline and vessel corrosion during production, transport, and storage.

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Desalting is necessary prior to further processing to remove these salts and other inorganic materials that would otherwise cause fouling and deposits in downstream heat exchanger equipment and/or form corrosive salts detrimental to crude oil processing equipment. Further, these metals can act as poisons for the catalysts used in downstream refinery units. Effective crude oil desalting can help minimize the effects of these contaminants on the crude unit and downstream operations. Proper desalter operations provide the following benefits to the refiner:

- Reduced crude unit corrosion.
 - Reduced crude preheat system fouling.
 - Reduced potential for distillation column damage.
 - Reduced energy costs.
- 5 • Reduced downstream process and product contamination.

Desalting is the resolution of the natural emulsion of water that accompanies the crude oil by creating another emulsion in which about 5 percent relative wash water is dispersed into the oil using a mix valve. The emulsion mix is directed into a desalter vessel containing a parallel series of

10 electrically charged plates. Under this arrangement, the oil and water emulsion is exposed to the applied electrical field. An induced dipole is formed on each water droplet within the emulsion that causes electrostatic attraction and coalescence of the water droplets into larger and larger droplets. Eventually, the emulsion resolves into two separate phases — the oil phase (top layer) and

15 the water phase (bottom layer). The streams of desalted crude oil and effluent water are separately discharged from the desalter.

The entire desalting process is a continuous flow procedure as opposed to a batch process. Normally, chemical additives are injected before the mix valve to help resolve the oil/water emulsion in addition to the use of

20 electrostatic coalescence. These additives effectively allow small water droplets to more easily coalesce by lowering the oil/water interfacial tension.

Crude oil that contains a high percent of particulate solids can complicate the desalting process. The particulate solids, by nature, would prefer to transfer to the water phase. However, much of the solids in a crude oil

25 from a field exists in tight water-in-oil emulsions. That is, oil-wetted solids in high concentration in the crude may help form tight oil and water emulsions that are difficult to resolve. These tight emulsions are often referred to as “rag” and may exist as a layer between the separated oil and water phases. The rag layer inside the desalter vessel may grow to such an extent that some of it will be

30 inadvertently discharged with the water phase. This is a problem for the waste water treatment plant since the rag layer still contains a high percentage of unresolved emulsified oil.

As mentioned, much of the solids encountered during crude oil desalting consists of iron, most commonly as particulate iron such as iron oxide, iron sulfide, etc. Other metals that are desirably removed include, but are not necessarily limited to, calcium, zinc, silicon, nickel, sodium, potassium, and the like, and typically a number of these metals are present. Some of the metals may be present in a soluble form. The metals may be present in inorganic or organic forms. In addition to complicating the desalter operation, iron and other metals are of particular concern to further downstream processing. This includes the coking operation since iron and other metals remaining in the processed hydrocarbon yields a lower grade of coke. Removing the metals from the crude oil early in the hydrocarbon processing stages is desired to eventually yield high quality coke as well as to limit corrosion and fouling processing problems.

Several treatment approaches have been made to reduce total metal levels and these all center on the removal of metals at the desalter unit. Normally, the desalter only removes water soluble inorganic salts such as sodium or potassium chlorides. Some crude oils contain water insoluble metal organic acid salts such as calcium naphthenate and iron naphthenate, which are soluble or dispersed as fine particulate matter in the oil but not in water.

It would thus be desirable to develop a composition and method employing it that would cause most or all of the metals in the crude oil to transfer from the oil phase in a desalter operation, with little or no oil carryunder in the aqueous phase. Nonyl phenol resins have been used as desalting additives in the past, but these materials have come under suspicion as possible hormonal mimics and are ineffective by themselves of removing metals such as calcium or iron.

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Summary of the Invention

Accordingly, it is an aspect of the present invention to provide a composition and method of using it that would transfer a large part of the metals and/or amines in the crude oil to the aqueous phase in a desalter operation.

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It is another aspect of the present invention to provide a composition and method for transferring metals and/or amines from a hydrocarbon into an aque-

ous phase in an emulsion breaking operation without causing oil undercarry into the aqueous phase.

In carrying out these and other aspects of the invention, there is provided, in one form, a method of transferring metals and/or amines from a hydrocarbon phase to a water phase involving adding to an emulsion of hydrocarbon and water, an effective amount of a composition to transfer metals and/or amines from a hydrocarbon phase to a water phase containing at least one water-soluble hydroxyacid. The water-soluble hydroxyacid may be glycolic acid, gluconic acid, C₂-C₄ alpha-hydroxy acids, poly-hydroxy carboxylic acids, thioglycolic acid, chloroacetic acid, polymeric forms of the above hydroxyacids, poly-glycolic esters, glycolate ethers, and ammonium salt and alkali metal salts of these hydroxyacids, and mixtures thereof. The emulsion is then resolved into hydrocarbon phase and an aqueous phase, where at least a portion of the metals and/or amines have been transferred to the aqueous phase. This is accomplished by converting the water insoluble salt such as calcium naphthenate into a water soluble salt such as calcium glycolate.

In another non-limiting embodiment of the invention, there is provided a composition for transferring metals and/or amines from a hydrocarbon phase to a water phase that includes a water-soluble hydroxyacid (as defined above, including the salts thereof), and a mineral acid.

There is provided in another non-limiting embodiment of the invention a composition for transferring metals and/or amines from a hydrocarbon phase to a water phase that includes a water-soluble hydroxyacid (as defined above, including the salts thereof) and at least one additional component that may be a hydrocarbon solvent, a corrosion inhibitor, a demulsifier, a scale inhibitor, metal chelants, wetting agents and mixtures thereof.

In still another non-limiting embodiment of the invention, there is provided a treated hydrocarbon emulsion that includes hydrocarbon, water, and a composition for transferring metals and/or amines from a hydrocarbon phase to a water phase comprising a water-soluble hydroxyacid (as defined above, including the salts thereof).

In accordance with an aspect of the present invention there is provided a method of transferring at least one of metals and from a hydrocarbon phase to a water phase in a refinery desalting process consisting of: adding to a wash water, an effective amount of a composition to transfer at least one of metals and amines from a hydrocarbon phase to a water phase

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comprising at least one water-soluble hydroxyacid selected from the group consisting of glycolic acid, gluconic acid, C₂-C₄ alpha-hydroxy acids, malic acid, lactic acid, poly-hydroxy carboxylic acids, thioglycolic acid, chloroacetic acid, polymeric forms of the above hydroxyacids, poly-glycolic esters, glycolate ethers, and ammonium salt and alkali metal salts of these hydroxyacids, and mixtures thereof; lowering the pH of the wash water to 6 or below, at a time that is at least one of before, during and after adding the composition; adding the wash water to crude oil to create an emulsion; and resolving the emulsion into hydrocarbon phase and an aqueous phase using electrostatic coalescence, where at least a portion of the at least one of metals and amines are transferred to the aqueous phase.

In accordance with a further aspect of the present invention there is provided a method of transferring at least one of metals and amines from a hydrocarbon phase to a water phase in a refinery desalting process consisting of: adding to a wash water, an effective amount of a composition to transfer at least one of metals and amines from a hydrocarbon phase to a water phase comprising a mineral acid and at least one water-soluble hydroxyacid selected from the group consisting of glycolic acid, gluconic acid, C₂-C₄ alpha-hydroxy acids, malic acid, lactic acid, poly-hydroxy carboxylic acids, thioglycolic acid, chloroacetic acid, polymeric forms of the above hydroxyacids, poly-glycolic esters, glycolate ethers, and ammonium salt and alkali metal salts of these hydroxyacids, and mixtures thereof, where the water-soluble hydroxyacid comprises from about 1 to about 100 wt. % of the composition and the composition further comprises a water or alcohol solvent; lowering the pH of the wash water to 6 or below, at a time that is at least one of before, during and after adding the composition; adding the wash water to crude oil to create an emulsion; and resolving the emulsion into hydrocarbon phase and an aqueous phase using electrostatic coalescence, where at least a portion of the at least one of metals and amines are transferred to the aqueous phase.

In accordance with a further aspect of the present invention there is provided a composition for transferring at least one of metals and amines from a hydrocarbon phase to a water phase consisting of: water; a water-soluble hydroxyacid selected from the group consisting of glycolic acid, gluconic acid, C₂-C₄ alpha-hydroxy acids, malic acid, lactic acid, poly-hydroxy carboxylic acids, thioglycolic acid, chloroacetic acid, polymeric forms of the above hydroxyacids, poly-glycolic esters, glycolate

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ethers, and ammonium salt and alkali metal salts of these hydroxyacids, and mixtures thereof; a mineral acid, and at least one demulsifier; where the pH of the composition is 6 or below.

In accordance with a further aspect of the present invention there is provided a treated hydrocarbon crude oil emulsion consisting of:

5 crude oil; a composition for transferring at least one of metals and amines from a hydrocarbon phase to a water phase comprising a water-soluble hydroxyacid selected from the group consisting of glycolic acid, gluconic acid, C₂-C₄ alpha-hydroxy acids, malic acid, lactic acid, poly-hydroxy

10 carboxylic acids, thioglycolic acid, chloroacetic acid, polymeric forms of the above hydroxyacids, poly-glycolic esters, glycolate ethers, and ammonium salt and alkali metal salts of these hydroxyacids, and mixtures thereof;

wash water where the pH of the wash water is 6 or below; a mineral acid; and at least one additional component selected from the group consisting of

15 a water or alcohol solvent, a corrosion inhibitor, a demulsifier, a scale inhibitor, metal chelants, wetting agents and mixtures thereof.

In accordance with a further aspect of the present invention there is provided a method of transferring amines from a hydrocarbon phase to a water phase in a refinery desalting process consisting of:

20 adding to a wash water, an effective amount of a composition to transfer amines from a hydrocarbon phase to a water phase comprising at least one water-soluble organic acid selected from the group consisting of glycolic acid, gluconic acid, citric acid, C₂-C₄ alpha-hydroxy acids, malic acid, lactic acid, poly-hydroxy carboxylic acids, thioglycolic acid, chloroacetic acid,

25 polymeric forms of the above hydroxyacids, poly-glycolic esters, glycolate ethers, and ammonium salt and alkali metal salts of these hydroxyacids, and mixtures thereof;

lowering the pH of the wash water to 6 or below, before, during or after adding the composition; adding the wash water to crude oil to create an

30 emulsion; and resolving the emulsion into hydrocarbon phase and an aqueous phase using electrostatic coalescence, where at least a portion of at least one of the metals and amines are transferred to the aqueous phase.

In accordance with a further aspect of the present invention there is provided a method of transferring at least one of metals and amines from a

35 hydrocarbon phase to a water phase in a refinery desalting process consisting of: adding to a wash water, an effective amount of a composition to transfer at least one of metals and amines from a hydrocarbon phase to a

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water phase comprising a mineral acid and at least one water-soluble organic acid selected from the group consisting of glycolic acid, gluconic acid, citric acid, C₂-C₄ alpha-hydroxy acids, malic acid, lactic acid, poly-hydroxy carboxylic acids, thioglycolic acid, chloroacetic acid, polymeric forms of the above hydroxyacids, poly-glycolic esters, glycolate ethers, and ammonium salt and alkali metal salts of these hydroxyacids, and mixtures thereof;

lowering the pH of the wash water to 6 or below, at a time that is at least one of before, during and after adding the composition; adding the wash water to crude oil to create an emulsion; and resolving the emulsion into hydrocarbon phase and an aqueous phase using electrostatic coalescence, where at least a portion of the at least one of metals and amines are transferred to the aqueous phase.

In accordance with an aspect of the present invention there is provided a composition for transferring at least one of metals and amines from a hydrocarbon phase to a water phase consisting of: water; a water-soluble organic acid selected from the group consisting of glycolic acid, gluconic acid, citric acid, C₂-C₄ alpha-hydroxy acids, malic acid, lactic acid, poly-hydroxy carboxylic acids, thioglycolic acid, chloroacetic acid, polymeric forms of the above hydroxyacids, poly-glycolic esters, glycolate ethers, and ammonium salt and alkali metal salts of these hydroxyacids, and mixtures thereof; a mineral acid, and at least one demulsifier; where the pH of the composition is 6 or below.

In accordance with a further aspect of the present invention there is provided a treated crude oil emulsion consisting of: crude oil; a composition for transferring amines from a hydrocarbon phase to a water phase comprising a water-soluble organic acid selected from the group consisting of glycolic acid, gluconic acid, citric acid, C₂-C₄ alpha-hydroxy acids, malic acid, lactic acid, poly-hydroxy carboxylic acids, thioglycolic acid, chloroacetic acid, polymeric forms of the above hydroxyacids, poly-glycolic esters, glycolate ethers, and ammonium salt and alkali metal salts of these hydroxyacids, and mixtures thereof; wash water where the pH of the wash water is 6 or below; a mineral acid; and at least one additional component selected from the group consisting of a water or alcohol solvent, a corrosion inhibitor, a demulsifier, a scale inhibitor, metal chelants, wetting agents and mixtures thereof.

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In accordance with a final aspect of the present invention there is provided a treated crude oil emulsion consisting of: crude oil; a composition for transferring at least one of metals and amines from a hydrocarbon phase to a water phase comprising a mineral acid and a water-soluble organic acid selected from the group consisting of glycolic acid, gluconic acid, citric acid, C₂-C₄ alpha-hydroxy acids, malic acid, lactic acid, poly-hydroxy carboxylic acids, thioglycolic acid, chloroacetic acid, polymeric forms of the above hydroxyacids, poly-glycolic esters, glycolate ethers, and ammonium salt and alkali metal salts of these hydroxyacids, and mixtures thereof; wash water where the pH of the wash water is 6 or below; a mineral acid; and at least one additional component selected from the group consisting of a water or alcohol solvent, a corrosion inhibitor, a demulsifier, a scale inhibitor, metal chelants, wetting agents and mixtures thereof.

In accordance with an aspect of the present invention, there is provided a method of transferring at least one of metals and amines from a hydrocarbon phase to a water phase in a refinery desalting process comprising: adding to a wash water, an effective amount of a composition to transfer at least one of metals and amines from a hydrocarbon phase to a water phase comprising at least one water-soluble hydroxylacid selected from the group comprising glycolic acid, gluconic acid, C₂-C₄ alpha-hydroxy acids, malic acid, lactic acid, poly-hydroxy carboxylic acids, thioglycolic acid, chloroacetic acid, polymeric forms of the above hydroxyacids, poly-glycolic esters, glycolate ethers, and ammonium salt and alkali metal salts of these hydroxyacids, and mixtures thereof; lowering the pH of the wash water to 6 or below, at a time that is at least one of before, during and after adding the composition; adding the wash water to crude oil to create an emulsion; and resolving the emulsion into hydrocarbon phase and an aqueous phase using electrostatic coalescence, where at least a portion of the at least one of metals and amines are transferred to the aqueous phase.

In accordance with another aspect of the present invention, there is provided a method of transferring at least one of metals and amines from a hydrocarbon phase to a water phase in a refinery desalting process comprising: adding to a wash water, an effective amount of a composition to

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transfer at least one of metals and amines from a hydrocarbon phase to a water phase comprising a mineral acid and at least one water-soluble hydroxyacid selected from the group comprising glycolic acid, gluconic acid, C₂-C₄ alpha-hydroxy acids, malic acid, lactic acid, poly-hydroxy carboxylic acids, thioglycolic acid, chloroacetic acid, polymeric forms of the above hydroxyacids, poly-glycolic esters, glycolate ethers, and ammonium salt and alkali metal salts of these hydroxyacids, and mixtures thereof, where the water-soluble hydroxyacid comprises from about 1 to about 100 wt. % of the composition and the composition further comprises a water or alcohol solvent; lowering the pH of the wash water to 6 or below, at a time that is at least one of before, during and after adding the composition; adding the wash water to crude oil to create an emulsion; and resolving the emulsion into hydrocarbon phase and an aqueous phase using electrostatic coalescence, where at least a portion of the at least one of metals and amines are transferred to the aqueous phase.

In accordance with another aspect of the present invention, there is provided a composition for transferring at least one of metals and amines from a hydrocarbon phase to a water phase comprising: water; a water-soluble hydroxyacid selected from the group comprising glycolic acid, gluconic acid, C₂-C₄ alpha-hydroxy acids, malic acid, lactic acid, poly-hydroxy carboxylic acids, thioglycolic acid, chloroacetic acid, polymeric forms of the above hydroxyacids, poly-glycolic esters, glycolate ethers, and ammonium salt and alkali metal salts of these hydroxyacids, and mixtures thereof; a mineral acid, and at least one demulsifier; where the pH of the composition is 6 or below.

In accordance with another aspect of the present invention, there is provided a treated hydrocarbon crude oil emulsion comprising: crude oil; a composition for transferring at least one of metals and amines from a hydrocarbon phase to a water phase comprising a water-soluble hydroxyacid selected from the group comprising glycolic acid, gluconic acid, C₂-C₄ alpha-hydroxy acids, malic acid, lactic acid, poly-hydroxy carboxylic acids, thioglycolic acid, chloroacetic acid, polymeric forms of the above hydroxyacids, poly-glycolic esters, glycolate ethers, and ammonium salt and alkali metal salts of these hydroxyacids, and mixtures thereof; wash water where the pH of the wash water is 6 or below; a mineral acid; and at least one additional component selected from the group comprising a water or alcohol

solvent, a corrosion inhibitor, a demulsifier, a scale inhibitor, metal chelants, wetting agents and mixtures thereof.

In accordance with another aspect of the present invention, there is provided a method of transferring amines from a hydrocarbon phase to a water phase in a refinery desalting process comprising: adding to a wash water, an effective amount of a composition to transfer amines from a hydrocarbon phase to a water phase comprising at least one water-soluble organic acid selected from the group comprising glycolic acid, gluconic acid, citric acid, C₂-C₄ alpha-hydroxy acids, malic acid, lactic acid, poly-hydroxy carboxylic acids, thioglycolic acid, chloroacetic acid, polymeric forms of the above hydroxyacids, poly-glycolic esters, glycolate ethers, and ammonium salt and alkali metal salts of these hydroxyacids, and mixtures thereof; lowering the pH of the wash water to 6 or below, before, during or after adding the composition; adding the wash water to crude oil to create an emulsion; and resolving the emulsion into hydrocarbon phase and an aqueous phase using electrostatic coalescence, where at least a portion of at least one of the metals and amines are transferred to the aqueous phase.

In accordance with another aspect of the present invention, there is provided a method of transferring at least one of metals and amines from a hydrocarbon phase to a water phase in a refinery desalting process comprising: adding to a wash water, an effective amount of a composition to transfer at least one of metals and amines from a hydrocarbon phase to a water phase comprising a mineral acid and at least one water-soluble organic acid selected from the group comprising glycolic acid, gluconic acid, citric acid, C₂-C₄ alpha-hydroxy acids, malic acid, lactic acid, poly-hydroxy carboxylic acids, thioglycolic acid, chloroacetic acid, polymeric forms of the above hydroxyacids, poly-glycolic esters, glycolate ethers, and ammonium salt and alkali metal salts of these hydroxyacids, and mixtures thereof; lowering the pH of the wash water to 6 or below, at a time that is at least one of before, during and after adding the composition; adding the wash water to crude oil to create an emulsion; and resolving the emulsion into hydrocarbon phase and an aqueous phase using electrostatic coalescence, where at least a portion of the at least one of metals and amines are transferred to the aqueous phase.

In accordance with another aspect of the present invention, there is provided a composition for transferring at least one of metals and amines

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from a hydrocarbon phase to a water phase comprising: water; a water-soluble organic acid selected from the group comprising glycolic acid, gluconic acid, citric acid, C₂-C₄ alpha-hydroxy acids, malic acid, lactic acid, poly-hydroxy carboxylic acids, thioglycolic acid, chloroacetic acid, polymeric forms of the above hydroxyacids, poly-glycolic esters, glycolate ethers, and ammonium salt and alkali metal salts of these hydroxyacids, and mixtures thereof; a mineral acid, and at least one demulsifier; where the pH of the composition is 6 or below.

In accordance with another aspect of the present invention, there is provided a treated crude oil emulsion comprising: crude oil; a composition for transferring amines from a hydrocarbon phase to a water phase comprising a water-soluble organic acid selected from the group comprising glycolic acid, gluconic acid, citric acid, C₂-C₄ alpha-hydroxy acids, malic acid, lactic acid, poly-hydroxy carboxylic acids, thioglycolic acid, chloroacetic acid, polymeric forms of the above hydroxyacids, poly-glycolic esters, glycolate ethers, and ammonium salt and alkali metal salts of these hydroxyacids, and mixtures thereof; wash water where the pH of the wash water is 6 or below; a mineral acid; and at least one additional component selected from the group comprising a water or alcohol solvent, a corrosion inhibitor, a demulsifier, a scale inhibitor, metal chelants, wetting agents and mixtures thereof.

In accordance with another aspect of the present invention, there is provided a treated crude oil emulsion comprising: crude oil; a composition for transferring at least one of metals and amines from a hydrocarbon phase to a water phase comprising a mineral acid and a water-soluble organic acid selected from the group comprising glycolic acid, gluconic acid, citric acid, C₂-C₄ alpha-hydroxy acids, malic acid, lactic acid, poly-hydroxy carboxylic acids, thioglycolic acid, chloroacetic acid, polymeric forms of the above hydroxyacids, poly-glycolic esters, glycolate ethers; and ammonium salt and alkali metal salts of these hydroxyacids, and mixtures thereof; wash water where the pH of the wash water is 6 or below; a mineral acid; and at least one additional component selected from the group comprising a water or alcohol solvent, a corrosion inhibitor, a demulsifier, a scale inhibitor, metal chelants, wetting agents and mixtures thereof.

In accordance with another aspect of the present invention, there is provided a method of transferring metals and/or amines from a hydrocarbon phase to a water phase in a refinery desalting process consisting of: adding to

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a wash water, an effective amount of a composition to transfer metals and/or amines from a hydrocarbon phase to a water phase, the composition comprising: at least one corrosion inhibitor, and at least one water-soluble hydroxyacid selected from the group consisting of glycolic acid, gluconic acid, citric acid, C₂-C₄ alpha-hydroxy acids, malic acid, lactic acid, poly-hydroxy carboxylic acids, thioglycolic acid, chloroacetic acid, polymeric forms of the above hydroxyacids, poly-glycolic esters, glycolate ethers, and ammonium salt and alkali metal salts of these hydroxyacids, and mixtures thereof; lowering the pH of the wash water to 6 or below, before, during and/or after adding the composition; adding the wash water to crude oil to create an emulsion; and resolving the emulsion into hydrocarbon phase and an aqueous phase using electrostatic coalescence, where at least a portion of the metals and/or amines are transferred to the aqueous phase.

In accordance with another aspect of the present invention, there is provided a method of transferring metals and/or amines from a hydrocarbon phase to a water phase in a refinery desalting process consisting of: adding to a wash water, an effective amount of a composition to transfer metals and/or amines from a hydrocarbon phase to a water phase, the composition comprising: at least one corrosion inhibitor; at least one demulsifier; and at least one water-soluble hydroxyacid selected from the group consisting of glycolic acid, gluconic acid, citric acid, C₂-C₄ alpha-hydroxy acids, malic acid, lactic acid, poly-hydroxy carboxylic acids, thioglycolic acid, chloroacetic acid, polymeric forms of the above hydroxyacids, poly-glycolic esters, glycolate ethers, and ammonium salt and alkali metal salts of these hydroxyacids, and mixtures thereof, where the water-soluble hydroxyacid comprises from about 1 to about 85 wt.% of the composition and the composition further comprises a water or alcohol solvent; lowering the pH of the wash water to 6 or below, before, during and/or after adding the composition; adding the wash water to crude oil to create an emulsion; and resolving the emulsion into hydrocarbon phase and an aqueous phase using electrostatic coalescence, where at least a portion of the metals and/or amines are transferred to the aqueous phase.

In accordance with another aspect of the present invention, there is provided a composition for transferring metals and/or amines from a hydrocarbon phase to a water phase consisting of: water; a water-soluble hydroxyacid selected from the group consisting of glycolic acid, gluconic acid, citric acid, C₂-C₄ alpha-hydroxy acids, malic acid, lactic

acid, poly-hydroxy carboxylic acids, thioglycolic acid, chloroacetic acid, polymeric forms of the above hydroxyacids, poly-glycolic esters, glycolate ethers, and ammonium salt and alkali metal salts of these hydroxyacids, and mixtures thereof; at least one corrosion inhibitor; and
5 at least one demulsifier; where the pH of the composition is 6 or below.

In accordance with another aspect of the present invention, there is provided a treated hydrocarbon crude oil emulsion consisting of: crude oil; a composition for transferring metals and/or amines from a hydrocarbon phase to a water phase comprising a water-soluble hydroxyacid selected from the
10 group consisting of glycolic acid, gluconic acid, citric acid, C₂-C₄ alpha-hydroxy acids, malic acid, lactic acid, poly-hydroxy carboxylic acids, thioglycolic acid, chloroacetic acid, polymeric forms of the above hydroxyacids, poly-glycolic esters, glycolate ethers, and ammonium salt and alkali metal salts of these hydroxyacids, and mixtures thereof; wash water
15 where the pH of the wash water is 6 or below; at least one corrosion inhibitor; and at least one additional component selected from the group consisting of a water or alcohol solvent, a demulsifier, a scale inhibitor, metal chelants, wetting agents and mixtures thereof.

Brief Description of the Drawing

The Figure is a graph of various amines and ammonia partitioning across desalters as a function of pH.

5

Detailed Description of the Invention

The inventors have discovered that the addition of glycolic acid (hydroxyacetic acid) and other water-soluble hydroxyacids to a crude oil can significantly reduce the amount of calcium and other metals and/or amines in the hydrocarbon when it is run through a desalter in a refinery. The inventors have compared the "normal" desalting on a reference crude oil containing higher than normal amounts of calcium and found minimal calcium removal. The addition of glycolic acid in levels of up to a 5:1 ratio with calcium, results in much lower metals and/or amine content of the desalted oil. The levels of metals other than calcium such as iron, zinc, silicon, nickel, sodium and potassium are also reduced. The removal of particulate iron in the form of iron oxide, iron sulfide, etc. is a specific, non-limiting embodiment of the invention. By "removing" the metals and/or amines from the hydrocarbon or crude is meant any and all partitioning, sequestering, separating, transferring, eliminating, dividing, removing, of one or more metal from the hydrocarbon or crude to any extent.

Being an aqueous additive, the glycolic acid is typically added to the wash water in the desalter. This improves distribution of the acid in the oil although addition to the aqueous phase should not be viewed as a requirement for the composition of the invention to work.

The composition and method of the invention will be valuable to produce high quality (*i.e.*, high purity) coke from crude that may originally have contained high concentrations of metals and/or amines and solids, including iron-based solids. Further, the invention advances the technology by removing inorganic material from the crude oil without discharging any oil or emulsion to the waste treatment plant.

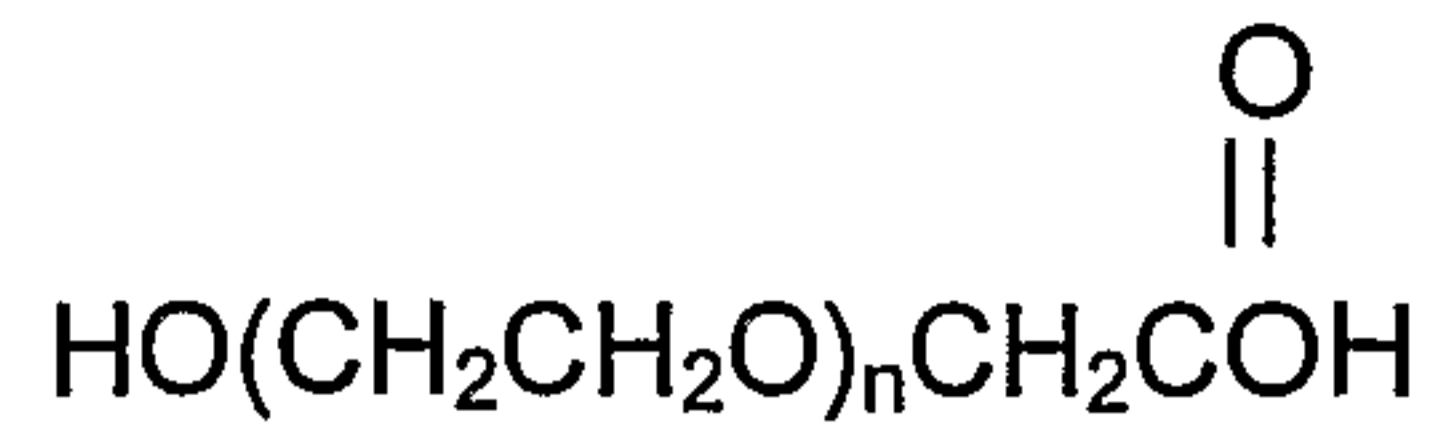
In this invention, it will be understood that the metals include, but are not necessarily limited to, those of Groups IA, IIA, VB, VIII, IIB and IVA of the Periodic Table (CAS version). In another non-limiting embodiment, the metals

include, but are not necessarily limited to calcium, iron, zinc, silicon, nickel, sodium, potassium, vanadium, and combinations thereof. In particular, nickel and vanadium are known poisons for catalysts used in fluid catalytic cracking units (FCCUs) downstream.

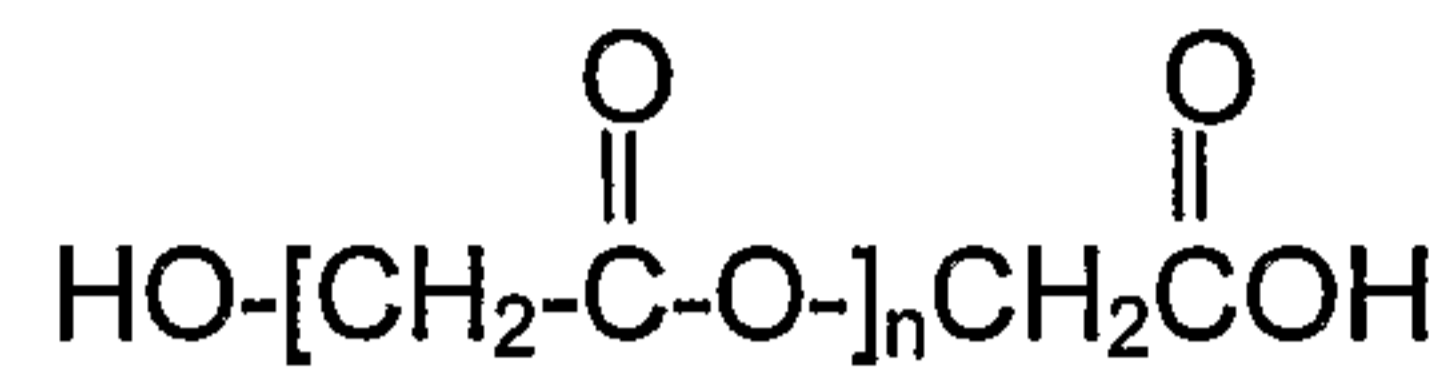
5 The amines removed in accordance with the method of this invention may include, but are not necessarily limited to, monoethanolamine (MEA); diethanolamine (DEA); triethanolamine (TEA); N-methylethanolamine; N,N-dimethylethanolamine (DMEA); morpholine; N-methyl morpholine; ethylenediamine (EDA); methoxypropylamine (MOPA); N-ethyl morpholine (EMO); N-
10 methyl ethanolamine, N-methyldiethanolamine and combinations thereof.

In one embodiment of the invention, the composition of the invention includes a water-soluble hydroxy acid. Hydroxy acids are defined herein as not including or exclusive of acetic acid. Acetic acid has sometimes been used to remove metals as well, but it has a high oil solubility and tends to stay with the
15 hydrocarbon coming from the desalter. The acidity of the acetic acid can then cause corrosion problems in the crude unit. The water-soluble hydroxy acids are much more water-soluble and will not partition as much into the crude oil, thus reducing downstream concerns. They are also less volatile and do not distill into the crude unit overhead system where they can increase corrosion
20 rates when combined with the water usually present at this location.

In one preferred, non-limiting embodiment of the invention, the water-soluble hydroxyacid is selected from the group consisting of glycolic acid, C₁-C₄ alpha-hydroxy acids, poly-hydroxy carboxylic acids, thioglycolic acid, chloroacetic acid, polymeric forms of the above hydroxyacids, glycolate ethers, poly-glycolic esters, and mixtures thereof. While thioglycolic acid and chloroacetic acid
25 are not strictly speaking hydroxyacids, they are functional equivalents thereof. For the purposes of this invention, they are defined as hydroxyacids. The alpha substituent on the C₁-C₄ alpha-hydroxy acids may be any C₁-C₄ straight or branched alkyl group. In one non-limiting embodiment of the invention, the
30 alpha substituent may be C₂-C₄ straight or branched alkyl group and lactic acid is not included. Gluconic acid, CH₂OH(CHOH)₄COOH, is a non-limiting but preferred polymer of glycolic acid. The glycolate ethers may have the formula:



5 where n ranges from 1-10. The glycolate esters may have a formula:



10 where n is as above. Thioglycolic acid and the ethers of glycolic acid may have the added benefits of a higher boiling point, and possibly increased water solubility. A higher boiling point means the additive will not distill into the distillate fractions in the crude unit and cause corrosion or product quality concerns. The higher water solubility also favors removal of the additive from the crude in the
 15 desalter and reduces the amount that may reach the downstream processing units.

In particular, the definition of water-soluble hydroxyacids includes ammonium salt and alkali metal salts (*e.g.* sodium and potassium salts, etc.) of these hydroxyacids alone or in combination with the other water-soluble hydroxyacids
 20 mentioned. Such salts would be formed in the desalter wash water as the system's pH was adjusted with pH adjusters such as sodium hydroxide, potassium hydroxide, ammonia, and the like.

In another non-limiting embodiment the water-soluble hydroxyacids do not include citric acid, malic acid, tartaric acid, mandelic acid, and lactic acid. In
 25 yet another non-limiting embodiment of the invention, the definition of water-soluble hydroxyacids does not include organic acid anhydrides, particularly acetic, propionic, butyric, valeric, stearic, phthalic and benzoic anhydrides.

In yet another non-limiting embodiment of the invention, glycolic acid and gluconic acid may be used to remove calcium and amines, and thioglycolic
 30 acid may be used for iron removal, from crude oil or another hydrocarbon phase.

It is expected that the water-soluble hydroxyacids will be used together with other additives including, but not necessarily limited to, corrosion inhibitors, demulsifiers, pH adjusters, metal chelants, scale inhibitors, hydrocarbon sol-

vents, and mixtures thereof, in a commercial process. Metal chelants are compounds that complex with metals to form chelates. In particular, mineral acids may be used since metal removal is best accomplished at an acidic pH. The use of combinations of water-soluble hydroxyacids, particularly glycolic acid or gluconic acid, and mineral acids may give the best economics in a commercial application. Suitable mineral acids for use in conjunction with the water-soluble hydroxyacids of this invention include, but are not necessarily limited to, sulfuric acid, hydrochloric acid, phosphoric acid, nitric acid, phosphorous acid, and mixtures thereof. As noted, in one embodiment of the invention, the method of this invention is practiced in a refinery desalting process that involves washing the crude emulsion with wash water. In one non-limiting embodiment of the invention, the amount of mineral acid used may be sufficient to lower the pH of the wash water to 6 or below. As noted below, in some embodiments of the invention, it may be necessary or preferred to lower the pH of the wash water to 5 or below, alternatively to 4 or below. The water-soluble hydroxyacids (and salts thereof) are expected to be useful over a wide pH range, although in some situations it may be necessary or desirable to adjust the pH to achieve the desired contaminant transfer or separation.

It will be appreciated that the necessary, effective or desired proportions of the hydroxyacid and/or the mineral acid will be difficult to predict in advance, since these proportions or dosages are dependent upon a number of factors, including, but not necessarily limited to, the nature of the hydrocarbon, the concentration of metal species and amine to be removed, the temperature and pressure conditions of method, the particular hydroxyacid and mineral acid used, etc. In general, the more of a species, such as calcium, there is to be removed, the more of the reactive acid that must be added. Since many undesirable species are affected, a successful metal removal process may require more reactive acid on a stoichiometric basis than would be indicated by the concentration of only the target species. It may therefore be insufficient to only just add enough acid to get the pH below 6. Nevertheless, in order to give some sense of the proportions that may be used, in one non-limiting embodiment of the invention, the composition may comprise down to about 1 wt.% water-soluble hydroxyacid; and up to about 20 wt.% mineral acid,

preferably from about 1 to about 100 wt.% water-soluble hydroxyacid; and from about 1 to about 20 wt.% mineral acid, and most preferably from about 25 to about 85 wt.% water-soluble hydroxyacid; and from about 15 to about 75 wt.% mineral acid. In some non-limiting embodiments of the invention, the mineral acid is optional and may be omitted.

The additive blend of this invention is injected into the wash water before the mix valve in neat form or diluted with water, alcohol or similar solvent suitable to keep all additive components in solution. The amount of solvent used may range from about 10 to about 95 wt.%, based on the total composition, preferably from about 20 to about 10 wt.%.

The concentration of the additive blend composition of this invention to be used in the crude oil to be effective is very difficult to predict in advance since it depends on multiple, interrelated factors including, but not limited to, the composition of the crude, the desalting conditions (temperature, pressure, etc.), the flow rate of the crude and its residence time in the desalter, among others. Nevertheless, for the purposes of non-limiting illustration, the proportion of the active water-soluble hydroxyacid that may be used in the crude (not including any solvent or mineral acid) may range from about 1 to about 2000 ppm-w, more preferably from about 10 to about 500 ppm-w and will depend on the concentration of metal species to be removed. The organic hydroxy acid reacts stoichiometrically with the organo metal and/or amine species to be removed. Thus an equivalent amount of organic hydroxy acid must be added compared to the concentration of metal species to be removed. A slight excess of the acid will ensure that the reaction goes to completion. In one non-limiting embodiment of the invention, the amount of water-soluble hydroxyacid is stoichiometric with the amount of metals and/or amines present, or greater than stoichiometric. For economic reasons the refinery may chose to leave some of the metal and/or amine species in the crude at an acceptably low level of contamination of hydrocarbon. In those cases the treatment level of the hydroxy acids can be correspondingly reduced.

It is most preferred, of course, that in the practice of this invention there be no oil carryunder in the aqueous phase, and that at least oil carryunder is minimized. Further, while it is preferred that all of the metals and/or amines

transfer to the aqueous phase, in one non-limiting theory of the invention, some of the metals and/or amines may be transferred from the oil phase into the rag. This proportion of metals and/or amines is then removed when the rag is cleaned out.

5 It is also most preferred, of course, that in the practice of this invention all of the metals and/or amines transfer to the aqueous phase. In another non-limiting embodiment of the invention, 25% or less metal and/or amine is present in the hydrocarbon phase after desalting, preferably 20% or less metal and/or amine remains, most preferably only 10% or less remains. In some
10 cases the refinery may chose to leave higher percentages of metal and/or amine contaminants in the crude if the detrimental effects are judged to be economically acceptable.

The invention will be illustrated further with reference to the following Examples, which are not intended to limit the invention, but instead illuminate it
15 further.

The following Electrostatic Desalting Dehydration Apparatus (EDDA) Test Method was employed to screen possible blend compositions. The EDDA is a laboratory test device to simulate the desalting process.

20 EDDA Test Method

1. Add 800, 600 or 400 ml of crude oil to be tested minus the percent of wash water (depending on the number of tubes the EDDA will hold) to a Waring blender.
2. Add the required percentage of wash water to the blender to bring the total
25 volume up to 800, 600 or 400 ml.
3. Mix at 50% speed (on the Variac) for 30 seconds. The speed can be reduced if the ΔP on the mix valve is low.
4. Pour the mixture into the EDDA tubes to just below the 100 ml line.
5. Place the tubes in the EDDA heating block that is at the desired test tem-
30 perature (99°C).
6. Add the desired quantity of demulsifier, in ppm, to each tube. With every test, a blank must be run for comparison purposes.

7. Place the screw top electrode in the tubes and allow the samples to heat for approximately 15 minutes.
8. Tighten the caps and shake each tube 100-200 times and place back in the heating block to reheat for five minutes.
- 5 9. Place the electrode cover over the tubes and lock into place. Make sure that there is good contact between the cover and the electrode caps.
10. Set the time for five minutes and run at 1500-3000 volts, depending on the test requirements.
11. At the end of the five minutes, pull the tubes out and check for the percent
10 water drop. Also check the quality of the interface and the quality of the water and record it.
12. Repeat steps 9, 10, and 11 until the desired total residence time is achieved.
13. Determine the best candidates and run a dehydration test on those
15 samples.
 - a) Fill the desired number of 12.5 ml centrifuge tubes to the 50% mark with xylene.
 - b) Use a glass syringe to pull 5.8 ml of dehydrated crude sample from the desired level in the tube and mix in with the xylene in the centrifuge
20 tubes.
 - c) Centrifuge the tubes at 2000 rpm for 4 minutes.
 - d) Check for the quantity of water, emulsion, and solids that are present in the bottom of the tube and record.

25 **ANALYSIS FOR CALCIUM**

After completing the EDDA test, use a glass syringe and cannula (long, wide bore needle), to withdraw two 20 ml aliquots of the EDDA desalted crude oil. Abstract the oil at a level in the EDDA tube that is at 25 ml and 70 ml below the surface of the oil. The two samples (top cut and bottom cut) are each ana-
30 lyzed for calcium concentration by whatever appropriate method (wet ash or microwave digestion, acidification, dilution, AA or ICP analysis). A similar procedure would be used to generate oil and water samples that could be analyzed by ion chromatography for other contaminants such as amine salts.

The crude oil used was from an African country that has a high calcium content.

Additive A = 70% glycolic acid, balance water.

5 Additive B = A blend of glycolic acid, phosphoric acid (pH adjuster), a pyridine quaternary ammonium compound (corrosion inhibitor), a dinonyl phenol/ethylene oxide oxyalkylate (co-solvent), isopropyl alcohol and water.

TABLE I

Sample A – 100% Crude

<u>Ex.</u>	<u>Metal</u>	<u>Additive</u>	<u>Raw Crude Oil, ppm</u>	<u>Desalted Crude Oil*</u>		<u>Water Phase, ppm</u>
				<u>Top Phase, ppm</u>	<u>Interface, ppm</u>	
1	Calcium	A	370	30	31	1700
2	"	B	370	76	76	1210
3	Iron	A	60	14	15	113
4	"	B	60	26	27	8
5	Zinc	A	35	6	4	163
6	"	B	35	17	16	34
7	Silicon	A	37	<2	<2	6
8	"	B	37	<2	2	7
9	Nickel	A	8	9	9	<2
10	"	B	8	9	10	<2
11	Sodium	A	97	9	10	416
12	"	B	97	13	12	404
13	Potassium	A	789	31	32	4030
14	"	B	789	34	32	3900

* Top Phase = 20 mL sample taken at 75 mL mark of 100 mL EDDA test tube.

- 5 Interface = 20 mL oil sample taken near oil/water interface present in EDDA test tube.

TABLE II

Sample B – 20% High Calcium Crude Blend

<u>Ex.</u>	<u>Metal</u>	<u>Additive</u>	<u>Raw Crude Oil, ppm</u>	<u>Desalted Crude Oil</u>		
				<u>Top Phase, ppm</u>	<u>Interface, ppm</u>	<u>Water Phase, ppm</u>
15	Calcium	A	Emulsion	Emulsion	Emulsion	Emulsion
16	"	B	58	8	5	362
17	Iron	A	Emulsion	Emulsion	Emulsion	Emulsion
18	"	B	10	2	<2	3.6
19	Zinc	A	Emulsion	Emulsion	Emulsion	Emulsion
20	"	B	6	5	22	32
21	Silicon	A	Emulsion	Emulsion	Emulsion	Emulsion
22	"	B	<2	11	20	2
23	Nickel	A	Emulsion	Emulsion	Emulsion	Emulsion
24	"	B	2	3	3	<2
25	Sodium	A	Emulsion	Emulsion	Emulsion	Emulsion
26	"	B	17	15	8	113
27	Potassium	A	Emulsion	Emulsion	Emulsion	Emulsion
28	"	B	79	3	4	91

From the data presented above it may be seen that the water-soluble hydroxyacid used (glycolic acid) effectively removed or transferred a variety of metals from the oil phase to the water phase. The inventive method was particularly effective on the high content metals such as calcium and potassium.

Tables III-VI provide additional data showing the transfer of various metals from a hydrocarbon phase to a water phase using the water-soluble hydroxyacids of the invention. The various components are defined as follows (all proportions are volume percents):

Additive C 70% glycolic acid, 30% water

Additive D 75% Additive C, 20% acrylic acid polymer scale inhibitor (which alone is designated SI1), 1.8% alkyl pyridine quaternary ammonium salt corrosion inhibitor, and 3.2% oxyalkylated alkyl phenol surfactant

Additive E 72% phosphorous acid scale control/pH adjuster compound, 14% oxyalkylated polyalkyleneamine, and 14% SI1.

Additive F 10% oxalic acid, 20% thioglycolic acid, 10% glycolic acid, 1.5% alkyl pyridine quaternary ammonium salt corrosion inhibitor, and 58.5%
5 water.

DA through DF designate Demulsifiers A through F, which are all various oxyalkylated alkylphenol resin demulsifiers. When used together with an additive of this invention, they may be abbreviated such as DA/D which indicates Demulsifier A is used together with Additive D in the ppm ratio
10 given in the next column.

SI2 Scale Inhibitor 2 that contains diammonium ethylenediamine tetracetic acid (EDTA).

SI3 Scale Inhibitor 3 that contains an amine phosphonate scale inhibitor.

SRA1 Scale Removal Additive 1, which is a blend of an alkyl pyridine quaternary ammonium salt corrosion inhibitor (same as in Additive D) with
15 phosphoric acid, glycolic acid and a demulsifier.

TABLE III
EDDA Test Results, Examples 29-40

Ex	Test Condition	Test Sample	Additive	Dose (ppm)		Metals Analysis											P							
						Na	K	Mg	Ca	Fe	Cu	Zn	Al	Sb	Ba	V		Pb	Mn	Ni	Si			
29	EDDA, 10% DI Wash Water	Crude A	C	1000 (in water)	Top Oil Interface Water	2.3	11.5	<1	85	51	<2	40.0	1.5	15	2.7	<1	8	10	10.0	1.3	8	8	<0.1	
30	"	"	lactic acid	1000 (in water)	Top Oil Interface Water	2.4	6.3	<1	37	39	<2	30.0	1.2	14	2.4	<1	7	6	8.0	<1	7	11	0.1	
31	"	"	Blank	none	Oil	164	765	4	306	49	<2	30.0	8.0	14	8.5	<1	8	11	7.0	10	8	8	8	
32	"	"	C	2000 (in water)	Oil	5	19	<3	24	16	<0.5	2.0	1.2	<0.5	0.7	<0.5	11.7	0.6	8.6	30.7	<2	<2	<2	
33	"	"	Blank	None	Oil	5	20	<3	24	16	<0.5	2.0	1.0	<0.5	0.7	<0.5	7.9	0.6	9.0	7.1	<2	<2	2.2	
34	"	"	SRA1	2000 (in water)	Top Oil Interface Water	425	4670	24	1640	93.8	0.2	162.0	1.5	0.4	33.8	0.2	3.1	56.4	1.0	5.5	5.5	2.2	2.8	
35	"	"	SI2	"	Top Oil Interface Water	87	919	5.8	363	68.6	<0.5	32.0	11.4	<0.5	8.4	<0.5	6.8	12.2	8.4	15.6	2.8	86	91	1300
36	"	"	C	"	Top Oil Interface Water	13	34		76	26		17.0			2		93	3	9.0	2	5	4	6	
37	"	"	SI3	"	Top Oil Interface Water	12	32		76	27		16.0			2		88	3	10.0	6	3	215	223	50
38	"	"	Blank	none	Oil	404	3900	21	1210	8		34.0			8		4	57	9.0	6	3	3	3	
39	"	"	SRA1	2000 (in water)	Top Oil Interface Water	11	14		192	29		7.0			6		80	13	12.0	14	11	11	5	
40	"	"	Blank	none	Oil	7	10		191	28		2.0			5		84	13	9.0	11	11	5	516	

TABLE IV
EDDA Test Results, Examples 41-54

Ex	Test Condition	Test Sample	Additive	Dose (ppm)	Na	K	Mg	Ca	Fe	Cu	Zn	Metals Analysis				Ba	V	Pb	Mn	Ni	Si	P
												Al	Sb	Al	Sb							
41	EDDA, 10% DI WW	Crude A	DA	15	5.9 626	17.1 <5	<3 17	371 210	58 <0.2	<3 <0.2	36.0 <0.2	4.0 <0.2	<3 <0.2	5 7	<3 <0.2	27 <0.4	14 <0.2	10.0 <0.2	13 10	4 <0.2		
42	"	"	DB	15	5 705	13 <5	<3 19	384 236	60 <0.2	<3 <0.2	36.0 <0.2	5.0 <0.2	<3 <0.2	5 8	<3 <0.2	22 <0.4	14 <0.2	10.0 <0.2	9 10	3 <0.2		
43	"	"	DC	15	11 579	32 <5	5 15	443 193	88 <0.2	<3 <0.2	38.0 <0.2	41.0 <0.2	<3 <0.2	6 7	<3 <0.2	33 <0.4	14 <0.2	11.0 <0.2	55 8	3 <0.2		
44	"	"	DD	15	8 698	27 <5	<3 17	368 234	57 <0.2	<3 <0.2	36.0 <0.2	4.0 <0.2	<3 <0.2	6 9	<3 <0.2	33 <0.4	14 <0.2	10.0 <0.2	8 9	4 <0.2		
45	"	"	DE	15	6 612	23 <5	3 16	366 204	55 <0.2	<3 <0.2	35.0 <0.2	4.0 <0.2	<3 <0.2	5 8	<3 <0.2	21 <0.4	14 <0.2	10.0 <0.2	66 8	<3 <0.2		
46	"	"	Blank	None	6 650	19 <5	<3 18	361 216	54 <0.2	<3 <0.2	35.0 <0.2	<3 <0.2	<3 <0.2	5 8	<3 <0.2	20 <0.4	13 <0.2	9.0 <0.2	8 9	3 <0.2		
47	"	Crude B	DA	15	4 147	<5 950	<3 7	40 143	7 <0.2	<3 <0.2	6.0 <0.2	<3 <0.2	<3 <0.2	<3 2	<3 <0.2	24 <0.4	<3 <0.2	<3 <0.2	6 2	<3 <0.2		
48	"	"	DB	15	5 134	<5 882	<3 6	41 129	6 <0.2	<3 <0.2	6.0 <0.2	<3 <0.2	<3 <0.2	<3 2	<3 <0.2	17 <0.4	<3 <0.2	<3 <0.2	6 2	<3 <0.2		
49	"	"	DC	15	5 147	<5 948	<3 7	39 140	7 <0.2	<3 <0.2	6.0 <0.2	<3 <0.2	<3 <0.2	<3 1	<3 <0.2	21 0.4	<3 <0.2	<3 <0.2	4 3	<3 <0.2		
50	"	"	DD	15	4 148	<5 954	<3 6	41 140	6 <0.2	<3 <0.2	6.0 <0.2	<3 <0.2	<3 <0.2	<3 1	<3 <0.2	21 <0.4	<3 <0.2	<3 <0.2	3 3	<3 <0.2		
51	"	"	DE	15	<5 943	<3 7	46 140	8 <0.2	<3 <0.2	6.0 <0.2	<3 <0.2	<3 <0.2	1 <0.2	8 <0.2	<3 <0.2	<3 <0.2	<3 <0.2	10 3	<3 <0.2	<3 <0.2		
52	"	"	Blank	none	5 130	<5 858	<3 5	48 122	6 <0.2	<3 <0.2	6.0 <0.2	<3 <0.2	<3 <0.2	<3 1	<3 <0.2	23 0.5	<3 <0.2	<3 <0.2	6 3	<3 <0.2		
53	"	Crude C	C	50	3 4 690	<1 <1 42	<1 <1 31	4 3 174	2 5 124	<1 <1 <1	<1 1.0 6.0	1.0 <1 2.0	<1 <1 <1	<1 <1 2	<1 <1 <1	<1 <1 <1	<1 <1 <1	6.0 6.0 <1	3 3 2	3 3 2	3 3 2	
54	"	"	Blank	none	46	4	3	14	22	<1	2.0	2.0	<1	<1	<1	<1	<1	6.0	4	4	4	

TABLE V

EDDA Test Results, Examples 55-67

Ex	Test Condition	Test Sample	Additive	Dose (ppm)		Metals Analysis															
						Na	K	Mg	Ca	Fe	Cu	Zn	Al	Sb	Ba	V	Pb	Mn	Ni	Si	P
55	EDDA, 4% DI WW	Crude D/G Blend	DA/D	15/50	Top Oil Water	6 338	29 40	3 40	225 383	0.2 0.2	29 0.2	3 <0.1	15.0 <0.1	4.0 <0.1	<0.1	5 17.5		11 1.1	8.0 <0.1	2 8.1	11 <0.1
56	"	"	DE/D	15/50	Top Oil Water	6 341	30 34	4 34	249 388	0.2 0.2	32 0.2	4 <0.1	15.0 <0.1	3.0 <0.1	<0.1	5 17.4		12 1.1	10.0 <0.1	3 7.1	<1 <0.1
57	"	"	DB/D	15/50	Top Oil Water	11 334	76 35	4 35	244 375	0.1 0.1	30 0.1	5 <0.1	14.0 <0.1	2.0 <0.1	<0.1	5 17.3		12 1.1	8.0 <0.1	2 8	6 <0.1
58	"	"	DA/D	25/50	Top Oil Water	8 339	30 39	2 39	216 382	0.2 0.2	26 0.2	7 <0.1	15.0 <0.1	3.0 <0.1	<0.1	5 18.6		11 1.2	7.0 <0.1	<1 9.6	9 <0.1
59	"	"	DE/D	25/50	Top Oil Water	338		37	380	0.2	0.2	<0.1	<0.1	<0.1	<0.1	19		1.1	<0.1	8	<0.1
60	"	"	DB/D	25/50	Top Oil Water	13 345	33 37	1 37	206 386	0.3 0.3	26 0.3	14 <0.1	15.0 <0.1	2.0 <0.1	<0.1	5 19		10 1.2	6.0 <0.1	1 8.9	8 <0.1
61	"	"	Blank	None	Oil	44	930	11	266	33	33	2	15.0	4.0	7		11	6.0	3	9	
62	"	"	DA/D	40/50	Top Oil Water	30 155	20 18	4 18	194 142	29 <0.1	29 <0.1	4 <0.1	12.0 <0.1	4.0 <0.1	3 <0.1	6.8		9 0.6	3.0 <0.1	5 3.5	14 114
63	"	"	DE/D	40/50	Top Oil Water	6 341	25 26	4 39	205 292	0.2 0.2	28 0.2	3 <0.1	13.0 <0.1	5.0 <0.1	2 <0.1	5 13.6		10 1.1	3.0 <0.1	5 6.9	15 180
64	"	"	DB/D	40/50	Top Oil Water	8 336	43 67	6 33.7	224 287	0.2 0.2	31 0.2	8 <0.1	17.0 <0.1	6.0 0.2	<1 <0.1	5 13.4		10 1.1	5.0 <0.1	2 7.1	18 180
65	"	"	DF/D	40/50	Top Oil Water	8 352	43 67	6 33.7	230 297	0.2 0.2	36 0.2	4 <0.1	19.0 <0.1	11.0 0.2	<1 <0.1	5 13.6		11 1	6.0 <0.1	3 6.8	18 187
66	"	"	DD/D	40/50	Top Oil Water	8 344	67 33	8 33	250 386	0.2 0.2	34 0.2	3 <0.1	21.0 0.2	10.0 1.0	<1 <0.1	6 13.4		12 1	8.0 <0.1	4 6.7	27 177
67	"	"	DC/D	40/50	Top Oil Water	7 352	33 33.2	5 33.2	211 300	0.2 0.2	34 0.2	4 <0.1	14.0 0.2	10.0 <0.5	<1 <0.1	5 13.6		10 1.1	4.0 <0.1	4 6.7	14 183

TABLE VI
EDDA Test Results, Examples 68-83

Ex	Test Condition	Test Sample	Additive	Dose (ppm)	Oil	Metals Analysis																		
						Na	K	Mg	Ca	Fe	Cu	Zn	Al	Sb	Ba	V	Pb	Mn	Ni	Si	P			
68	EDDA. 7.5% DI WW	Crude E	Blank	None		63	1590	12.2	475	23.8	0.5	13.0	0.6	<0.4	11	<0.4	<0.4	<0.4	<0.4	<0.4	10.4	10.6	3.9	2.9
69	"	"	DA/E	30/70	Top Oil Water	6.1	20.5	7.8	482	25	0.8	14.5	2.1	<0.4	9.2	<0.4	<0.4	<0.4	<0.4	<0.4	11.3	13.2	5.3	26.2
70	"	"	DE/E	30/70	Top Oil Water	5.6	17.7	7.4	435	25.2	0.6	14.7	0.5	<0.4	9.4	<0.4	<0.4	<0.4	<0.4	<0.4	11.6	13.6	2.4	25.5
71	"	"	DB/E	30/70	Top Oil Water	6	17.2	7.7	420	24	0.8	15.1	0.2	<0.4	8.6	<0.4	<0.4	<0.4	<0.4	<0.4	11.3	13.8	3.4	27.2
72	"	"	DF/E	30/70	Top Oil Water	6.2	19.6	7.5	485	24.8	0.8	14.7	0.6	<0.4	9.4	<0.4	<0.4	<0.4	<0.4	<0.4	11.4	14.2	2.6	25.3
73	"	"	DD/E	30/70	Top Oil Water	7	18.5	6.6	415	24.5	0.4	14.5	<0.4	<0.4	8.9	<0.4	<0.4	<0.4	<0.4	<0.4	11.3	13.6	3	26.6
74	"	"	DC/E	30/70	Top Oil Water	6	24.6	7.6	398	23.4	<0.4	15.0	<0.4	<0.4	8.4	<0.4	<0.4	<0.4	<0.4	<0.4	10.9	14.8	4	29.2
75	EDDA 5.0% DI Wash W.	Crude G	acetic acid	1000 (in water)	Top Oil Water	<0.4	12.6	2.5	22.6	25.2	0.9	10.6	2.1	<0.4	0.6	<0.4	<0.4	<0.4	<0.4	<0.4	2.5	11.6	1.1	4.2
76	"	Crude F	F	1000 (in water)	Top Oil Water	0.8	7	3.9	190	31.8	0.7	15.2	3.0	<0.4	3.9	<0.4	<0.4	<0.4	<0.4	<0.4	12.8	11.7	2.4	4
77	"	Blend E	Blank	None	Oil	11	320	3.3	100	11.3	0.4	4.2	1.1	<0.4	2.5	<0.4	<0.4	<0.4	<0.4	<0.4	4.1	3.5	0.7	1.5
78	"	+ Other Crude	acetic acid	1000 (in water)	Top Oil Water	1.4	7.7	1.2	21.5	3.5	<0.4	13.8	9.9	<0.4	0.9	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	4.1	1.3	2.2
79	"	30/70 Refiner	F	1000 (in water)	Top Oil	3	1.2	1	24.7	1.1	<0.4	0.6	1.0	<0.4	0.6	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	4.0	<0.4	2.1
80	"	Blend	lactic acid	1000 (in water)	Water	140	3170	29.3	408	118	<0.1	52.4	2.2	<0.1	4.2	<0.4	<0.4	<0.4	<0.4	<0.4	38.8	0.5	4.9	0.6
81	"	"	glycolic acid	1000 (in water)	Top Oil Water	2.4	22.9	1.2	25.9	2.7	<0.4	0.9	1.5	<0.4	0.8	<0.4	<0.4	<0.4	<0.4	<0.4	1.1	3.9	2.6	2.2
82	"	"	S11	1000 (in water)	Top Oil Water	2	7.9	1.9	75	11.1	0.5	5.0	1.1	<0.4	1.7	<0.4	<0.4	<0.4	<0.4	<0.4	4.2	3.8	<0.4	1.9
83	"	"	Oxalic acid	1000 (in water)	Top Oil Water	6.6	21.9	2.5	80	11.4	0.5	4.7	1.0	<0.4	1.6	<0.4	<0.4	<0.4	<0.4	<0.4	4.2	3.9	<0.4	2.3

The Figure presents a graph showing the partitioning across desalters of various amines and ammonia as a function of pH. The addition of water-soluble hydroxyacids of this invention such as glycolic and gluconic acid to the desalter wash water at the use
5 rates specified herein will reduce the water's pH to the range of about 3- 6.5.

In the foregoing specification, the invention has been described with reference to specific embodiments thereof, and has been demonstrated as effective in transferring metals, e.g. calcium, potassium, etc., and/or amines from crude oil to the aqueous phase in bench scale desalting testing, as non-limiting examples. However, it will be evident
10 that various modifications and changes can be made thereto without departing from the scope of the invention as set forth in the appended claims. Accordingly, the specification is to be regarded in an illustrative rather than a restrictive sense. For example, specific water-soluble hydroxyacids, and combinations thereof with other mineral acids, other than those specifically exemplified or mentioned, or in different proportions, falling within
15 the claimed parameters, but not specifically identified or tried in a particular application to transfer metals and/or amines into the aqueous phase, are within the scope of this invention. Similarly, it is expected that the inventive compositions will find utility as metal transfer compositions for other fluids besides crude oil emulsions.

CLAIMS

1. A method of transferring at least one of metals and amines from a hydrocarbon phase to a water phase in a refinery desalting process consisting of:
 - adding to a wash water, an effective amount of a composition to transfer at least one of metals and amines from a hydrocarbon phase to a water phase comprising at least one water-soluble hydroxyacid selected from the group consisting of glycolic acid, gluconic acid, C₂-C₄ alpha-hydroxy acids, malic acid, lactic acid, poly-hydroxy carboxylic acids, thioglycolic acid, chloroacetic acid, polymeric forms of the above hydroxyacids, poly-glycolic esters, glycolate ethers, and ammonium salt and alkali metal salts of these hydroxyacids, and mixtures thereof;
 - lowering the pH of the wash water to 6 or below, at a time that is at least one of before, during and after adding the composition; adding the wash water to crude oil to create an emulsion;
 - and resolving the emulsion into hydrocarbon phase and an aqueous phase using electrostatic coalescence, where at least a portion of the at least one of metals and amines are transferred to the aqueous phase.
2. The method of claim 1 where in the adding of the composition, the composition additionally comprises a mineral acid.
3. The method of claim 2 where in the adding of the composition, the composition further comprises down to about 1 wt. % water-soluble hydroxyacid; and up to about 20 wt. % mineral acid.
4. The method of claim 2 where the amount of mineral acid is sufficient to lower the pH of the wash water to 6 or below.
5. The method of claim 1 where in the adding of the composition, the water-soluble hydroxyacid is present in the emulsion in an amount ranging from about 1 to about 2000 ppm.
6. The method of claim 1 where in the adding of the composition, the composition further comprises water or alcohol solvent.

7. A method of transferring at least one of metals and amines from a hydrocarbon phase to a water phase in a refinery desalting process consisting of:

adding to a wash water, an effective amount of a composition to transfer at least one of metals and amines from a hydrocarbon phase to a water phase comprising a mineral acid and at least one water-soluble hydroxyacid selected from the group consisting of glycolic acid, gluconic acid, C₂-C₄ alpha-hydroxy acids, malic acid, lactic acid, poly-hydroxy carboxylic acids, thioglycolic acid, chloroacetic acid, polymeric forms of the above hydroxyacids, poly-glycolic esters, glycolate ethers, and ammonium salt and alkali metal salts of these hydroxyacids, and mixtures thereof, where the water-soluble hydroxyacid comprises from about 1 to about 100 wt. % of the composition and the composition further comprises a water or alcohol solvent;

lowering the pH of the wash water to 6 or below, at a time that is at least one of before, during and after adding the composition;

adding the wash water to crude oil to create an emulsion; and resolving the emulsion into hydrocarbon phase and an aqueous phase using electrostatic coalescence, where at least a portion of the at least one of metals and amines are transferred to the aqueous phase.

8. The method of claim 7 where the amount of mineral acid is sufficient to lower the pH of the wash water to 6 or below.

9. A composition for transferring at least one of metals and amines from a hydrocarbon phase to a water phase consisting of:

water;

a water-soluble hydroxyacid selected from the group consisting of glycolic acid, gluconic acid, C₂-C₄ alpha-hydroxy acids, malic acid, lactic acid, poly-hydroxy carboxylic acids, thioglycolic acid, chloroacetic acid, polymeric forms of the above hydroxyacids, poly-glycolic esters, glycolate ethers, and ammonium salt and alkali metal salts of these hydroxyacids, and mixtures thereof;

a mineral acid, and at least one demulsifier;

where the pH of the composition is 6 or below.

10. The composition of claim 9 where the composition further comprises: down to about 1 wt. % water-soluble hydroxyacid; and up to about 20 wt. % mineral acid.
11. The composition of claim 9 where the water-soluble hydroxyacid comprises from about 1 to about 85 wt % of the composition.
12. A treated hydrocarbon crude oil emulsion consisting of:
 - crude oil;
 - a composition for transferring at least one of metals and amines from a hydrocarbon phase to a water phase comprising a water-soluble hydroxyacid selected from the group consisting of glycolic acid, gluconic acid, C₂-C₄ alpha-hydroxy acids, malic acid, lactic acid, poly-hydroxy carboxylic acids, thioglycolic acid, chloroacetic acid, polymeric forms of the above hydroxyacids, poly-glycolic esters, glycolate ethers, and ammonium salt and alkali metal salts of these hydroxyacids, and mixtures thereof;
 - wash water where the pH of the wash water is 6 or below;
 - a mineral acid;
 - and at least one additional component selected from the group consisting of a water or alcohol solvent, a corrosion inhibitor, a demulsifier, a scale inhibitor, metal chelants, wetting agents and mixtures thereof.
13. The treated crude oil emulsion of claim 12 where the composition further comprises: down to about 1 wt. % water-soluble hydroxyacid; and up to about 20 wt. % mineral acid.
14. The treated crude oil emulsion of claim 12 where the amount of mineral acid is sufficient to lower the pH of the wash water to 6 or below.
15. The treated crude oil emulsion of claim 12 where the water-soluble hydroxyacid is present in the emulsion in an amount ranging from about 1 to about 2000 ppm.
16. The treated crude oil emulsion of claim 12 where the hydrocarbon component contains more than 10 ppm iron or calcium.
17. The method of claim 1 where the composition additionally comprises at least one

additional component selected from the group consisting of a water or alcohol solvent, a corrosion inhibitor, a demulsifier, a scale inhibitor, metal chelants, wetting agents and mixtures thereof.

18. A method of transferring amines from a hydrocarbon phase to a water phase in a refinery desalting process consisting of:

adding to a wash water, an effective amount of a composition to transfer amines from a hydrocarbon phase to a water phase comprising at least one water-soluble organic acid selected from the group consisting of glycolic acid, gluconic acid, citric acid, C₂-C₄ alpha-hydroxy acids, malic acid, lactic acid, poly-hydroxy carboxylic acids, thioglycolic acid, chloroacetic acid, polymeric forms of the above hydroxyacids, poly-glycolic esters, glycolate ethers, and ammonium salt and alkali metal salts of these hydroxyacids, and mixtures thereof;

lowering the pH of the wash water to 6 or below, before, during or after adding the composition;

adding the wash water to crude oil to create an emulsion;

and resolving the emulsion into hydrocarbon phase and an aqueous phase using electrostatic coalescence, where at least a portion of at least one of the metals and amines are transferred to the aqueous phase.

19. The method of claim 18 where in the adding of the composition, the composition additionally comprises a mineral acid.

20. The method of claim 18 where the composition additionally comprises at least one additional component selected from the group consisting of a water or alcohol solvent, a corrosion inhibitor, a demulsifier, a scale inhibitor, metal chelants, wetting agents and mixtures thereof.

21. A method of transferring at least one of metals and amines from a hydrocarbon phase to a water phase in a refinery desalting process consisting of:

adding to a wash water, an effective amount of a composition to transfer at least one of metals and amines from a hydrocarbon phase to a water phase comprising a mineral acid and at least one water-soluble organic acid selected from the group consisting of glycolic acid, gluconic acid, citric acid, C₂-C₄ alpha-hydroxy acids, malic acid, lactic acid,

poly-hydroxy carboxylic acids, thioglycolic acid, chloroacetic acid, polymeric forms of the above hydroxyacids, poly-glycolic esters, glycolate ethers, and ammonium salt and alkali metal salts of these hydroxyacids, and mixtures thereof;

lowering the pH of the wash water to 6 or below, at a time that is at least one of before, during and after adding the composition; adding the wash water to crude oil to create an emulsion;

and resolving the emulsion into hydrocarbon phase and an aqueous phase using electrostatic coalescence, where at least a portion of the at least one of metals and amines are transferred to the aqueous phase.

22. The method of claim 21 where the composition additionally comprises at least one additional component selected from the group consisting of a water or alcohol solvent, a corrosion inhibitor, a demulsifier, a scale inhibitor, metal chelants, wetting agents and mixtures thereof.

23. A composition for transferring at least one of metals and amines from a hydrocarbon phase to a water phase consisting of:

water;

a water-soluble organic acid selected from the group consisting of glycolic acid, gluconic acid, citric acid, C₂-C₄ alpha-hydroxy acids, malic acid, lactic acid, poly-hydroxy carboxylic acids, thioglycolic acid, chloroacetic acid, polymeric forms of the above hydroxyacids, poly-glycolic esters, glycolate ethers, and ammonium salt and alkali metal salts of these hydroxyacids, and mixtures thereof;

a mineral acid, and at least one demulsifier;

where the pH of the composition is 6 or below.

24. A treated crude oil emulsion consisting of:

crude oil;

a composition for transferring amines from a hydrocarbon phase to a water phase comprising a water-soluble organic acid selected from the group consisting of glycolic acid, gluconic acid, citric acid, C₂-C₄ alpha-hydroxy acids, malic acid, lactic acid, poly-hydroxy carboxylic acids, thioglycolic acid, chloroacetic acid, polymeric forms of the above hydroxyacids, poly-glycolic esters, glycolate ethers, and ammonium salt and alkali metal salts of these hydroxyacids, and mixtures thereof;

wash water where the pH of the wash water is 6 or below;

a mineral acid;

and at least one additional component selected from the group consisting of a water or alcohol solvent, a corrosion inhibitor, a demulsifier, a scale inhibitor, metal chelants, wetting agents and mixtures thereof.

25. A treated crude oil emulsion consisting of:

crude oil;

a composition for transferring at least one of metals and amines from a hydrocarbon phase to a water phase comprising a mineral acid and a water-soluble organic acid selected from the group consisting of glycolic acid, gluconic acid, citric acid, C₂-C₄ alpha-hydroxy acids, malic acid, lactic acid, poly-hydroxy carboxylic acids, thioglycolic acid, chloroacetic acid, polymeric forms of the above hydroxyacids, poly-glycolic esters, glycolate ethers, and ammonium salt and alkali metal salts of these hydroxyacids, and mixtures thereof;

wash water where the pH of the wash water is 6 or below;

a mineral acid;

and at least one additional component selected from the group consisting of a water or alcohol solvent, a corrosion inhibitor, a demulsifier, a scale inhibitor, metal chelants, wetting agents and mixtures thereof.

26. A method of transferring at least one of metals and amines from a hydrocarbon phase to a water phase in a refinery desalting process comprising:

adding to a wash water, an effective amount of a composition to transfer at least one of metals and amines from a hydrocarbon phase to a water phase comprising at least one water-soluble hydroxyacid selected from the group comprising glycolic acid, gluconic acid, C₂-C₄ alpha-hydroxy acids, malic acid, lactic acid, poly-hydroxy carboxylic acids, thioglycolic acid, chloroacetic acid, polymeric forms of the above hydroxyacids, poly-glycolic esters, glycolate ethers, and ammonium salt and alkali metal salts of these hydroxyacids, and mixtures thereof;

lowering the pH of the wash water to 6 or below, at a time that is at least one of before, during and after adding the composition; adding the wash water to crude oil to create an emulsion;

and resolving the emulsion into hydrocarbon phase and an aqueous phase using electrostatic coalescence, where at least a portion of the at least one of metals and amines are transferred to the aqueous phase.

27. The method of claim 26 where in the adding of the composition, the composition additionally comprises a mineral acid.

28. The method of claim 27 where in the adding of the composition, the composition further comprises down to about 1 wt. % water-soluble hydroxyacid; and up to about 20 wt. % mineral acid.

29. The method of claim 27 where the amount of mineral acid is sufficient to lower the pH of the wash water to 6 or below.

30. The method of claim 26 where in the adding of the composition, the water-soluble hydroxyacid is present in the emulsion in an amount ranging from about 1 to about 2000 ppm.

31. The method of claim 26 where in the adding of the composition, the composition further comprises water or alcohol solvent.

32. A method of transferring at least one of metals and amines from a hydrocarbon phase to a water phase in a refinery desalting process comprising:

adding to a wash water, an effective amount of a composition to transfer at least one of metals and amines from a hydrocarbon phase to a water phase comprising a mineral acid and at least one water-soluble hydroxyacid selected from the group comprising glycolic acid, gluconic acid, C₂-C₄ alpha-hydroxy acids, malic acid, lactic acid, poly-hydroxy carboxylic acids, thioglycolic acid, chloroacetic acid, polymeric forms of the above hydroxyacids, poly-glycolic esters, glycolate ethers, and ammonium salt and alkali metal salts of these hydroxyacids, and mixtures thereof, where the water-soluble hydroxyacid comprises from about 1 to about 100 wt. % of the composition and the composition further comprises a water or alcohol solvent;

lowering the pH of the wash water to 6 or below, at a time that is at least one of before, during and after adding the composition;

adding the wash water to crude oil to create an emulsion; and resolving the emulsion into hydrocarbon phase and an aqueous phase using electrostatic coalescence, where at least a portion of the at least one of metals and amines are transferred to the aqueous phase.

33. The method of claim 32 where the amount of mineral acid is sufficient to lower the pH of the wash water to 6 or below.

34. A composition for transferring at least one of metals and amines from a hydrocarbon phase to a water phase comprising:

water;

a water-soluble hydroxyacid selected from the group comprising glycolic acid, gluconic acid, C₂-C₄ alpha-hydroxy acids, malic acid, lactic acid, poly-hydroxy carboxylic acids, thioglycolic acid, chloroacetic acid, polymeric forms of the above hydroxyacids, poly-glycolic esters, glycolate ethers, and ammonium salt and alkali metal salts of these hydroxyacids, and mixtures thereof;

a mineral acid, and at least one demulsifier;

where the pH of the composition is 6 or below.

35. The composition of claim 34 where the composition further comprises: down to about 1 wt. % water-soluble hydroxyacid; and up to about 20 wt. % mineral acid.

36. The composition of claim 34 where the water-soluble hydroxyacid comprises from about 1 to about 85 wt % of the composition.

37. A treated hydrocarbon crude oil emulsion comprising:
crude oil;

a composition for transferring at least one of metals and amines from a hydrocarbon phase to a water phase comprising a water-soluble hydroxyacid selected from the group comprising glycolic acid, gluconic acid, C₂-C₄ alpha-hydroxy acids, malic acid, lactic acid, poly-hydroxy carboxylic acids, thioglycolic acid, chloroacetic acid, polymeric forms of the above hydroxyacids, poly-glycolic esters, glycolate ethers, and ammonium salt and alkali metal salts of these hydroxyacids, and mixtures thereof;

wash water where the pH of the wash water is 6 or below;

a mineral acid;

and at least one additional component selected from the group comprising a water or alcohol solvent, a corrosion inhibitor, a demulsifier, a scale inhibitor, metal chelants, wetting agents and mixtures thereof.

38. The treated crude oil emulsion of claim 37 where the composition further comprises: down to about 1 wt. % water-soluble hydroxyacid; and up to about 20 wt. % mineral acid.

39. The treated crude oil emulsion of claim 37 where the amount of mineral acid is sufficient to lower the pH of the wash water to 6 or below.

40. The treated crude oil emulsion of claim 37 where the water-soluble hydroxyacid is present in the emulsion in an amount ranging from about 1 to about 2000 ppm.

41. The treated crude oil emulsion of claim 37 where the hydrocarbon component contains more than 10 ppm iron or calcium.

42. The method of claim 26 where the composition additionally comprises at least one additional component selected from the group comprising a water or alcohol solvent, a corrosion inhibitor, a demulsifier, a scale inhibitor, metal chelants, wetting agents and mixtures thereof.

43. A method of transferring amines from a hydrocarbon phase to a water phase in a refinery desalting process comprising:

adding to a wash water, an effective amount of a composition to transfer amines from a hydrocarbon phase to a water phase comprising at least one water-soluble organic acid selected from the group comprising glycolic acid, gluconic acid, citric acid, C₂-C₄ alpha-hydroxy acids, malic acid, lactic acid, poly-hydroxy carboxylic acids, thioglycolic acid, chloroacetic acid, polymeric forms of the above hydroxyacids, poly-glycolic esters, glycolate ethers, and ammonium salt and alkali metal salts of these hydroxyacids, and mixtures thereof;

lowering the pH of the wash water to 6 or below, before, during or after adding the composition;

adding the wash water to crude oil to create an emulsion;

and resolving the emulsion into hydrocarbon phase and an aqueous phase using electrostatic coalescence, where at least a portion of at least one of the metals and amines are transferred to the aqueous phase.

44. The method of claim 43 where in the adding of the composition, the composition additionally comprises a mineral acid.

45. The method of claim 43 where the composition additionally comprises at least one additional component selected from the group comprising a water or alcohol solvent, a corrosion inhibitor, a demulsifier, a scale inhibitor, metal chelants, wetting agents and mixtures thereof.

46. A method of transferring at least one of metals and amines from a hydrocarbon phase to a water phase in a refinery desalting process comprising:

adding to a wash water, an effective amount of a composition to transfer at least one of metals and amines from a hydrocarbon phase to a water phase comprising a mineral acid and at least one water-soluble organic acid selected from the group comprising glycolic acid, gluconic acid, citric acid, C₂-C₄ alpha-hydroxy acids, malic acid, lactic acid, poly-hydroxy carboxylic acids, thioglycolic acid, chloroacetic acid, polymeric forms of the above hydroxyacids, poly-glycolic esters, glycolate ethers, and ammonium salt and alkali metal salts of these hydroxyacids, and mixtures thereof;

lowering the pH of the wash water to 6 or below, at a time that is at least one of before, during and after adding the composition; adding the wash water to crude oil to create an emulsion;

and resolving the emulsion into hydrocarbon phase and an aqueous phase using electrostatic coalescence, where at least a portion of the at least one of metals and amines are transferred to the aqueous phase.

47. The method of claim 46 where the composition additionally comprises at least one additional component selected from the group comprising a water or alcohol solvent, a corrosion inhibitor, a demulsifier, a scale inhibitor, metal chelants, wetting agents and mixtures thereof.

48. -A composition for transferring at least one of metals and amines from a hydrocarbon phase to a water phase comprising:

water;

a water-soluble organic acid selected from the group comprising glycolic acid, gluconic acid, citric acid, C₂-C₄ alpha-hydroxy acids, malic acid, lactic acid, poly-hydroxy carboxylic acids, thioglycolic acid, chloroacetic acid, polymeric forms of the above hydroxyacids, poly-glycolic esters, glycolate ethers, and ammonium salt and alkali metal salts of these hydroxyacids, and mixtures thereof;

a mineral acid, and at least one demulsifier;

where the pH of the composition is 6 or below.

49. A treated crude oil emulsion comprising:

crude oil;

a composition for transferring amines from a hydrocarbon phase to a water phase comprising a water-soluble organic acid selected from the group comprising glycolic acid, gluconic acid, citric acid, C₂-C₄ alpha-hydroxy acids, malic acid, lactic acid, poly-hydroxy carboxylic acids, thioglycolic acid, chloroacetic acid, polymeric forms of the above hydroxyacids, poly-glycolic esters, glycolate ethers, and ammonium salt and alkali metal salts of these hydroxyacids, and mixtures thereof;

wash water where the pH of the wash water is 6 or below;

a mineral acid;

and at least one additional component selected from the group comprising a water or alcohol solvent, a corrosion inhibitor, a demulsifier, a scale inhibitor, metal chelants, wetting agents and mixtures thereof.

50. A treated crude oil emulsion comprising:

crude oil;

a composition for transferring at least one of metals and amines from a hydrocarbon phase to a water phase comprising a mineral acid and a water-soluble organic acid selected from the group comprising glycolic acid, gluconic acid, citric acid, C₂-C₄ alpha-hydroxy acids, malic acid, lactic acid, poly-hydroxy carboxylic acids, thioglycolic acid, chloroacetic acid, polymeric forms of the above hydroxyacids, poly-glycolic esters, glycolate ethers, and ammonium salt and alkali metal salts of these hydroxyacids, and mixtures thereof;

wash water where the pH of the wash water is 6 or below;

a mineral acid;

and at least one additional component selected from the group comprising a water or alcohol solvent, a corrosion inhibitor, a demulsifier, a scale inhibitor, metal chelants, wetting agents and mixtures thereof.

51. A method of transferring metals and/or amines from a hydrocarbon phase to a water phase in a refinery desalting process consisting of:

adding to a wash water, an effective amount of a composition to transfer metals and/or amines from a hydrocarbon phase to a water phase, the composition comprising:

at least one corrosion inhibitor, and

at least one water-soluble hydroxyacid selected from the group

consisting of glycolic acid, gluconic acid, citric acid, C₂-C₄ alpha-hydroxy acids, malic acid, lactic acid, poly-hydroxy carboxylic acids, thioglycolic acid, chloroacetic acid, polymeric forms of the above hydroxyacids, poly-glycolic esters, glycolate ethers, and ammonium salt and alkali metal salts of these hydroxyacids, and mixtures thereof;

lowering the pH of the wash water to 6 or below, before, during and/or after adding the composition;

adding the wash water to crude oil to create an emulsion; and

resolving the emulsion into hydrocarbon phase and an aqueous phase using electrostatic coalescence, where at least a portion of the metals and/or amines are transferred to the aqueous phase.

52. The method of claim 51 where in the adding of the composition, the composition further comprises down to about 1 wt.% water-soluble hydroxyacid.

53. The method of claim 51 where in the adding of the composition, the water-soluble hydroxyacid is present in the emulsion in an amount ranging from about 1 to about 2000 ppm.

54. The method of claim 51 where in the adding of the composition, the

composition further comprises water or alcohol solvent.

55. The method of claim 51 where the composition additionally comprises at least one additional component selected from the group consisting of a water or alcohol solvent, a demulsifier, a scale inhibitor, metal chelants, wetting agents and mixtures thereof.

56. The method of claim 51 where the composition additionally comprises at least one demulsifier.

57. A method of transferring metals and/or amines from a hydrocarbon phase to a water phase in a refinery desalting process consisting of:

adding to a wash water, an effective amount of a composition to transfer metals and/or amines from a hydrocarbon phase to a water phase, the composition comprising:

at least one corrosion inhibitor;

at least one demulsifier; and

at least one water-soluble hydroxyacid selected from the group consisting of glycolic acid, gluconic acid, citric acid, C₂-C₄ alpha-hydroxy acids, malic acid, lactic acid, poly-hydroxy carboxylic acids, thioglycolic acid, chloroacetic acid, polymeric forms of the above hydroxyacids, poly-glycolic esters, glycolate ethers, and ammonium salt and alkali metal salts of these hydroxyacids, and mixtures thereof, where the water-soluble hydroxyacid comprises from about 1 to about 85 wt.% of the composition and the composition further comprises a water or alcohol solvent;

lowering the pH of the wash water to 6 or below, before, during and/or after adding the composition;

adding the wash water to crude oil to create an emulsion; and

resolving the emulsion into hydrocarbon phase and an aqueous phase using electrostatic coalescence, where at least a portion of the metals and/or amines are transferred to the aqueous phase.

58. A composition for transferring metals and/or amines from a hydrocarbon phase to a water phase consisting of:

water;

a water-soluble hydroxyacid selected from the group consisting of glycolic acid, gluconic acid, citric acid, C₂-C₄ alpha-hydroxy acids, malic acid, lactic acid, poly-hydroxy carboxylic acids, thioglycolic acid, chloroacetic acid, polymeric forms of the above hydroxyacids, poly-glycolic esters, glycolate ethers, and ammonium salt and alkali metal salts of these hydroxyacids, and mixtures thereof;

at least one corrosion inhibitor; and

at least one demulsifier;

where the pH of the composition is 6 or below.

59. The composition of claim 58 where the composition further comprises down to about 1 wt.% water-soluble hydroxyacid.

60. The composition of claim 58 where the water-soluble hydroxyacid comprises from about 1 to about 85 wt% of the composition.

61. A treated hydrocarbon crude oil emulsion consisting of:

crude oil;

a composition for transferring metals and/or amines from a hydrocarbon phase to a water phase comprising a water-soluble hydroxyacid selected from the group consisting of glycolic acid, gluconic acid, citric acid, C₂-C₄ alpha-hydroxy acids, malic acid, lactic acid, poly-hydroxy carboxylic acids, thioglycolic acid, chloroacetic acid, polymeric forms of the above hydroxyacids, poly-glycolic esters, glycolate ethers, and ammonium salt and alkali metal salts of these hydroxyacids, and mixtures thereof;

wash water where the pH of the wash water is 6 or below;

at least one corrosion inhibitor; and

at least one additional component selected from the group consisting of a water or alcohol solvent, a demulsifier, a scale inhibitor, metal chelants, wetting agents and mixtures thereof.

62. The treated crude oil emulsion of claim 61 where the composition further comprises down to about 1 wt.% water-soluble hydroxyacid.
63. The treated crude oil emulsion of claim 61 where the water-soluble hydroxyacid is present in the emulsion in an amount ranging from about 1 to about 2000 ppm.
64. The treated crude oil emulsion of claim 61 where the hydrocarbon component contains more than 10 ppm iron or calcium.
65. The treated crude oil emulsion of claim 61 where the at least one additional component is at least one demulsifier.

Amine/Ammonia Partitioning Across Desalters
As a Function of pH

