INTELLECTUAL
PROPERTY **INDIA**
एकस्व/PATENTS|अभिकल्प/DESIGNS|
व्यापार चिह्न/TRADE MARKS|भौगोलिक
उपदर्शन/GEOGRAPHICAL INDICATIONS

सत्यमेव जयते

भारत सरकार
GOVERNMENT OF INDIA

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प्लॉट न. 32/ PLOT NO. 32
सैक्टर -14/ SECTOR 14, द्वारका/ DWARKA
नई दिल्ली/NEW DELHI -110078
दूरभाष /Tel. No.: 011-25300200
फ़ैक्स /Fax : 011-28034301/02/15
ई मेल /Email : delhi-patent@nic.in
वेबसाइट /Website:http://ipindia.nic.in

सं. \ No. 3955/DEL/2012

दिनांक \ Dated the 27/06/2019

सेवा मे, \ To :
Address of Service:- LEX ORBIS 709/710, Tolstoy House 15-17, Tolstoy Marg New Delhi – 110 001 India
Email Id:- mail@lexorbis.com

विषय :- पेटेंट आवेदन संख्या 3955/DEL/2012 के संबंध मे अधिनियम की धारा 43 के तहत पेटेंट अनुदान तथा पेटेंट रजिस्टर मे प्रविष्टि की सूचना
Sub :- Intimation of the grant and recordal of patent under section 43 of the Act in respect of patent application no. 3955/DEL/2012

महोदय/महोदया,
Sir/Madam,

आपको सूचित किया जाता है कि पेटेंट अधिनिय, 1970 की धारा 12 व 13 तथा उस आधार पर बने नियम के तहत उपर्युक्त पेटेंट आवेदन के परीक्षण [व -------- को हुई सुनवाई] के उपरांत एतद्द्वारा पेटेंट अनुदान किया जाता है। तथा पेटेंट अनुदान की प्रविष्टि 27/06/2019 को पेटेंट रजिस्टर मे कर दी गयी है।

This is to Inform you that following the examination of above mentioned patent application under section 12 and 13 of The Patents Act, 1970 and Rules made thereunder [and hearing held on -------] a patent is hereby granted and recorded in the Register of Patents on the 27/06/2019. The Patent Certificate is enclosed herewith.

पेटेंट संख्या \ Patent No : 314878
आवेदक का नाम \ Name Of Applicant : BL Technologies, Inc.
पेटेंट दिनांक \ Date of Patent : 21/12/2012
पूर्विक्ता तिथि \ Priority Date : 21/12/2012
परीक्षण हेतु अनुरोध दाखिल करने की तिथि \ Filling date of Request for examination : 18/12/2016
शीर्षक \ Title : DEMULSIFYING COMPOSITIONS AND METHODS OF USE
दावों की संख्या \ Number of claims : 28

उपर्युक्त पेटेंट के अनुदान का प्रकाशन अधिनियम की धारा 43 के तहत पेटेंट कार्यालय के आधिकारिक जर्नल मे किया जाएगा।
The grant of above mentioned patent will be published in the Official Journal of the patent Office under section 43 of the Act.

पेटेंट अधिनियम 1970 यथा संशोधित पेटेंट (संशोधन) नियम, 2005/ पेटेंट नियम, 2003 यथा संशोधित पेटेंट (संशोधन) नियम, 2016 की धारा 142 की उप-धारा (4) के प्रावधानों के तहत उपरोक्त प्रविष्टि की तिथि से 3 माह के भीतर इस कार्यालय मे नवीकरण शुल्क जमा किया जाना चाहिए।
The payment of renewal fee is required to be made at this office within three(3) months from the aforesaid date of recording according to the proviso in sub-section(4) of Section 142 of The Patents Act,1970, as amended by The Patents (Amendment) Act, 2005 / The Patents Rules, 2003 as amended by The Patents (Amendment) Rules, 2016.

Piyush Garg
(नियंत्रक पेटेंट)
Controller of Patents

टिप्पणी / Note :

1. संशोधित नवीकरण शुल्क हेतु कृपया महानियंत्रक पेटेंट, अभिकल्प एवं व्यापार चिह्न की आधिकारिक वैबसाइट www.ipindia.gov.in पर उपलब्ध पेटेंट (संशोधन) नियम 2016 की प्रथम अनुसूची (शुल्क) देखें।
For revised renewal fees kindly refer to the First Schedule (fees) of The Patents (Amendment) Rules 2016 available on the official website of Controller General of Patents, Designs and Trade Marks www.ipindia.gov.in
2. कार्यालय द्वारा पेटेंट प्रमाणपत्र की कोई भी कागजी प्रति अलग से जारी नहीं की जाएगी।
No hard copy of Patent Certificate shall be issued separately by the office.

WE CLAIM:

1. A method of resolving an emulsion present in a hydrocarbon stream comprising: contacting said hydrocarbon stream with a demulsifying composition, wherein said demulsifying composition is colloidal, said demulsifying composition comprising at least one C_4-C_{12} alkyl phenol-formaldehyde resin alkoxylate, an oil phase, and an aqueous phase, wherein said oil and aqueous phase form an inverse colloidal micellar solution.

2. The method as claimed in claim 1, wherein the C_4-C_{12} alkyl phenol-formaldehyde resin alkoxylate has a polymerization number of 2-20 and a degree of alkoxylation greater than about 30% and less than about 90% relative to the weight of the resin.

3. The method as claimed in claim 1, wherein said demulsifying composition comprises 0.1 wt% to about 90 wt% water based on a total weight of said demulsifying composition.

4. The method as claimed in claim 1, wherein said C_4-C_{12} alkyl phenol-formaldehyde resin alkoxylate comprises at least two alkyl phenol-formaldehyde resin alkoxylates having different amounts of alkoxylation.

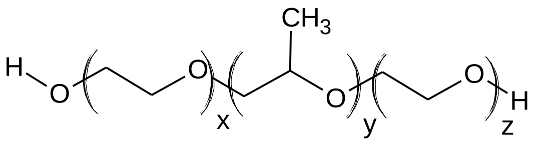
5. The method as claimed in claim 4, wherein the two alkyl phenol-formaldehyde resin alkoxylates comprise a first alkyl phenol-formaldehyde resin alkoxylate, having a percent A by weight of alkoxylation, and a second alkyl phenol-formaldehyde resin alkoxylate, having a percent B by weight of alkoxylation, wherein A minus B is 10-50%, and wherein the ratio by weight of an amount of the first alkyl phenol-formaldehyde resin alkoxylate relative to the second alkyl phenol-formaldehyde resin alkoxylate is 1:9 to 9:1.

6. The method as claimed in claim 1, wherein said demulsifying composition is added to said hydrocarbon stream in an amount ranging from about 1 to about 200 ppm by volume of said hydrocarbon stream.

7. The method as claimed in claim 1, wherein the demulsifying composition further comprises at least one polyalkylene oxide polyol with a degree of ethoxylation greater than about 30% and less than about 85% and a molecular weight ranging from about 1000 to about 25,000, and wherein a ratio of said C_4-C_{12} alkyl phenol-formaldehyde resin alkoxylate to said polyalkylene oxide polyol ranges from about 1:9 to about 9:1.

8. The method as claimed in claim 7, wherein the at least one polyalkylene oxide polyol comprises at least two polyalkylene oxide polyols, and wherein at least one of said polyalkylene oxide polyols is selected from the group consisting of ethylene oxide/propylene oxide block polymers, ethylenediamine alkoxylates, polyethylenimine alkoxylates, glycerol alkoxylates, trimethylpropane alkoxylates, and sorbitol alkoxylates.

9. The method as claimed in claim 8, wherein a first polyalkylene oxide polyol is an ethylene oxide/propylene oxide block copolymer having the formula:



wherein x, y, and z are any integer greater than one and the molecule has a molecular weight of 1000-9000; and wherein a second polyalkylene oxide polyol is an oxide block copolymer with a molecular weight of 3000-25000 and 2-6 branches, each branch comprising at least one polyalkoxylate block.

10. The method as claimed in claim 1, wherein said demulsifying composition comprises at least one member selected from the group consisting of an acid, a non-polar organic solvent, a base, a wetting agent, a water-soluble reverse emulsion breaker and a water-soluble corrosion inhibitor.

11. The method as claimed in claim 10, wherein the water-soluble reverse emulsion breaker comprises a water soluble cationic polymer.

12. The method as claimed in claim 11, wherein the water soluble cationic polymer comprises a polyamine polymer, a dialkyldiallylammonium polymer, and/or an acrylamide-based polymer.

13. The method as claimed in claim 11, wherein said corrosion inhibitor comprises at least one member selected from the group consisting of amidoethyl imidazoline, hydroxyethyl imidazoline, and aminoethyl imidazoline.

14. The method as claimed in claim 10, wherein said acid is at least one selected from the group consisting of acetic acid, citric acid, malic acid, maleic acid, succinic acid, glycolic acid, methane sulfonic acid, dodecylbenzenesulfonic acid, naphthalene sulfonic acid, and p-toluene sulfonic acid, and wherein said non-polar organic solvent is at least one selected from the group consisting of naptha, light aromatic naptha, heavy aromatic naptha, pentane, cyclopentane, hexane, cyclohexane, benzene, ethyl benzene, 1,2,4-trimethyl benzene, 1,3,5-trimethyl benzene, toluene, xylene, cumene, 1,4-dioxane, choloroform, diethyl ether, methyl esters of fatty acids (biodiesel), and diethylene glycol butyl ether, and wherein said base is at least one selected from the group consisting of sodium hydroxide and potassium hydroxide; and wherein the wetting agent is at least one selected from the group consisting of sodium dioctyl sulfosuccinic acid and sodium dodecylbenzene sulfonic acid; and wherein said dispersant is an adduct of at least

one mono- or polycarboxylic acid or anhydride and an acylating reagent selected from the group consisting of fumaric acid, maleic anhydride, maleic acid, succinic anhydride, and succinic acid.

15. The method as claimed in claim 1, wherein said C_4-C_{12} alkyl phenol-formaldehyde resin alkoxylate comprises at least one member selected from the group consisting of: a) a mixed resin with units of nonylphenol formaldehyde alkoxylate and units of butylphenol formaldehyde alkoxylate; b) a resin with units of nonylphenol formaldehyde alkoxylate; and c) a resin with units of amylphenol formaldehyde alkoxylate.

16. The method as claimed in claim 1, wherein said hydrocarbon steam comprises crude oil.

17. A demulsifying composition for treating a hydrocarbon stream, said demulsifying composition comprising at least one C_4-C_{12} alkyl phenol-formaldehyde resin alkoxylate, an oil phase, and an aqueous phase, wherein said demulsifying composition is colloidal, wherein said oil and aqueous phase forms an inverse colloidal micellar solution, and wherein said demulsifying composition comprises 0.1 wt% to about 90 wt% water based on a total weight of said demulsifying composition.

18. The demulsifying composition as claimed in claim 17, wherein the C_4-C_{12} alkyl phenol-formaldehyde resin alkoxylate has a polymerization number of 2-20 and a degree of alkoxylation greater than about 30% and less than about 90% relative to the weight of the resin.

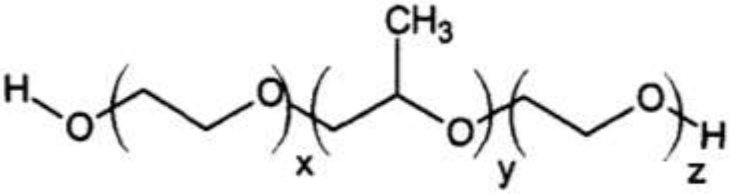
19. The demulsifying composition as claimed in claim 17, wherein said C_4-C_{12} alkyl phenol-formaldehyde resin alkoxylate comprises at least two alkyl phenol-formaldehyde resin alkoxylates having different amounts of alkoxylation, and

wherein the two alkyl phenol-formaldehyde resin alkoxylates comprise a first alkyl phenol-formaldehyde resin alkoxylate, having a percent A by weight of alkoxylation, and a second alkyl phenol-formaldehyde resin alkoxylate, having a percent B by weight of alkoxylation, wherein A minus B is 10-50%, and wherein the ratio by weight the first alkyl phenol-formaldehyde resin alkoxylate relative to the second alkyl phenol-formaldehyde resin alkoxylate is 1:9 to 9:1.

20. The demulsifying composition as claimed in claim 17, wherein the demulsifying composition further comprises at least one polyalkylene oxide polyol with a degree of ethoxylation greater than about 30% and less than about 85% and a molecular weight ranging from about 1000 to about 25,000, and wherein a weight ratio of said C_4-C_{12} alkyl phenol-formaldehyde resin alkoxylate to said polyalkylene oxide polyol ranges from about 1:9 to about 9:1.

21. The demulsifying composition as clamed in claim 20, wherein the at least one polyalkylene oxide polyol comprises at least two polyalkylene oxide polyols, and wherein one of said polyalkylene oxide polyols is selected from the group consisting of ethylene oxide/propylene oxide block polymers, ethylenediamine alkoxylates, polyethylenimine alkoxylates, glycerol alkoxylates, trimethylpropane alkoxylates, and sorbitol alkoxylates.

22. The demulsifying composition as claimed in claim 21, wherein a first polyalkylene oxide polyol is an ethylene oxide block copolymer having the formula:



wherein x, y, and z are any integer greater than one and the molecule has a molecular weight of 1000-9000; and wherein a second polyalkylene oxide polyol is an oxide block copolymer with a molecular weight of 3000-25000 and 2-6 branches, each branch comprising at least one polyalkoxylate block.

23. The demulsifying composition as claimed in claim 17, wherein said composition further comprises at least one member selected from the group consisting of an acid, a non-polar organic solvent, a base, a wetting agent, a dispersant, a corrosion inhibitor, and a water-soluble reverse emulsion breaker.

24. The demulsifying composition as claimed in claim 23, wherein the water-soluble reverse emulsion breaker comprises a water soluble cationic polymer.

25. The demulsifying composition as claimed in claim 24, wherein the water soluble cationic polymer comprises a polyamine polymer, a dialkyldiallylammonium polymer, or an acrylamide-based polymer.

26. The demulsifying composition as claimed in claim 23, wherein said corrosion inhibitor comprises at least one member selected from the group consisting of amidoethyl imidazoline, hydroxyethyl imidazoline, and aminoethyl imidazoline.

27. The demulsifying composition as claimed in claim 23, wherein said acid is at least one selected from the group consisting of acetic acid, citric acid, malic acid, succinic acid, glycolic acid, methane sulfonic acid, dodecylbenzenesulfonic acid, naphthalene sulfonic acid, and p-toluene sulfonic acid; and wherein said non-polar organic solvent is at least one selected from the group consisting of naptha, light aromatic naptha, heavy aromatic naptha, pentane, cyclopentane, hexane, cyclohexane, benzene, ethyl benzene, 1,2,4-trimethyl benzene, 1,3,5-trimethyl benzene, toluene, xylene, cumene, 1,4-dioxane, chloroform, diethyl ether, methyl esters of fatty acids (biodiesel), and diethylene glycol butyl ether; and wherein said base is at least one selected from the group consisting of sodium hydroxide and potassium hydroxide; and wherein the wetting agent is at least one selected from

the group consisting of sodium dioctyl sulfosuccinic acid and sodium dodecylbenzene sulfonic acid; and wherein said dispersant is an adduct of at least one acid of mono- or polycarboxylic acid or anhydride and an acylating reagent selected from the group consisting of fumaric acid, maleic anhydride, maleic acid, succinic anhydride, and succinic acid.

28. The demulsifying composition as claimed in claim 17, wherein said C_4-C_{12} alkyl phenol-formaldehyde resin alkoxylate comprises at least one member selected from the group consisting of: a) a mixed resin with units of nonylphenol formaldehyde alkoxylate and units of butylphenol formaldehyde alkoxylate; b) a resin with units of nonylphenol formaldehyde alkoxylate; and c) a resin with units of amylphenol formaldehyde alkoxylate.

Dated this the 21st day of December, 2012

Manisha Singh
Agent for the Applicant [IN/PA-740]
LEXORBIS
/Digitally Signed/

FIELD OF THE INVENTION

The present invention relates to compositions and processes for breaking emulsions in crude oil. More particularly, the compositions and processes may be used to break water-in-oil emulsions at an oilfield or in a desalter in a crude oil refinery.

BACKGROUND OF THE INVENTION

Crude oil is produced from geological formations where it is in intimate contact with brine (salt water). As the oil and brine are produced, their movement through geological formations produces an emulsion of water-in-oil, wherein tiny droplets of water are suspended in a continuous phase of oil. Generally, the amount of water produced from the formation in the oil field ranges from 1-2% and may even be higher than 90%. Refineries operate with much lower water content in the crude oil, generally not exceeding 0.5%.

In oilfield industries, these water-in-oil emulsions are often referred to as primary emulsions. Though less common, oil-in-water emulsions, wherein tiny droplets of oil are suspended in a continuous phase of water, also occur and are often referred to as reverse emulsions. Another type of emulsion is a multiple, or complex, emulsion where tiny droplets are suspended in bigger droplets that are suspended in a continuous phase.

To render the crude oil more suitable for refining, the crude oil is demulsified by separating the primary or reverse emulsions into separate oil and water phases. While the water in the oil is a problem for refiners, it is the dissolved salts which cause the most problems since they can deposit and foul heat transfer surfaces. Calcium chloride and magnesium chloride decompose at operating temperatures of the refinery to produce HCl (hydrochloric acid) which corrodes the distillation towers. To remove the brine and the salts it contains, the crude oil is heated to around 120° C and mixed with about 5% fresh water by passing the water and oil through a mixing valve and thence to a vessel, such as an oil refinery desalter, where it has a residence time of about 30 minutes to allow the emulsion to break and the oil and water to separate.

Generally, the steps in demulsification are flocculation followed by coalescence and, finally, sedimentation. During the flocculation step, the suspended droplets aggregate to form larger droplets. During coalescence, the larger droplets come together to form a large drop. Sedimentation takes advantage of the fact that water is denser than oil. During sedimentation the water and oil phases become stratified into distinct layers as large drops of water fall to the bottom. There are several methods for demulsifying oil field emulsions, including thermal, mechanical, electrical, and chemical methods.

Chemical methods employ the use of chemicals that neutralize the effects of emulsion stabilizing agents and to accelerate the demulsification process by reducing the interfacial tension. These demulsifying chemicals are often referred to as emulsion "breakers" because they break, or separate the emulsions into the separate oil and water phases. Demulsifying chemicals used to break water-in-oil emulsions, or primary emulsions, are often referred to as primary emulsion breakers. Primary emulsion breakers are added to the continuous oil phase and are generally oil-soluble, though they may be water-soluble. Likewise, demulsifying chemicals used to break oil-in-water emulsions, or reverse emulsions, are often referred to as reverse emulsion breakers. Reverse emulsion breakers are generally water-soluble, though they may be oil-soluble, and are added to the continuous water phase. Some of the water is removed from the crude oil by adding surfactant chemicals to demulsify the water and oil at the well or near the point of production. These surfactants are optimized to separate, or "break", the oil and water at relatively low temperatures, common in the oil field. Without emulsion breakers, more time is required to separate the phases, limiting the amount of oil the refinery can process.

The most effective demulsifying chemistries and formulations typically vary with the crude composition. The crude composition, however, continuously varies based on the crude source or well, the treatment, if any, at the well, well stimulation practices, "smearing", or contamination effects from adjacent pipeline transports, and the crude blend composition. The crude composition may be further altered by a myriad of chemistries that may have been added to the crude between the time it is collected at the well and the time it enters a desalter at a refinery. Such chemistries may include, but are not limited to, corrosion inhibitors, biocides, drag reducers, H_2S scavengers, etc.

Most of the effects on crude composition mentioned above are beyond a refinery's control, yet the refinery is often left with the burden of analyzing the crude composition and determining the most effective demulsifying treatment.

BRIEF DESCRIPTION OF THE INVENTION

It was surprisingly discovered, however, that blends of one or more C_4-C_{12} alkyl phenol-formaldehyde resin alkoxylates with a surfactant produced a robust demulsifying composition that was effective at resolving emulsions in a variety of crude types.

Accordingly, in one embodiment, a method of resolving an emulsion present in a hydrocarbon stream is disclosed. The method may comprise providing the hydrocarbon stream and providing a demulsifying composition. The demulsifying composition may comprise 1) at least one C_4-C_{12} alkyl phenol-formaldehyde resin alkoxylate and 2) at least one surfactant, wherein the surfactant comprises at least two blocks of alkylene oxide units. The hydrocarbon stream may be contacted with the demulsifying composition, thereby coalescing aqueous droplets from the emulsion to form an aqueous stream. The aqueous stream may then be removed.

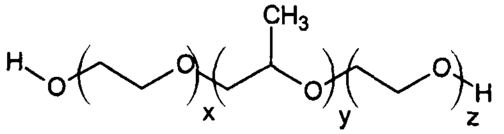
In another embodiment, the hydrocarbon stream may comprise crude oil. In yet another embodiment, the coalescing of aqueous droplets from the emulsion to form an aqueous stream may occur in a desalter.

In another embodiment, at least one C_4-C_{12} alkyl phenol-formaldehyde resin alkoxylate may comprise 30-90% alkoxylate units by weight and may have a polymerization number of 2-20. In another embodiment, the C_4-C_{12} alkyl phenol-formaldehyde resin alkoxylate may comprise ethylene oxide units. The C_4-C_{12} alkyl phenol-formaldehyde resin alkoxylate may be nonylphenol formaldehyde resin ethoxylate.

In yet another embodiment, the C_4-C_{12} alkyl phenol-formaldehyde resin alkoxylate may comprise at least two alkyl phenol-formaldehyde resin alkoxylates having different amounts of alkoxylation. The two alkyl phenol-formaldehyde resin alkoxylates may comprise a first alkyl phenol-formaldehyde resin alkoxylate having a percent A by weight of alkoxylation and a second alkyl phenol-formaldehyde resin alkoxylate having a percent B by weight of alkoxylation. A minus B may be 10-50%. The ratio by weight of an amount of the first alkyl phenol-formaldehyde resin alkoxylate relative to the second alkyl phenol-formaldehyde resin alkoxylate may be 1:9 to 9:1. In another embodiment, the C_4-C_{12} alkyl phenol-formaldehyde resin alkoxylate may comprise a mixed resin with units of nonylphenol formaldehyde alkoxylate and units of butylphenol formaldehyde alkoxylate. Alternatively, the C_4-C_{12} alkyl phenol-formaldehyde resin alkoxylate may comprise a first resin with units of nonylphenol formaldehyde alkoxylate and a second resin with units of amylphenol formaldehyde alkoxylate.

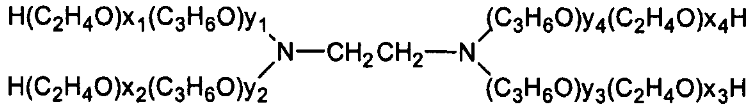
In another embodiment, at least one surfactant may comprise ethylene oxide units and propylene oxide units wherein the ratio by weight of the ethylene oxide units to the total number of ethylene and propylene oxide units is 30-50%.

In yet another embodiment, at least one surfactant may comprise a polyalkylene oxide triblock polyol having the formula:



wherein x, y, and z are any integer greater than one where the molecule has a molecular weight of 1000-9000.

Alternatively, at least one surfactant may comprises a molecule with 2-6 branches each comprising at least one polyalkoxylate block, and wherein said molecule has a molecular weight of 3000-25000. The surfactant may have the formula:



$$\left.\begin{array}{l}H(C_2H_4O)x_1(C_3H_6O)y_1\\H(C_2H_4O)x_2(C_3H_6O)y_2\end{array}\right\rangle N-CH_2CH_2-N\left\langle\begin{array}{l}(C_3H_6O)y_4(C_2H_4O)x_4H\\(C_3H_6O)y_3(C_2H_4O)x_3H\end{array}\right.$$

where x1, x2, x3, and x4 may be the same or different and represent the number of polyethylene oxide units and where y1, y2, y3, and y4 may be the same or different and represent the number of polypropylene oxide units, and wherein a ratio of the polyethylene oxide units to polypropylene oxide units is from 10:90 to 90:10.

In another embodiment, the surfactant may comprise at least two surfactants.

In yet another embodiment, the demulsifying composition may further comprise at least one non-polar organic solvent and/or at least one aqueous solvent. Suitable non-polar organic solvents include, but are not limited to, naphtha, light aromatic naphtha, heavy aromatic naphtha, pentane, cyclopentane, hexane, cyclohexane, benzene, ethyl benzene, 1,2,4-trimethyl benzene, 1,3,5-trimethyl benzene, toluene, xylene, cumene, 1,4-dioxane, chloroform, diethyl ether, methyl esters of fatty acids (biodiesel), and diethylene glycol butyl ether. In yet another embodiment, the demulsifying composition may comprise an organic solvent and an aqueous solvent in an aggregate amount of about 10 wt% to about 90 wt% based on a total weight of the demulsifying composition. The demulsifying composition may be a colloidal micellar solution including an oil phase and an aqueous phase.

In yet another embodiment, the demulsifying composition may be added to the hydrocarbon stream in an amount ranging from about 1 to about 200 ppm by volume of the hydrocarbon stream.

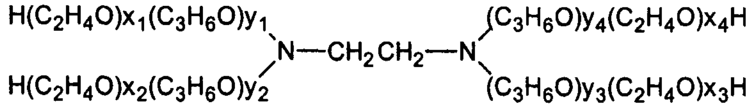
In another embodiment, the method may further comprise contacting the hydrocarbon stream with a dispersant, wherein the dispersant is an adduct of at least one acid ester of mono- or polycarboxylic acid and an acylating reagent. Suitable acylating reagents include, but are not limited to fumaric acid, maleic anhydride, maleic acid, succinic anhydride, and succinic acid. In another embodiment, the acid ester may have a polyisobutenyl and a pentaerythritol moiety and the acylating reagent may be succinic anhydride or succinic acid. In yet another embodiment, the dispersant may be a polyisobutenyl succinic anhydride derived ester with a molecular weight, $\overline{Mw}$, of about 20,000 to about 25,000 in an aromatic solvent.

In yet another embodiment, the dispersant may be added in an amount of about 1 to about 1000 ppm by volume of the hydrocarbon stream.

In another embodiment, a demulsifying composition for treating a hydrocarbon stream is disclosed. The demulsifying composition may comprise 1) at least one C_4-C_{12} alkyl phenol-formaldehyde resin alkoxylate, wherein the C_4-C_{12} alkyl phenol-formaldehyde resin alkoxylate comprises 30-90% alkoxylate units by weight and has a polymerization number of 2-20 and 2) at least one surfactant, wherein the surfactant comprises ethylene oxide units and propylene oxide units and the ratio by weight of the ethylene oxide units to the total number of ethylene and propylene oxide units is 30-50%.

In another embodiment, the C_4-C_{12} alkyl phenol-formaldehyde resin alkoxylate may comprise at least two alkyl phenol-formaldehyde resin alkoxylates having different amounts of alkoxylation. The two alkyl phenol-formaldehyde resin alkoxylates may comprise a first alkyl phenol-formaldehyde resin alkoxylate having a percent A by weight of alkoxylation and a second alkyl phenol-formaldehyde resin alkoxylate having a percent B by weight of alkoxylation. A minus B may be 10-50%. The ratio by weight of an amount of the first alkyl phenol-formaldehyde resin alkoxylate relative to the second alkyl phenol-formaldehyde resin alkoxylate may be 1:9 to 9:1. In yet another embodiment, the C_4-C_{12} alkyl phenol-formaldehyde resin alkoxylate may be nonylphenol formaldehyde resin ethoxylate. In another embodiment, the C_4-C_{12} alkyl phenol-formaldehyde resin alkoxylate may comprise a mixed resin with units of nonylphenol formaldehyde alkoxylate and units of butylphenol formaldehyde alkoxylate. Alternatively, the C_4-C_{12} alkyl phenol-formaldehyde resin alkoxylate may comprise a first resin with units of nonylphenol formaldehyde alkoxylate and a second resin with units of amylphenol formaldehyde alkoxylate.

In yet another embodiment, at least one surfactant has formula:



$$\begin{array}{lcl} H(C_2H_4O)x_1(C_3H_6O)y_1 & & (C_3H_6O)y_4(C_2H_4O)x_4H \\ & N-CH_2CH_2-N & \\ H(C_2H_4O)x_2(C_3H_6O)y_2 & & (C_3H_6O)y_3(C_2H_4O)x_3H \end{array}$$

where x1, x2, x3, and x4 may be the same or different and represent the number of polyethylene oxide units and where y1, y2, y3, and y4 may be the same or different and represent the number of polypropylene oxide units, and wherein a ratio of the polyethylene oxide units to polypropylene oxide units is from 10:90 to 90:10.

In another embodiment, the demulsifying composition may further comprise at least one non-polar organic solvent and/or at least one aqueous solvent. Suitable non-polar organic solvents include, but are not limited to, naphtha, light aromatic naphtha, heavy aromatic naphtha, pentane, cyclopentane, hexane, cyclohexane, benzene, ethyl benzene, 1,2,4-trimethyl benzene, 1,3,5-trimethyl benzene, toluene, xylene, cumene, 1,4-dioxane, chloroform, diethyl ether, methyl esters of fatty acids (biodiesel), and diethylene glycol butyl ether. In yet another embodiment, the demulsifying composition may comprise an organic solvent and an aqueous solvent in an aggregate amount of about 10 wt% to about 90 wt% based on a total weight of the demulsifying composition. The demulsifying composition may be a colloidal micellar solution including an oil phase and an aqueous phase.

In yet another embodiment, the demulsifying composition may further comprise a dispersant comprising a polyisobutenyl succinic anhydride derived ester with a molecular weight, $\overline{Mw}$, of about 20,000 to about 25,000 in an aromatic solvent.

DETAILED DESCRIPTION OF EXEMPLARY EMBODIMENTS

It was surprisingly discovered that blends of one or more C_4-C_{12} alkyl phenol-formaldehyde resin alkoxylates with one or more surfactants produced a robust demulsifying composition that was effective at resolving emulsions in a variety of crude types. Specifically, these demulsifying compositions were more effective than current formulations in resolving emulsions in some types of heavy crudes. For example, embodiments of the demulsifying composition are particularly effective on crudes or crude blends with an American Petroleum Institute ("API") gravity ranging from about 22 to 40 (degrees). The crudes or crude blends may comprise greater than, or equal to, about 0.5 wt% asphaltenes. These crudes may also have more than about 60 pounds of filterable solids per thousand barrels; such as 20-500 lbs., or 20-200 lbs., or 60-200 lbs. Exemplary blends for which the demulsifying composition is particularly effective include blends of Canadian crude oils with American shale oils, sweet crudes, or Bakken crude. In particular, blends of crude oil containing Western Canadian Select are preferred. The present invention is particularly applicable to oil blends having between 1-70%, such as 20-50%, by volume of Western Canada Select crudes.

While an organic solvent may be used as part of the formulation, it was also surprisingly discovered that water may be used as a solvent for the demulsifying compositions. Water is generally less expensive than the organic solvents and alcohols frequently used in demulsifying compositions. Accordingly, novel demulsifying compositions are disclosed comprising ethoxylated surfactants in water. These demulsifying compositions are stable as the oil phase does not separate from the aqueous phase.

Without limiting this specification to any particular theory of operation, it is thought that the demulsifying compositions with water are stable because they are colloidal solutions and not true solutions as previously thought.

Colloidal solutions of surfactants contain micelles. Micelles are groups of surfactant molecules dispersed in a liquid forming a colloidal solution. Typically, micelles are spherical with the hydrophilic portion of the surfactant molecules forming the outside of the micelle and the hydrophobic portion filling the micelle's interior. Based upon factors such as concentration and temperature as well as the surfactant's chemical structure, other shapes are possible such as rods, tubes, or sheets.

The micelles only form when the concentration of the surfactant in the liquid is greater than the critical micelle concentration ("CMC"). The CMC may vary depending on the surfactant and the liquid used. Other factors that affect the CMC are temperature, pressure, and the presence of any other compounds that affect the surface tension of the liquid.

Primary emulsion breakers typically have multiple components, including, but not limited to, ethoxylated surfactants in an organic solvent, or "oil", like naphtha or toluene. An "oil" is any liquid that is soluble in another oil or organic solvent, but is not soluble in water. Thus the micelles in primary emulsion breakers are "inverse" micelles because the hydrophobic portion of the surfactant forms the outside of the micelle, and the hydrophilic portion fills the interior. It is thought that when added to primary emulsion breakers, aqueous solvents, such as water, enter into the interior of the micelles and "hydrate" the hydrophilic, or polar portion, of the ethylene oxide molecules. The organic solvents may include aromatic and/or non-aromatic organic solvents.

It was surprisingly discovered, however, that replacing some or all of the organic solvents, like naphtha or toluene, with water, resulted in stable demulsifying compositions, even though the primary emulsion breakers may comprise oil-based components. Without limiting the invention to one theory, it is thought that instead of "inverse" micelles, typical micelles are formed, where the hydrophilic portions of the surfactant molecules form the outside of the micelle and the hydrophobic portions, or non-polar regions of the surfactant molecules, fill the micelle's interior. Accordingly, demulsifying compositions and methods of use are disclosed wherein the demulsifying compositions may comprise an oil phase and an aqueous phase that form a colloidal micellar solution.

The present invention is directed to a demulsifying composition and a method of demulsifying an emulsion with such demulsifying composition. In one embodiment, a method of resolving an emulsion present in a hydrocarbon stream is disclosed. The method may comprise: providing a hydrocarbon stream; providing a demulsifying composition comprising an oil phase and/or a water phase in contact with the hydrocarbon stream. If the solvents are all organic, than an oil phase will be present. If the only solvent is water, then a water phase will be present. If the solvents are a mixture of oil and water, then this will result in a dispersed phase and a continuous phase, depending on the amount of organic solvents and water present. In another method, the hydrocarbon stream may comprise crude oil. In yet another method the emulsion may be resolved in a desalter of a crude oil refinery. The demulsifying composition may be added to the desalter or, preferably, upstream of the desalter. The demulsifying composition may be added right before the mixing valve upstream of the desalter.

The amount of the demulsifying composition used will vary with refineries and the amount of emulsification present in the hydrocarbon stream. Accordingly, in another method, the demulsifying composition may be added to the hydrocarbon stream in an amount ranging from about 1 to about 200 ppm by volume of the hydrocarbon stream. Alternatively, the demulsifying composition may be added to the hydrocarbon stream in an amount ranging from about 1 to about 100 ppm, or about 1 to about 30 ppm, or about 2 to about 25 ppm by volume of the hydrocarbon stream.

The hydrocarbon stream may be contacted with the demulsifying composition to coalesce aqueous droplets from the emulsion form an aqueous stream. The aqueous stream may then be removed.

The demulsifying composition may comprise one or more C_4-C_{12} alkyl phenol-formaldehyde resin alkoxylates, each of which shall be individually referred to herein as a "demulsifying resin" and collectively as "demulsifying resins". The demulsifying composition may also comprise one or more surfactants. The surfactants may be polymers which include two or more blocks of polyalkoxylates, such as polyethylene oxide, polypropylene oxide, and/or polybutylene oxide. The polymers which include two or more blocks of polyalkoxylates shall be referred to herein individually as a "block polyalkoxylates surfactant" and collectively as "block polylkoxylate surfactants". The demulsifying composition may also comprise an aqueous and/or an organic solvent. The demulsifying composition may also include other components as more specifically identified below.

In another embodiment, the demulsifying composition may comprise a demulsifying resin and a block polyalkoxylate surfactant. The demulsifying resin may be present in an amount of about 90-50% by weight based upon a combined weight of the demulsifying resin and the block polyalkoxylate surfactant, and the block polyalkoxylate surfactant may be present in an amount of about 10-50% by weight based upon a combined weight of the demulsifying resin and the block polyalkoxylate surfactant.

The demulsifying composition preferably comprises one or two demulsifying resins. Each demulsifying resin is preferably a C_4-C_{12} alkyl phenol-formaldehyde resin alkoxylate, such as a C_5-C_9 alkyl phenol-formaldehyde resin alkoxylate, and may be present in from 1-20%, such as 3-11%, of the weight of the demulsifying composition. Preferably, each alkyl phenol formaldehyde resin alkoxylate is present in the demulsifying composition at or above its critical micelle concentration.

Each demulsifying resin may contain 30-90% alkoxylate by weight, such as 35-85, 50-85%, 60-85%, 80-85%, 35-60%, or 50-55% alkoxylate by weight. Each demulsifying resin may have a polymerization number (i.e. the number of alkyl phenol formaldehyde units) of 2-20, 2-9, 2-8, 6-8, 8-9, or 9. The alkoxylate portion can include ethylene oxide ("EO") units, propylene oxide ("PO") units, or a mixture of EO and PO units, but EO units are preferred. The demulsifying resin is preferably nonylphenol formaldehyde resin alkoxylate and is more preferably nonylphenol formaldehyde resin ethoxylate.

In yet another embodiment, the demulsifying composition may comprise at least two different demulsifying resins. The two different demulsifying resins may differ in terms of the degree of polymerization, amount of alkoxylation, the type of alkyl phenol, etc. Preferably, there is a difference in alkoxylation where one of the demulsifying resins has an alkoxylation that is 50-85%, 60-85%, or 80-85% of the weight of the molecule, while the other demulsifying resin has an alkoxylation that is 30-60%, or 35-60%, or 50-55% of the weight of the molecule. Preferably, the difference in alkoxylation between a first demulsifying resin and a second demulsifying resin ranges from 10-50%, or any range within this range, such as 25-30%. Thus, if one resin has 85% alkoxylation, and the other one has 35% alkoxylation, then the difference is 50%. If one demulsifying resin has 60% alkoxylation and the other has 50%, then the difference is 10%. Similarly, if one has 85% alkoxylation and the other one has 55%, then the difference is 30%, and if one has 80% and the other has 55%, then the difference is 25%. By using two different demulsifying resins with a different amount of alkoxylation, as identified above, the performance of the demulsifying composition is improved, particularly with the types of crude oils mentioned above. Each of the two demulsifying resins would be used as 1-20%, or more preferably, 3-11% by weight of the demulsifying composition. The ratio of the amount of one demulsifying resin to the other may be 1:9 to 9:1, 1:3 to 3:1, and 1:1. As stated above, the preferred alkoxylation is with EO and/or PO. The two resins are each preferably used in the demulsifying composition at or above their critical micelle concentration. At least one of the demulsifying resins may be a nonylphenol formaldehyde resin alkoxylate with a degree of polymerization of about 8-9 and is about 55% ethylene oxide by weight.

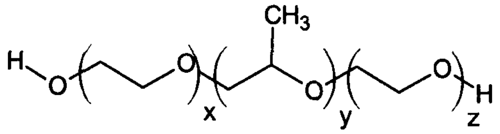
In yet another embodiment, the demulsifying resin may comprise an adduct of at least one C_4-C_{12} alkyl phenol-formaldehyde resin alkoxylate and the nonylphenol formaldehyde resin alkoxylate that is at least 50% ethylene oxide by weight. For example, the demulsifying resin may be an adduct of monomers of a nonylphenol formaldehyde resin alkoxylate that is at least 50% ethylene oxide by weight, such as 50-90% ethylene oxide, or 70-90% ethylene oxide, and monomers of a butylphenol formaldehyde resin alkoxylate that is at least 50% ethylene oxide by weight, such as 50-90% ethylene oxide, or 70-90% ethylene oxide by weight. The total degree of polymerization for both monomers may be 3-10 or 6-9. The ratio of the number of monomers containing butylphenol versus nonylphenol in the final resin may be 9:1 to 1:9, or preferably 2:1 to 1:2. This particular resin is appropriate for crudes having an API of 28-40. The amount of this resin that can be used is 1-20%, preferably 3-11 % by weight relative to the demulsifying composition. This resin may be used by itself or in conjunction with another demulsifying resin described in the present application. Accordingly, the demulsifying resin may comprise two different resins, each resin with different alkyl phenol units. For example, the demulsifying resin may comprise a nonylphenol formaldehyde resin alkoxylate and an amyphenol formaldehyde resin alkoxylate. Alternatively, the demulsifying resin may comprise different alkyl phenol units, such as nonylphenol and butylphenol, within one resin.

In another embodiment, at least one C_4-C_{12} alkyl phenol-formaldehyde resin alkoxylate may be a nonylphenol formaldehyde resin alkoxylate that is at least 50% ethylene oxide by weight. In another embodiment, at least one C_4-C_{12} alkyl phenol-formaldehyde resin alkoxylate may be a nonylphenol formaldehyde resin alkoxylate with a degree of polymerization of about 8-9 and is about 55% ethylene oxide by weight. In another embodiment, the C_4-C_{12} alkyl phenol-formaldehyde resin alkoxylate may be amyl phenol-formaldehyde resin alkoxylate.

As stated above the demulsifying composition also may comprise one or more surfactants. The surfactants may be polymers which include two or more blocks of polyalkoxylates, such as polyethylene oxide, polypropylene oxide, and/or polybutylene oxide. Thus, the surfactant may be a polyalkylene oxide block copolymer. The demulsifying composition may contain between 0.5-10% by weight of each block polyalkoxylate surfactant in the demulsifying composition, and preferably 1.5-6%. Preferably, the amount of the surfactant is at or above its critical micelle concentration.

The block polyalkoxylate surfactant may be a triblock polyol where the ratio between EO and PO by weight relative to the total aggregate amount of EO and PO may be 30-50% EO and 50-70% PO, and more preferably 40-50% EO and 50-60% PO. Thus, the block polyalkoxylate surfactant may be less than about 50% ethylene oxide by weight. In the triblock polyol, there are preferably two blocks of EO (EO1 and EO2), and one block of PO. The ratio by weight between EO1 and EO2 relative to the total aggregate amount of EO may be 30-70% EO1 and 30-70% EO2, preferably 45-55% EO1 and 45-55% EO2, and most preferably, EO1 is about the same as EO2. The block polyalkoxylate surfactant, such as the triblock polyol, may have a molecular weight of 1000-9000, preferably from 4000-5000, and usually has an average molecular weight, $\overline{M}_w$, less than about 6,000 g/mol. Preferably, the demulsifying composition contains one or two block polyalkoxylate surfactants, one of which is preferably the triblock polyol.

In yet another method, the surfactant may be a polyalkylene oxide triblock polyol having the formula:

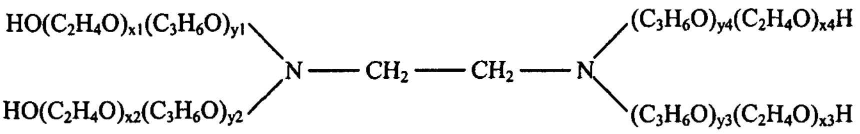


wherein x, y, and z are each preferably 20, 40, and 20 moles, respectively, and wherein $\overline{Mw}$ is about 4,200. Also, x, y, and z may be 76 moles, 32 moles, and 76 moles, respectively wherein $\overline{Mw}$ is about 8,400 g/mol. However, x, y, and z may be any integer greater than one where the molecule has a molecular weight of 1000-9000, preferably from 4000-5000. The ratio between EO and PO by weight relative to the total aggregate amount of EO and PO may be 30-50% EO and 50-70% PO, and more preferably 40-50% EO and 50-60% PO. Thus, the block polyalkoxylate surfactant may be less than about 50% ethylene oxide by weight. In the triblock polyol, there are preferably two blocks of EO, and one block of PO, and the ratio between the first block of EO and the second block of EO by weight relative to the total aggregate amount of EO may be 30-70% of the first block of EO and 30-70% of the second block of EO, preferably 45-55% of the first block of EO and 45-55% of the second block of EO, and most preferably , the two EO blocks have about the same weight as each other. The triblcok polyol may have a molecular weight of 1000-9000, preferably from 4000-5000, and usually has an average molecular weight, $\overline{Mw}$ less than about 6,000 g/mol. Preferably, the demulsifying composition contains one or two block polyalkoxylate surfactants, one of which is preferably the triblock polyol.

In another embodiment, the block polyalkoxylate surfactant may comprise polyalkoxylate blocks on two or more branches of the block polyalkoxylate surfactant, such as 2-6 branches and preferably 4-6 branches, most preferably four branches. The polyalkoxylate blocks may be blocks of ethylene oxide ("EO") units, and/or propylene oxide ("PO") units, and/or butylene oxide ("BO") units. The molecular weight of the block polyalkoxylate surfactant with two or more branches with polyalkoxylate blocks may be 3000-25000, or preferably 4000-10500, or more preferably 4700-7000. Preferably, the block polyalkoxylate surfactant contains at least one block of EO units and at least one block of PO units on each of its 2-6 branches. Preferably, each of these branches includes only one block of EO units and one block PO units. Also preferably, the PO blocks are closer to the branch point than the EO blocks. The block polyalkoxylate surfactant with two or more branches may be included in the demulsifying composition in an amount of 0.5% to 10%, or preferably 1% to 4% weight relative to the total demulsifying composition. Preferably, the block polyalkoxylate surfactant is used in the demulsifying composition at or above its critical micelle concentration.

Examples of this block polyalkoxylate surfactant with two or more branches with polyalkoxylate blocks may include block copolymers based on ethylenediamine, propylenediamine, diethylenetriamine, or triethylenetetramine. Examples of these types of copolymers are ethylenediamine ethylene oxide / propylene oxide copolymer, propylenediamine ethylene oxide / propylene oxide copolymer, diethylenetriamine ethylene oxide / propylene oxide copolymer, and triethylenetetramine ethylene oxide / propylene oxide copolymer.

One example of the block polyalkoxylate surfactant with two or more branches may have the formula:



where x1, x2, x3, and x4 may be the same or different and represent the number of polyethylene oxide units and where y1, y2, y3, and y4 may be the same or different and represent the number of polypropylene oxide units. The ratio of the polyethylene oxide units to polypropylene oxide units may range from 10:90 to 90:10, or 50:50 to 30:70, and may be about 30:70 or about 50:50. The ethylenediamine ethylene oxide / propylene oxide copolymer may have about 40% EO by weight and an average molecular weight, $\overline{Mw}$, of about 6,700.

In yet another method, the oil phase may comprise at least one non-polar organic solvent. Suitable non-polar organic solvents include, but are not limited to, naphtha, light aromatic naphtha, heavy aromatic naphtha, pentane, cyclopentane, hexane, cyclohexane, benzene, ethyl benzene, 1,2,4-trimethyl benzene, toluene, xylene, cumene, 1,4-dioxane, chloroform, diethyl ether, methyl esters of fatty acids (biodiesel), and diethylene glycol butyl ether (butyl carbitol).

In another method, the demulsifying composition may comprise an aqueous solvent. The aggregate amount of solvent, whether organic or aqueous, may be about 10% to 90%, such as 40-90% or 10-75%, or 50-85%, and is preferably 55-75% by weight of the demulsifying composition. The oil phase and the aqueous phase in the demulsifying composition may form a colloidal micellar solution. Any ratio of organic solvent to aqueous solvent is within the scope of the present invention, with the extremes being 100% aqueous solvent or 100% organic solvent relative to the amount of solvent. Preferably, the ratio of aqueous solvent to organic solvent is 90:10 to 70:30.

In another method embodiment, the demulsifying composition may further comprise a coupling agent or stabilizer, to further stabilize the demulsifying composition and prevent the phase separation. Suitable stabilizers include, but are not limited to, diethylene glycol butyl ether, hexylene glycol, methyl cellosolve (2-methoxyethanol), butanol, and octanol. The coupling agent or stabilizer may be present in an amount of 5-50%, such as 5-25%, and such as 5-20% of the demulsifying composition. The coupling agent may be an organic solvent, an example being diethylene glycol butyl ether (i.e. butyl carbitol). Accordingly, in another embodiment, the demulsifying composition may further comprise diethylene glycol butyl ether.

In other embodiments, the demulsifying composition may further comprise one or more aqueous or oil-based crude oil treatments or additives to aid in demulsification. Accordingly, the aqueous phase may comprise one or more components, including, but not limited to a pH adjuster, a water-soluble surfactant, a pH adjuster, a water-soluble surfactant, a flocculant, a wetting agent, a metal complexing agent, a reverse emulsion breaker, or a corrosion inhibitor. Some of these components are described in other portions of this disclosure in more specificity. It is also anticipated that the aqueous phase of the demulsifying composition may comprise one or more water-soluble additives that aid in demulsification.

In one embodiment, the aqueous phase may comprise a water-soluble pH adjusting agent. The pH adjusting agent may be a base or an acid. Suitable bases may be hydroxide bases of Group IA and IIA metals. In one embodiment the hydroxide base may be sodium or potassium hydroxide. In another embodiment, the pH adjuster may be an organic acid, mineral acid, or a carboxylic acid. Examples of suitable acids include, citric acid, propane-1,2,3-tricarboxylic acid, glycolic acid, formic acid, acetic acid, propanoic acid, butanoic acid, pentanoic acid, oxalic acid, glutaric acid, succinic acid, malonic acid, ascorbic acid, and lactic acid. Citric acid has the added advantage in that is also a metal complexing agent and may reduce the amount of metals in the stream being treated. The pH adjusting agent, such as the hydroxide bases, may be added in effective amounts such that the demulsifying composition will result in a pH of 6-8.

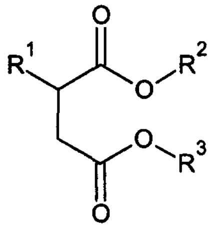
In one embodiment, the demulsifying composition comprises one or more inorganic flocculants or coagulants, such as hydrated chlorides and sulfates. Suitable hydrated chlorides include, but are not limited to, aluminum chloride, aluminum chlorohydrate, iron chloride, and zinc chloride. Suitable sulfates include, but are not limited to, aluminum sulfate, and iron sulfate.

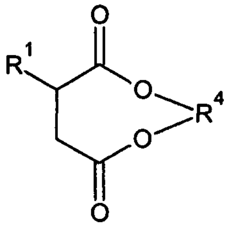
In another embodiment, the aqueous phase may comprise one or more wetting agents like sulfonates and their acids. Suitable sulfonates include, but are not limited to, sodium dioctyl sulfosuccinate and sodium dodecylbenzene sulfonate and acids thereof. In another embodiment, the demulsifying composition may further comprise, by weight, 0.5-5%, or preferably, 1-2% of a wetting agent, such as dodecylbenzene sulfonic acid.

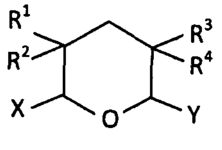
In yet another embodiment, the demulsifying composition may comprise a water-soluble or oil-soluble corrosion inhibitor. The corrosion inhibitor may comprise at least one imidazoline such as hydroxyethyl imidazoline, aminoethyl imidazoline, and amidoethyl imidazoline.

In another embodiment, a dispersant, such as an alkyl succinic anhydride based material, may be used in conjunction with the demulsifying composition to improve performance. The alkyl succinic anhydride based material may be a polyisobutenyl succinic anhydride based material. While a polyisobutenyl succinic anhydride-based material may have been used as an antifoulant for crude oil, such as in upstream applications, this material has special properties that will work conjunctively with the demulsifying composition to better resolve emulsions in downstream applications. Asphaltenes in the crude oil are believed to have hydrophilic functionalities which may result in a colloidal aggregation or flocculation of the asphaltenes at the interface of the aqueous phase and oil phase in a desalter. These hydrophilic functionalities decrease the ability of the dispersed phases to migrate towards respective continuous phases to resolve the emulsion. Thus, asphaltenes make resolving emulsions in a desalter difficult. The polyisobutenyl succinic anhydride based material is believed to adsorb onto the asphaltenes and decrease the colloidal aggregation or flocculation and deposition of the asphaltenes at the oil-water interface, thereby accelerating the speed at which the emulsion may be resolved by the demulsifying composition. The polyisobutenyl succinic anhydride based material may be added together with the demulsifying composition or separately, such as upstream of the addition of the demulsifying composition. The advantage of the separate addition is that the addition may be selective for crudes which have an asphaltene content of 0.5% or more, such as 0.5% to 50%, or 0.5% to 10%, or 0.5% to 8%.

The dispersant may be a treated ester that is a mono- or polycarboxylic acid ester that is further treated with an acylating reagent. The mono- or polycarboxylic acid ester may have at least one moiety that is a polyol as shown in any of the following three formulas:



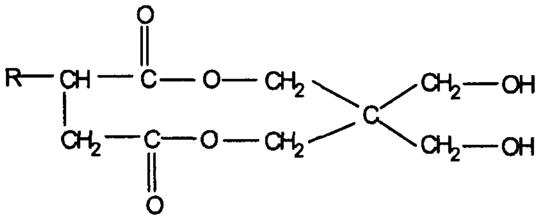




where R^1, R^2, R^3, and R^4 are the same or different and are selected from the group consisting of H, an alkyl, and $-CH(OH)(R^5)$; wherein R^5 is H or C_1 to C_{10} alkyl; and wherein X and Y are the same or different and are H or C_1 to C_{10} alkyl, with the proviso that at least one of R^1, R^2, R^3, and R^4 is the $-CH(OH)(R^5)$ moiety. Suitable alkyls may be polyalkenes, including interpolymers of various alkenes, and may include, but are not limited to, ethylene, propene, isoprene, 1-butene, 2-butene, isobutene, 3-pentene, 1-hexene, 1-octene, 4-oxtene, 2-methyl-1-heptene, 3-cyclohexyl-1-butene, 2-methyl-5-propyl-1-hexene, styrene, butadiene, and piperylene. The $-CH(OH)(R^5)$ moiety may be mono or polyhydric alcohols, preferably polyhydric, such as glycerol, erythritol, pentaerythritol, mannitol, and sorbitol.

The acylating reagent may be aliphatic mono- or polycarbocylic acids, anhydrides, or halides. Suitable acylating reagents may include, but are not limited to, fumaric acid, maleic anhydride, maleic acid, succinic anhydride, and succinic acid.

In a preferred embodiment, the acid ester has a polyisobutenyl and pentaerythritol moiety and is treated with succinic anhydride or succinic acid such that dispersant is a polyisobutenyl succinic anhydride ester ("PiBS ester") with a polyol moiety as in the following formula:



wherein R is a polyisobutenyl moiety.

Accordingly, in another embodiment, an alkyl succinic anhydride based material, such as a polyisobutenyl succinic anhydride based material may be used as the dispersant. The dispersant, such as the polyisobutylenyl succinic anhydride based material may be added to the desalter or upstream of the desalter in an amount of 1-1000 ppm, or 2-200 ppm, or more preferably, 20-200 ppm by volume of the hydrocarbon stream.

The polyisobutenyl succinic anhydride based material may be a polyisobutenyl succinic anhydride derived ester with a molecular weight, $\overline{Mw}$, of about 20,000 to about 25,000 in an aromatic solvent. The % actives may range from about 10-50% and the solvent may be aromatic naphtha.

In one embodiment, a method of resolving an emulsion present in a hydrocarbon stream is disclosed. The method may comprise providing the hydrocarbon stream and providing a demulsifying composition. The demulsifying composition may comprise 1) at least one C_4-C_{12} alkyl phenol-formaldehyde resin alkoxylate and 2) at least one surfactant, wherein the surfactant comprises at least two blocks of alkylene oxide units. The hydrocarbon stream may be contacted with the demulsifying composition, thereby coalescing aqueous droplets from the emulsion to form an aqueous stream. The aqueous stream may then be removed.

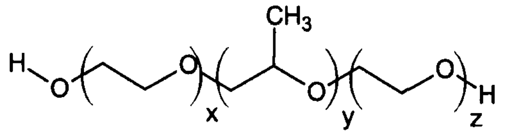
In another embodiment, the hydrocarbon stream may comprise crude oil. In yet another embodiment, the coalescing of aqueous droplets from the emulsion to form an aqueous stream may occur in a desalter.

In another embodiment, at least one C_4-C_{12} alkyl phenol-formaldehyde resin alkoxylate may comprise 30-90% alkoxylate units by weight and may have a polymerization number of 2-20. In another embodiment, the C_4-C_{12} alkyl phenol-formaldehyde resin alkoxylate may comprise ethylene oxide units. The C_4-C_{12} alkyl phenol-formaldehyde resin alkoxylate may be nonylphenol formaldehyde resin ethoxylate.

In yet another embodiment, the C_4-C_{12} alkyl phenol-formaldehyde resin alkoxylate may comprise at least two alkyl phenol-formaldehyde resin alkoxylates having different amounts of alkoxylation. The two alkyl phenol-formaldehyde resin alkoxylates may comprise a first alkyl phenol-formaldehyde resin alkoxylate having a percent A by weight of alkoxylation and a second alkyl phenol-formaldehyde resin alkoxylate having a percent B by weight of alkoxylation. A minus B may be 10-50%. The ratio by weight of an amount of the first alkyl phenol-formaldehyde resin alkoxylate relative to the second alkyl phenol-formaldehyde resin alkoxylate may be 1:9 to 9:1. In another embodiment, the C_4-C_{12} alkyl phenol-formaldehyde resin alkoxylate may comprise a mixed resin with units of nonylphenol formaldehyde alkoxylate and units of butylphenol formaldehyde alkoxylate (i.e., one resin with different alkylphenol units). Alternatively, the C_4-C_{12} alkyl phenol-formaldehyde resin alkoxylate may comprise a first resin with units of nonylphenol formaldehyde alkoxylate and a second resin with units of amylphenol formaldehyde alkoxylate.

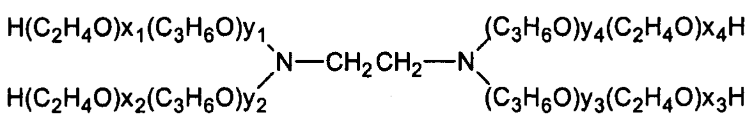
In another embodiment, at least one surfactant may comprise ethylene oxide units and propylene oxide units wherein the ratio by weight of the ethylene oxide units to the total number of ethylene and propylene oxide units is 30-50%.

In yet another embodiment, at least one surfactant may comprise a polyalkylene oxide triblock polyol having the formula:



wherein x, y, and z are any integer greater than one where the molecule has a molecular weight of 1000-9000.

Alternatively, at least one surfactant may comprises a molecule with 2-6 branches each comprising at least one polyalkoxylate block, and wherein said molecule has a molecular weight of 3000-25000. The surfactant may have the formula:



$$\begin{matrix} H(C_2H_4O)x_1(C_3H_6O)y_1 & & (C_3H_6O)y_4(C_2H_4O)x_4H \\ & N-CH_2CH_2-N & \\ H(C_2H_4O)x_2(C_3H_6O)y_2 & & (C_3H_6O)y_3(C_2H_4O)x_3H \end{matrix}$$

where x1, x2, x3, and x4 may be the same or different and represent the number of polyethylene oxide units and where y1, y2, y3, and y4 may be the same or different and represent the number of polypropylene oxide units, and wherein a ratio of the polyethylene oxide units to polypropylene oxide units is from 10:90 to 90:10.

In another embodiment, the surfactant may comprise at least two surfactants.

In yet another embodiment, the demulsifying composition may further comprise at least one non-polar organic solvent and/or at least one aqueous solvent. Suitable non-polar organic solvents include, but are not limited to, naphtha, light aromatic naphtha, heavy aromatic naphtha, pentane, cyclopentane, hexane, cyclohexane, benzene, ethyl benzene, 1,2,4-trimethyl benzene, 1,3,5-trimethyl benzene, toluene, xylene, cumene, 1,4-dioxane, chloroform, diethyl ether, methyl esters of fatty acids (biodiesel), and diethylene glycol butyl ether. In yet another embodiment, the demulsifying composition may comprise an organic solvent and an aqueous solvent in an aggregate amount of about 10 wt% to about 90 wt% based on a total weight of the demulsifying composition. The demulsifying composition may be a colloidal micellar solution including an oil phase and an aqueous phase.

In yet another embodiment, the demulsifying composition may be added to the hydrocarbon stream in an amount ranging from about 1 to about 200 ppm by volume of the hydrocarbon stream.

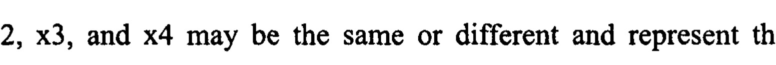
In another embodiment, the method may further comprise contacting the hydrocarbon stream with a dispersant, wherein the dispersant is an adduct of at least one acid ester of mono- or polycarboxylic acid and an acylating reagent. Suitable acylating reagents include, but are not limited to fumaric acid, maleic anhydride, maleic acid, succinic anhydride, and succinic acid. In another embodiment, the acid ester may have a polyisobutenyl and a pentaerythritol moiety and the acylating reagent may be succinic anhydride or succinic acid. In yet another embodiment, the dispersant may be a polyisobutenyl succinic anhydride derived ester with a molecular weight, $\overline{Mw}$, of about 20,000 to about 25,000 in an aromatic solvent.

In yet another embodiment, the dispersant may be added in an amount of about 1 to about 1000 ppm by volume of the hydrocarbon stream.

In another embodiment, a demulsifying composition for treating a hydrocarbon stream is disclosed. The demulsifying composition may comprise 1) at least one C_4-C_{12} alkyl phenol-formaldehyde resin alkoxylate, wherein the C_4-C_{12} alkyl phenol-formaldehyde resin alkoxylate comprises 30-90% alkoxylate units by weight and has a polymerization number of 2-20 and 2) at least one surfactant, wherein the surfactant comprises ethylene oxide units and propylene oxide units and the ratio by weight of the ethylene oxide units to the total number of ethylene and propylene oxide units is 30-50%.

In another embodiment, the C_4-C_{12} alkyl phenol-formaldehyde resin alkoxylate may comprise at least two alkyl phenol-formaldehyde resin alkoxylates having different amounts of alkoxylation. The two alkyl phenol-formaldehyde resin alkoxylates may comprise a first alkyl phenol-formaldehyde resin alkoxylate having a percent A by weight of alkoxylation and a second alkyl phenol-formaldehyde resin alkoxylate having a percent B by weight of alkoxylation. A minus B may be 10-50%. The ratio by weight of an amount of the first alkyl phenol-formaldehyde resin alkoxylate relative to the second alkyl phenol-formaldehyde resin alkoxylate may be 1:9 to 9:1. In yet another embodiment, the C_4-C_{12} alkyl phenol-formaldehyde resin alkoxylate may be nonylphenol formaldehyde resin ethoxylate. In another embodiment, the C_4-C_{12} alkyl phenol-formaldehyde resin alkoxylate may comprise a mixed resin with units of nonylphenol formaldehyde alkoxylate and units of butylphenol formaldehyde alkoxylate. Alternatively, the C_4-C_{12} alkyl phenol-formaldehyde resin alkoxylate may comprise a first resin with units of nonylphenol formaldehyde alkoxylate and a second resin with units of amylphenol formaldehyde alkoxylate.

In yet another embodiment, at least one surfactant has formula:



$$\begin{array}{lcl} H(C_2H_4O)x_1(C_3H_6O)y_1 & & (C_3H_6O)y_4(C_2H_4O)x_4H \\ & \diagdown N{-}CH_2CH_2{-}N \diagup & \\ & \diagup \qquad\qquad\qquad \diagdown & \\ H(C_2H_4O)x_2(C_3H_6O)y_2 & & (C_3H_6O)y_3(C_2H_4O)x_3H \end{array}$$

where x1, x2, x3, and x4 may be the same or different and represent the number of polyethylene oxide units and where y1, y2, y3, and y4 may be the same or different and represent the number of polypropylene oxide units, and wherein a ratio of the polyethylene oxide units to polypropylene oxide units is from 10:90 to 90:10.

In another embodiment, the demulsifying composition may further comprise at least one non-polar organic solvent and/or at least one aqueous solvent. Suitable non-polar organic solvents include, but are not limited to, naphtha, light aromatic naphtha, heavy aromatic naphtha, pentane, cyclopentane, hexane, cyclohexane, benzene, ethyl benzene, 1,2,4-trimethyl benzene, 1,3,5-trimethyl benzene, toluene, xylene, cumene, 1,4-dioxane, chloroform, diethyl ether, methyl esters of fatty acids (biodiesel), and diethylene glycol butyl ether. In yet another embodiment, the demulsifying composition may comprise an organic solvent and an aqueous solvent in an aggregate amount of about 10 wt% to about 90 wt% based on a total weight of the demulsifying composition. The demulsifying composition may be a colloidal micellar solution including an oil phase and an aqueous phase.

In yet another embodiment, the demulsifying composition may further comprise a dispersant comprising a polyisobutenyl succinic anhydride derived ester with a molecular weight, $\overline{\mathrm{Mw}}$, of about 20,000 to about 25,000 in an aromatic solvent.

EXAMPLES

Exemplary formulations are shown in Table 1. The exemplary formulations may comprise 10 to 40% actives with the remainder of the formulations comprising an organic or aqueous solvent or a combination thereof. The actives may include a polyalkylene oxide triblock polyol with about 40% EO by weight and an average molecular weight, $\overline{\mathrm{Mw}}$ of about 4,200 ("EO/PO Surf. 40% EO") and at least one alkyl phenol-formaldehyde resin alkoxylate. The EO/PO Surf. 40% EO may be present in an amount ranging from about 10 wt% to about 50 wt% based on a combined weight of the alkyl phenol-formaldehyde resin alkoxylate and the EO/PO Surf.

Suitable alkyl phenol-formaldehyde resin alkoxylates include nonylphenol formaldehyde resin alkoxylates ("NPF") and/or amylphenol formaldehyde resin alkoxylates ("APF") with a degree of polymerization ranging from about 4 to about 12 and are about 40% to about 80% ethylene oxide by weight. As shown in Table 1, one such APF may be an amylphenol formaldehyde resin alkoxylate with a degree of polymerization of about 7-8 and is about 40% ethylene oxide by weight ("APF 40% EO"). Also shown in Table 1 are suitable NPF. One such NPF may be a nonylphenol formaldehyde resin alkoxylate with a degree of polymerization of about 6-7 and is about 50% ethylene oxide by weight ("NPF 50% EO"). Another NPF may be a nonylphenol formaldehyde resin alkoxylate with a degree of polymerization of about 8-9 and is about 55% ethylene oxide by weight ("NPF 55% EO"). Another suitable NPF may be a nonylphenol formaldehyde resin alkoxylate with a degree of polymerization of about 2-8 and is about 80% ethylene oxide by weight ("NPF 80% EO"). The alkyl phenol-formaldehyde resin alkoxylates may also be adducts of at least two alkyl phenol-formaldehyde resin alkoxylates. In one embodiment, the adduct may be an adduct of a nonylphenol formaldehyde resin alkoxylate that is at least 50% ethylene oxide by weight and a butylphenol formaldehyde resin alkoxylate that is at least 50% ethylene oxide by weight ("NPF/BPF"). In other words, the NPF/BPF is a mixed resin with units of both nonylphenol formaldehyde alkoxylate and butylphenol formaldehyde alkoxylate.

The actives may also comprise one or more aqueous or oil-based crude oil treatments or additives to aid in demulsification. One such additive may be an ethylenediamine ethylene oxide / propylene oxide copolymer with about 40% EO by weight and an average molecular weight, $\overline{M}w$, of about 6,700 ("ED EO/PO"). The ED EO/PO may be present in an amount ranging from about 1 to about 10 wt% of a total weight of the demulsifying composition. Alternatively, the ED EO/PO may be present in an amount ranging from about 2 to about 4 wt% of a total weight of the demulsifying composition.

Another additive example is a wetting agent such as dodecylbenzene sulfonic acid ("DDBSA"). In one embodiment, the DDBSA may be present in an amount ranging from about 1 to about 10 wt% of a total weight of the demulsifying composition. Alternatively, the DDBSA may be present in an amount ranging from about 2 to about 4 wt%.

TABLE 1 – DEMULSIFIER FORMULATIONS

	Raw Materials (wt%)									
	Actives							Solvents		
	APF 40% EO	**NPF 55% EO**	**NPF 80% EO**	**NPF/ BPF**	**ED EO/PO**	**EO/PO Surf. 40% EO**	**DDBSA**	**Heavy Naph.**	**$C_8H_{18}O_3$**	**H_2O**
Ex A		10.70	10.70		3.43	5.14		55.03	15.00	
Ex B		7.13	7.13		2.29	3.43		65.02	15.00	
Ex C		7.14	7.14		2.29	3.43			20.00	60.00
Ex D		3.57	3.57		1.15	1.71			20.00	70.00
Ex E		7.14	7.14		2.29	4.43	3.00		15.00	62.00
Ex F		3.57	3.57		1.15	1.71	3.00		15.00	72.00
Ex G	7.14	7.14			2.29	3.43			20.00	60.00
Ex H	3.57	3.57			1.15	1.71			20.00	70.00
Ex I	7.14	7.14			2.29	3.43	3.00		15.00	62.00
Ex J	3.57	3.57			1.15	1.71	3.00		15.00	72.00
Ex K			22.50	7.50		5.00				65.00
Ex J			22.50	7.50		5.00			5.00	60.00

Note: $C_8H_{18}O_3$ is diethylene glycol butyl ether (butyl carbitol)

The efficacy of similar demulsifying formulations was tested on U.S. and Canadian crude oils. The formulations tested are listed in Table 2.

All the formulations in Table 2 comprised a surfactant that was a polyalkylene oxide triblock polyol with about 40% EO by weight and an average molecular weight, $\overline{Mw}$ of about 4,200 ("EO/PO Surf. 40% EO") and at least one alkyl phenol-formaldehyde resin alkoxylate (see Table 2). Comparative example 2 ('Comp 2") comprised an amylphenol formaldehyde resin alkoxylate with a degree of polymerization of about 7-8 and was about 40% EO by weight ("APF 40% EO"). All the rest of the formulations tested comprised at least one nonylphenol formaldehyde resin alkoxylate ("NPF"). The first NPF was a nonylphenol formaldehyde resin alkoxylate with a degree of polymerization of about 6-7 and was about 50% ethylene oxide by weight ("NPF 50% EO"). The second NPF was a nonylphenol formaldehyde resin alkoxylate with a degree of polymerization of about 8-9 and was about 55% ethylene oxide by weight ("NPF 55% EO"). The third NPF was a nonylphenol formaldehyde resin alkoxylate with a degree of polymerization of about 2-8 and was about 80% ethylene oxide by weight ("NPF 80% EO").

Comparative examples 1 and 2 ("Comp 1" and "Comp 2" respectively) have no water in the formulations. Comp 2 also comprised an oil-soluble surfactant that was a polyalkylene oxide triblock polyol with about 10% EO and an average molecular weight, $\overline{M_w}$ of about 4,400 ("EO/PO Surf. 10% EO").

The resulting formulations, Examples 1 through 4 (i.e. Ex 1- Ex 4), all had water in the formulations and were stable, micellar solutions that did not separate when stored at ambient temperature for more than 30 days. Examples 1 through 4 also included an ethylenediamine ethylene oxide / propylene oxide copolymer ("ED EO/PO") that was about 40% EO by weight and had an average molecular weight, $\overline{M_w}$, of about 6,700.

TABLE 2 – DEMULSIFIER FORMULATIONS

	Raw Materials (wt%)											
	Actives							**Solvents**				
	APF 40% EO	**NPF 50% EO**	**NPF 55% EO**	**NPF 80% EO**	**ED EO/PO**	**EO/PO Surf. 10% EO**	**EO/PO Surf. 40% EO**	**Heavy Naph.**	**Light Naph.**	**$C_6H_{14}O_2$**	**$C_8H_{18}O_3$**	**H_2O**
Comp 1		27.0	23.5				4.5	45.0				
Comp 2	28.0					6.0	6.0	30.0	20.0	10.0		
Ex 1			12.5	12.5	4.0		6.0	55.0				10.0
Ex 2			12.5	12.5	4.0		6.0				5.0	60.0
Ex 3		12.5	12.5		4.0		6.0	55.0				10.0
Ex 4		12.5	12.5		4.0		6.0				5.0	60.0

Note: $C_6H_{14}O_2$ is hexylene glycol; $C_8H_{18}O_3$ is diethylene glycol butyl ether (butyl carbitol)

EXAMPLE SET 1 – CANADIAN CRUDE AND AMERICAN SHALE OIL BLEND

A desalter process with an electric field and desalter mix valve was simulated to evaluate the effect the emulsion breaker (demulsifier) formulations in Table 1 had on breaking water and crude oil emulsions. The crude oil used was a blend of Canadian crudes and American shale oils. The Basic Sediments and Water ("BS&W") of the crude was about 50 pounds of solids per thousand barrels and 0.1 wt% water. Comp 1 was used as the comparative example. For these examples, 95 vol% crude oil was mixed with 5 vol% wash water (pH = 7) in a test tube. Then 3 ppm by volume of a demulsifier was added to the crude oil and wash water mixture and mixed at 6,000 rpm in a blender for 2 seconds. For the sedimentation step, the mixture was allowed to settle at a temperature of about 110 °C and at an electrical field strength of 10 kV. The volume of free water (mL) was measured at 2, 4, 8, 16, and 32 minutes.

The mean water drop is the average measured volume of free water. The mean water drop indicates both the speed of water drop and the amount of water that had separated from the emulsion. The water drop with respect to time for Example Set 1 is shown in FIG. 1. The mean water drop for the various demulsifier formulations are shown in FIG. 2.

EXAMPLE SET 2 – CANADIAN CRUDE OIL

A desalter process with an electric field and desalter mix valve was simulated to evaluate the effect the emulsion breaker (demulsifier) formulations in Table 1 had on breaking water and crude oil emulsions. The crude oil used was Canadian crude oil from Sarnia, Ontario. The BS&W of the crude was about 50 pounds of solids per thousand barrels and 0.1 wt% water. Comp 2 was used as the comparative example. For these examples, 95 vol% crude oil was mixed with 5 vol% wash water (pH = 7) in a test tube. Then 3 ppm by volume of a demulsifier was added to the crude oil and wash water mixture and mixed at 13,000 rpm in a blender for 4 seconds. For the sedimentation step, the mixture was allowed to settle at a temperature of about 120 °C and at an electrical field strength of 10 kV. The volume of free water (mL) was measured at 2, 4, 8, 16, and 32 minutes.

The mean water drop is the average measured volume of free water. The mean water drop test indicates both the speed of water drop and the amount of water that had separated from the emulsion. The water drop with respect to time for Example Set 2 is shown in FIG. 3. The mean water drop for the various demulsifier formulations are shown in FIG. 4.

EXAMPLE SET 3 – VENEZUELAN HEAVY CRUDE OIL

A desalter process with an electric field and desalter mix valve was simulated to evaluate the synergistic effect a dispersant, in this case a polyisobutenyl succinic anhydride based ester ("PiB ester"), had on breaking water and crude oil emulsions. For this test, diluted crude oil similar to Venezuelan heavy crude oil was prepared. The BS&W of the crude was about 84 pounds of solids per thousand barrels and 0.1 wt% water. Comp 1 was used as the comparative example. For these examples, 95 vol% crude oil was mixed with 5 vol% wash water (pH = 7) in a test tube. Then 3 ppm of a demulsifier (Comp 1) and/or 100 ppm of a dispersant (PiBS ester) was added to the crude oil and wash water mixture and mixed at 13,000 rpm in a blender for 4 seconds.

For the sedimentation step, the mixture was allowed to settle at a temperature of about 120 °C and at an electrical field strength of 10 kV. The volume of free water (mL) was measured at 2, 4, 8, 16, and 32 minutes.

The mean water drop is the average measured volume of free water. The mean water drop test indicates both the speed of water drop and the amount of water that had separated from the emulsion. The water drop with respect to time for Example Set 3 is shown in FIG. 5. The mean water drop results for the various demulsifier and/or dispersant treatments are shown in FIG. 6.

This written description uses examples to disclose the invention, including the best mode, and also to enable any person skilled in the art to practice the invention, including making and using any devices or systems and performing any incorporated methods. The patentable scope of the invention is defined by the claims, and may include other examples that occur to those skilled in the art. For example, those skilled in the art will recognize that the demulsification compositions have multiple applications, including but not limited to, oil-field or "down-hole" applications or in crude oil refining applications. Such other examples are intended to be within the scope of the claims if they have structural elements that do not differ from the literal language of the claims, or if they include equivalent structural elements with insubstantial differences from the literal languages of the claims.

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DEMULSIFYING COMPOSITIONS AND METHODS OF USE

Abstract Of The Invention

Methods for resolving emulsions in a hydrocarbon stream by contacting the hydrocarbon stream with a demulsifying composition are disclosed. Demulsifying compositions for treating a hydrocarbon stream are also disclosed, wherein the demulsifying composition comprises at least one C_4-C_{12} alkyl phenol-formaldehyde resin alkoxylate and at least one surfactant, wherein the surfactant comprises at least two blocks of alkylene oxide units.

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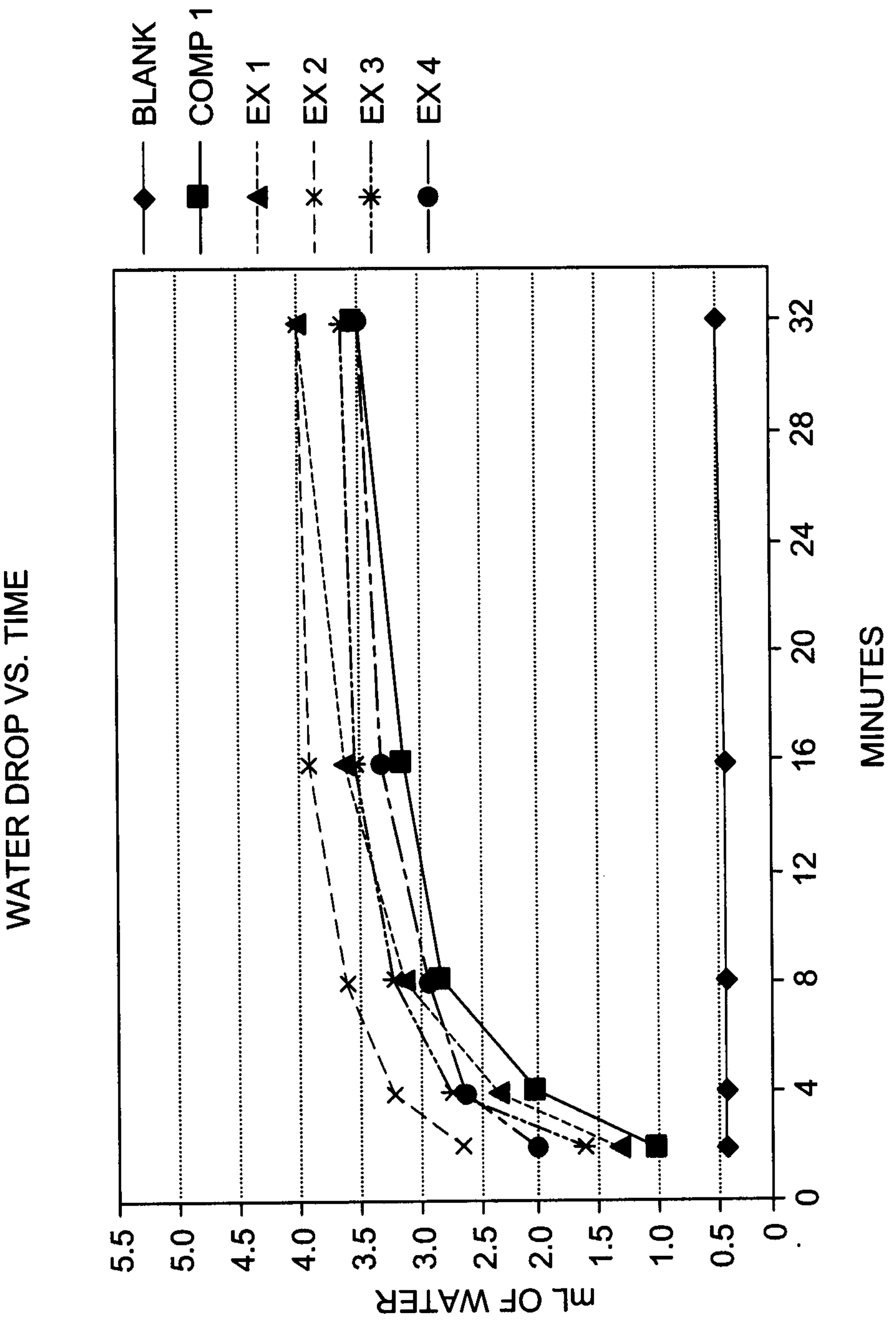

FIG. 1

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MANISHA SINGH NAIR
Agent for the Applicant - IN/PA-740
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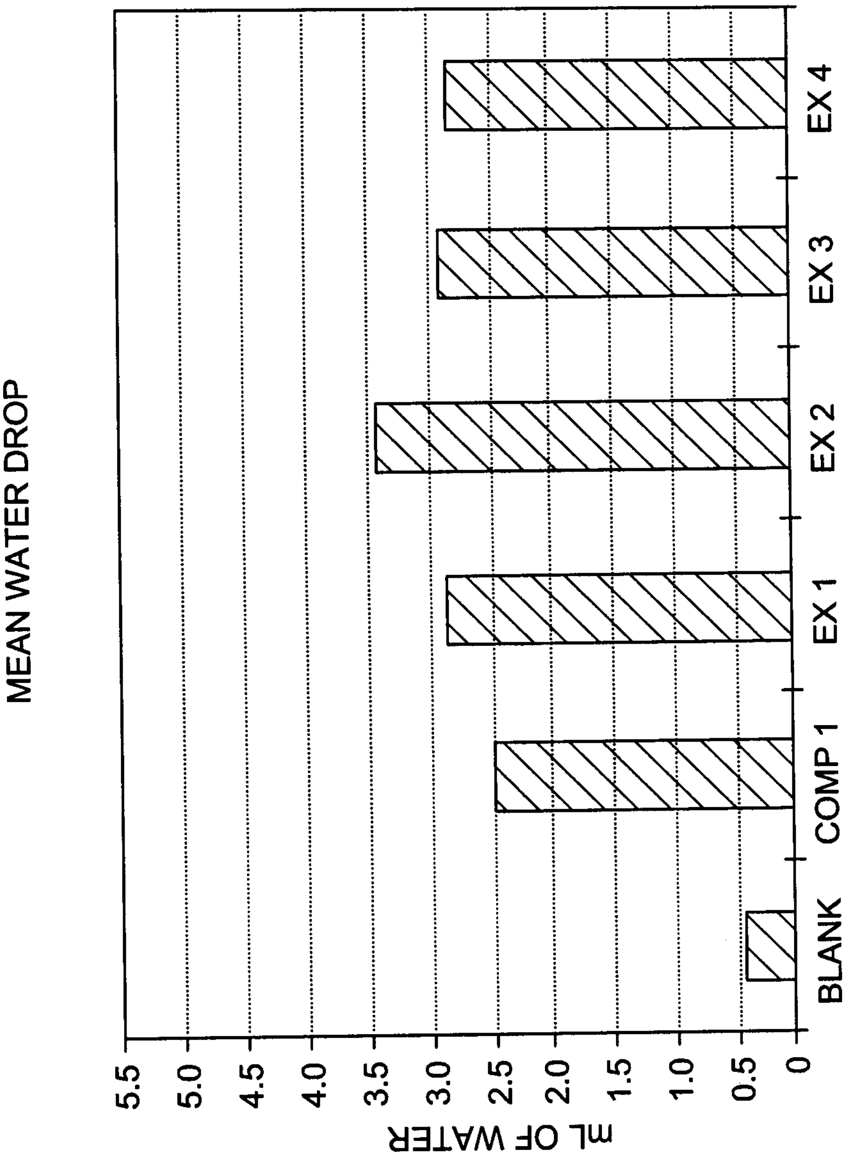

FIG. 2

Manisha Singh Nair

MANISHA SINGH NAIR
Agent for the Applicant - IN/PA-740
LEX ORBIS IP PRACTICE

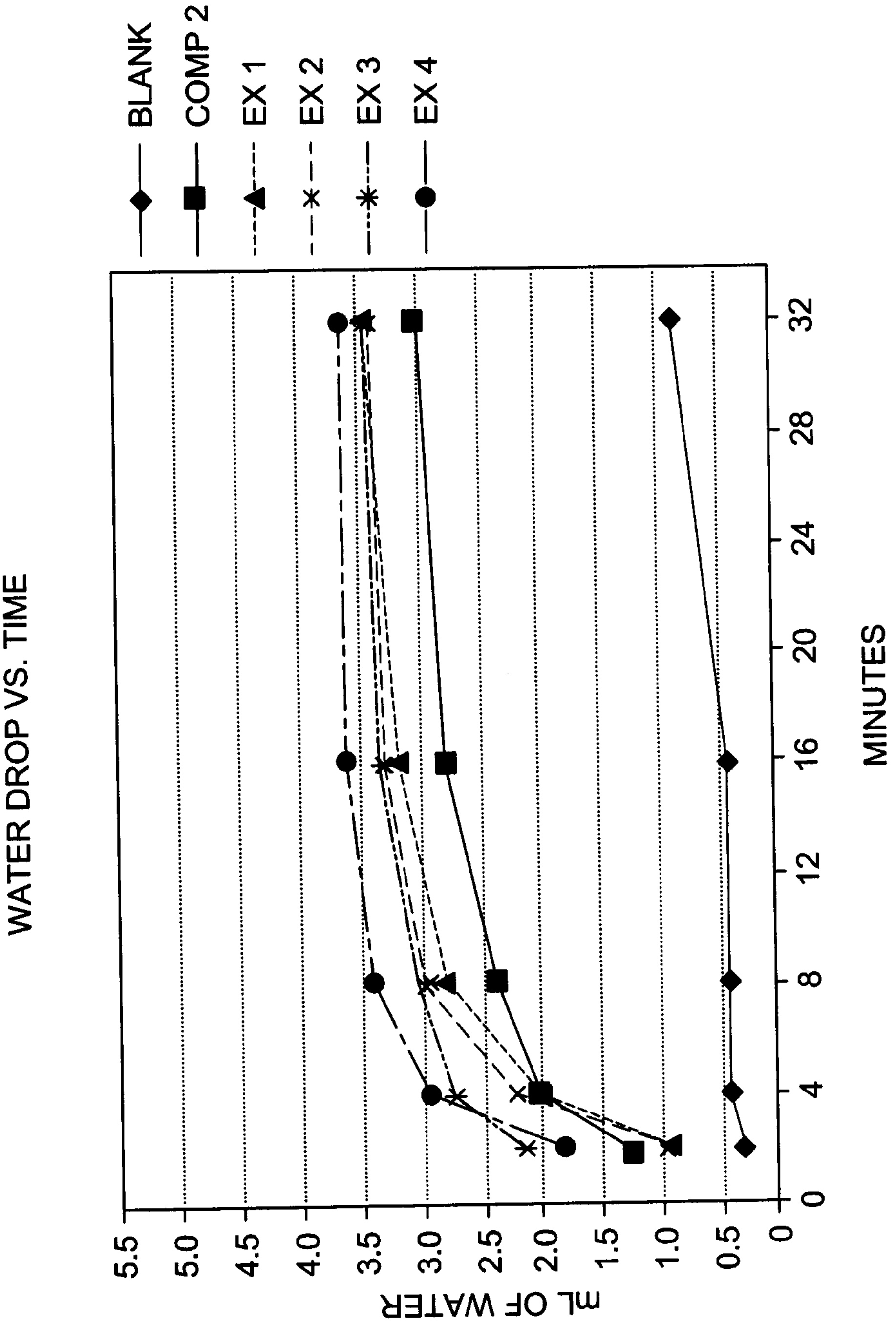

FIG. 3

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MANISHA SINGH NAIR
Agent for the Applicant - IN/PA-740
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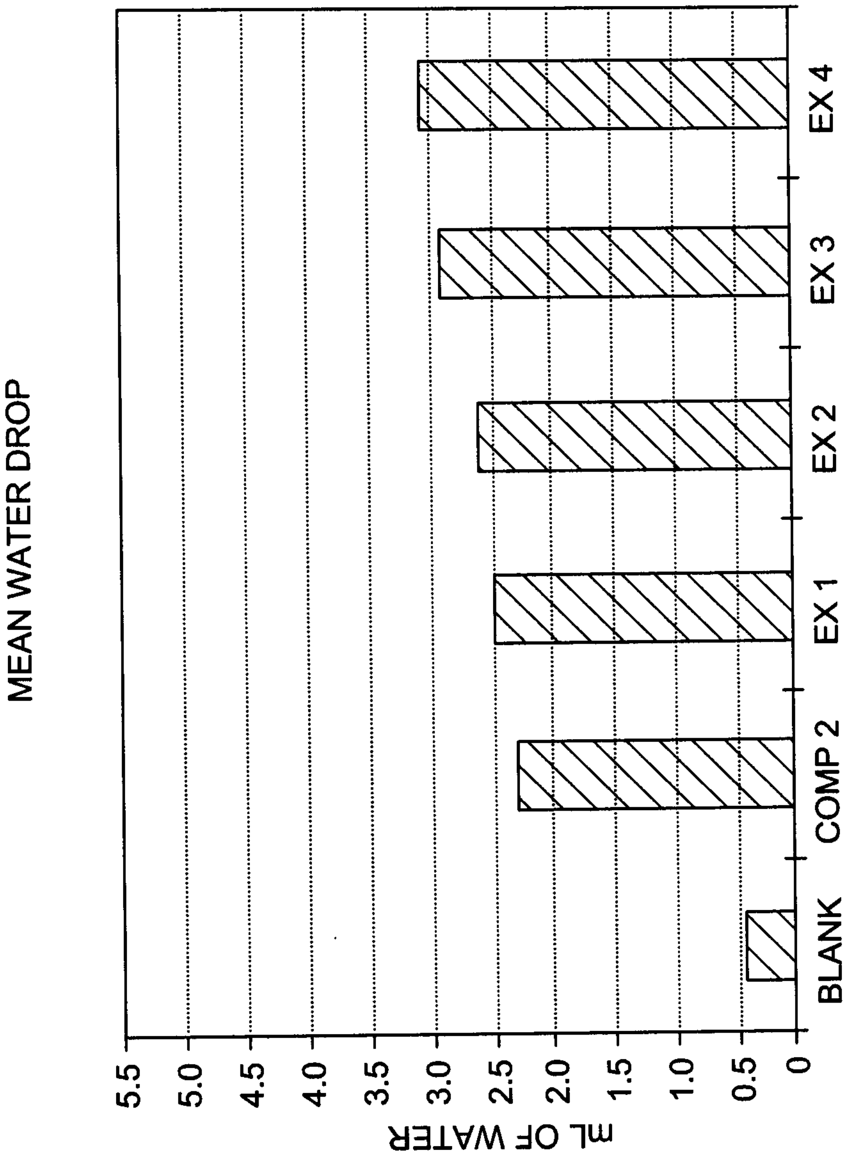

FIG. 4

Manisha Singh Nair
MANISHA SINGH NAIR
Agent for the Applicant - IN/PA-740
LEX ORBIS IP PRACTICE

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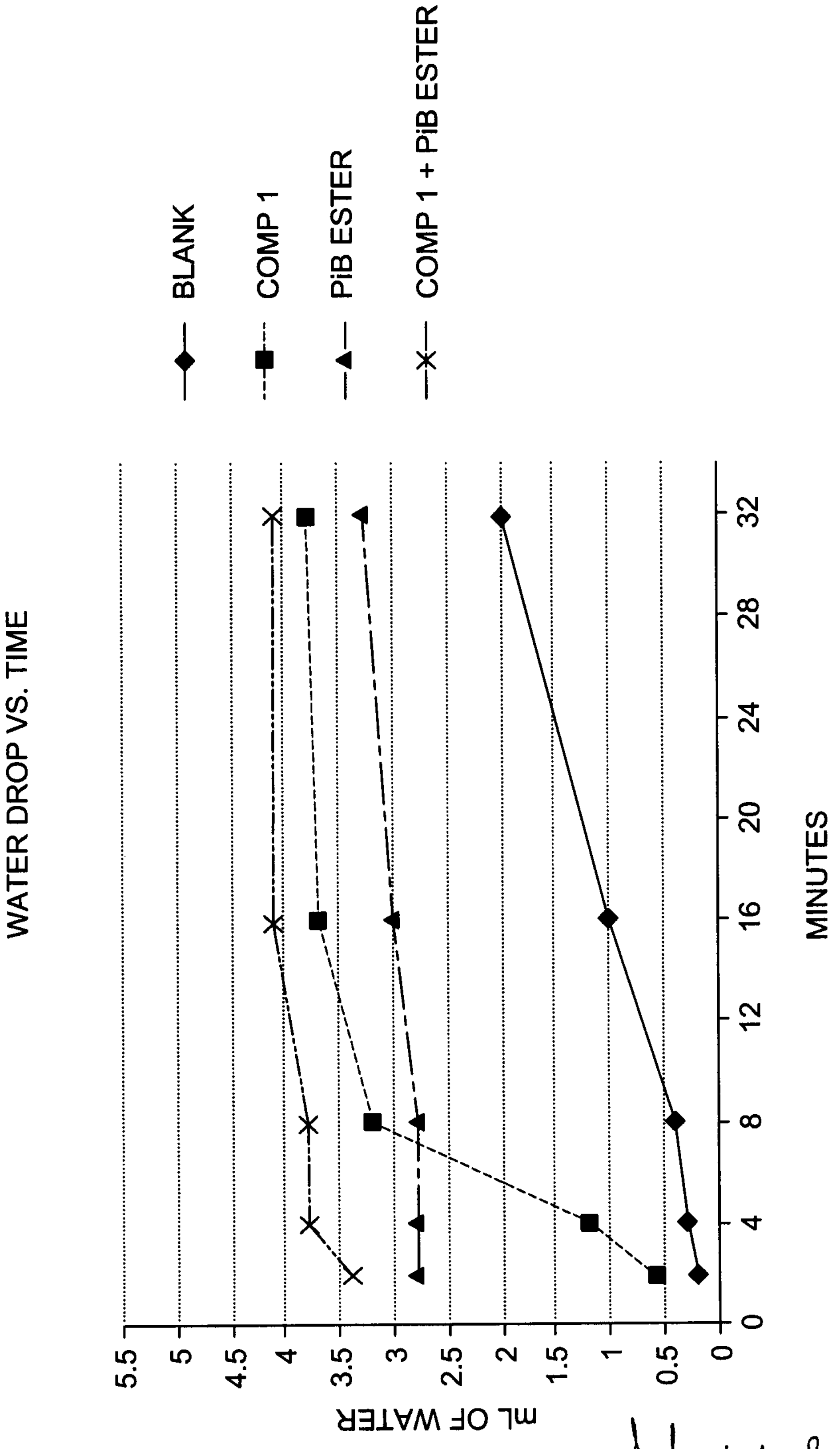

FIG. 5

Manisha Singh Nair
MANISHA SINGH NAIR
Agent for the Applicant - IN/PA-740
LEX ORBIS IP PRACTICE

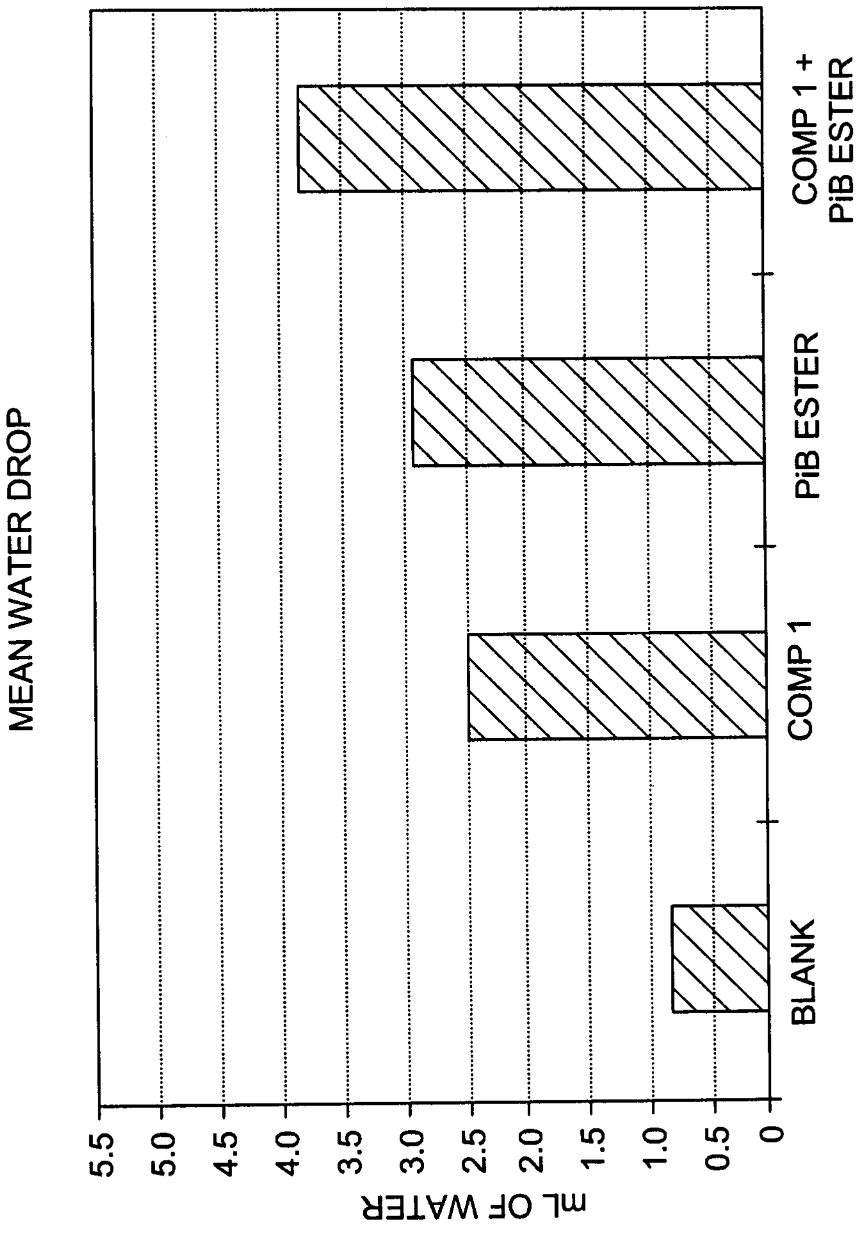

FIG. 6

Manisha Singh Nair
MANISHA SINGH NAIR
Agent for the Applicant - IN/PA-740
LEX ORBIS IP PRACTICE