

Title of the invention:

Demulsification Additive composition, and method of use thereof, and method of demulsification.

Field of the invention:

The present invention relates to demulsification additive composition for demulsification of water-in-oil emulsion.

In particular, the present invention relates to demulsification additive composition for demulsification of water-in-oil emulsion caused by mixing of wash water and crude oil, more particularly caused by mixing of wash water and crude oil in the desalter unit of the refinery.

Even more particularly, the present invention relates to demulsification additive composition for demulsification of water-in-oil emulsion caused by mixing of wash water and crude oil in the desalter unit of the refinery, wherein the demulsification additive composition comprises at least a combination of:

- (a) one or more demulsifiers;
- (b) a compound selected from the group comprising glyoxal, neutralized glyoxal and mixture thereof; and
- (c) further comprises phosphoric acid.

In one embodiment, the present invention relates to a method of demulsification of water-in-oil emulsions, particularly of water-in-oil emulsions caused by mixing of wash water and crude oil, more particularly of water-in-oil emulsions caused by mixing of wash water and crude oil in the desalter unit of the refinery by employing the demulsification additive composition of the present invention.

In another embodiment, the present invention relates to a method of using the demulsification additive composition of the present invention for demulsification of water-in-oil emulsions, particularly of water-in-oil emulsions caused by mixing of wash water and crude oil, more particularly of water-in-oil emulsions caused by mixing of wash water and crude oil in the desalter unit of the refinery.

Background of the invention:

The water-in-oil emulsions are formed in various industrial operations, and are responsible for substantial loss of various industrial ingredients including difficulties in separation of oil. Therefore, breaking of water-in-oil emulsions during the processing of oil is the requirement of the industry, particularly of the crude oil refinery industry

wherein the wash water gets mixed with crude oil in the desalter unit of the refinery and forms water-in-oil emulsion.

Presently, the water-in-oil emulsion caused by mixing of wash water and crude oil is broken by addition of demulsifier to the wash water.

The main problem of using the demulsifiers is that these are to be used in higher amounts and required continuously through the processing of crude oil, which results in substantial increase in cost of processing of crude oil.

Another problem of using the demulsifiers is that these are expensive, which also results in substantial increase in cost of processing of crude oil.

More importantly, the presently used demulsifiers are condensation product of nonyl phenols, and presently, there is a need to reduce consumption of nonyl phenols in view of their cost and environmental adverse effects.

Need of the invention:

Therefore, there is a need to reduce, if total elimination is not possible, the requirement of demulsifiers so that above-discussed problems of use of demulsifiers may, at least, be minimized without loss of or sacrificing the industrial output of the crude oil processing units.

Problem to be solved by the Invention:

Therefore, the present invention aims at providing a solution to above-described existing industrial problems by providing:

- i) an improved and effective demulsification additive composition for demulsification of water-in-oil emulsions, and
- ii) method of using the demulsification additive composition of the present invention for demulsification of water-in-oil emulsions, and
- iii) method for demulsification of water-in-oil emulsions by employing the demulsification additive composition of the present invention.

Objects of the invention:

Accordingly, the main object of the present invention is to provide:

- i) a demulsification additive composition for demulsification of water-in-oil emulsions, particularly of water-in-oil emulsions caused by mixing of wash water and crude oil, more particularly of water-in-oil emulsions caused by mixing of wash water and crude oil in the desalter unit of the refinery.

Accordingly, the other object of the present invention is to provide:

1 ii) a method of demulsification of water-in-oil emulsions, particularly of
2 water-in-oil emulsions caused by mixing of wash water and crude oil, more particularly
3 of water-in-oil emulsions caused by mixing of wash water and crude oil in the desalter
4 unit of the refinery by employing the demulsification additive composition of the present
5 invention.

6 Accordingly, another object of the present invention is to provide:

7 iii) a method of using the demulsification additive composition of the present
8 invention for demulsification of water-in-oil emulsions, particularly of water-in-oil
9 emulsions caused by mixing of wash water and crude oil, more particularly of water-in-
10 oil emulsions caused by mixing of wash water and crude oil in the desalter unit of the
11 refinery.

12 Accordingly, an object of the present invention is to provide a demulsification
13 additive composition for demulsification of water-in-oil emulsions, which is preferably
14 caused by mixing of wash water and crude oil, more preferably for demulsification of the
15 water-in-oil emulsions caused by mixing of wash water and crude oil in the desalter unit
16 of the refinery so as to reduce the amount of the presently used demulsifiers, which are
17 condensation product of nonyl phenols, and hence, to reduce consumption of nonyl
18 phenols or condensation product of nonyl phenols, and thereby to reduce cost of
19 processing and associated environmental adverse effects.

20 Other objects and advantages of present invention will become more apparent
21 from the following description when read in conjunction with examples, which are not
22 intended to limit scope of present invention.

23 **Description and Preferred Embodiments of the Invention:**

24 With aim to overcome above-described industrial problems of the prior art and to
25 achieve above-described objects of the present invention, the inventor has found that a
26 composition comprising:

- 27 (a) one or more demulsifiers (may be referred to as component (a)); and
28 (b) a compound selected from the group comprising glyoxal, neutralized
29 glyoxal, glyoxal derivative and a mixture thereof (may be referred to as
30 component (b)), and
31 (c) further comprising phosphoric acid (may be referred to as component (c)),
32 surprisingly and unexpectedly, substantially improves demulsification efficiency
33 of the demulsifier (the component (a)), and thereby, results in substantial reduction of

1 requirement of amount of the demulsifier, which results in substantial decrease in cost of
2 processing of crude oil, and associated environmental adverse effects.

3 The inventor has also found that the composition of the present invention
4 comprising a combination of the component (a), the component (b), and the component
5 (c), surprisingly and unexpectedly, also substantially improves demulsification
6 efficiency:

7 of the composition consisting of a combination of the component (a) and the
8 component (b), and

9 of the composition consisting of a combination of the component (a) and the
10 component (c).

11 Further, as the glyoxal and neutralized glyoxal are less expensive than the
12 demulsifiers, it further results in substantial decrease in cost of processing of the crude
13 oil.

14 Accordingly, the present invention relates to a demulsification additive
15 composition for demulsification of water-in-oil emulsion caused due to wash water in the
16 crude oil, wherein the composition comprises:

- 17 (a) one or more demulsifiers (the component (a)); and
18 (b) a compound selected from the group comprising glyoxal, glyoxal
19 derivative, neutralized glyoxal, and a mixture thereof (the component (b)),
20 and
21 (c) further comprises phosphoric acid (the component (c)).

22 The inventor has further found that the composition comprising a combination of
23 the component (a) and the component (b), or comprising a combination of the
24 component (a) and the component (b), and the component (c), wherein

25 the component (b) comprises one or more of the following:

26 Glycolic acid;

27 Glyoxylic Acid;

28 Citric acid; or

29 Maleic anhydride, and

30 the component (c) comprises phosphoric acid,

31 do not show an improvement in demulsification efficiency of the composition
32 consisting of the component (a) of the present invention.

33 Therefore, in accordance with one of the embodiments of the present invention,
34 the present composition does not comprise one or more of the following:

1 Glycolic acid;
2 Glyoxylic Acid;
3 Citric acid; or
4 Maleic anhydride.

5 In accordance with the present invention, the neutralized glyoxal is glyoxal
6 having pH neutral to basic. The inventor has observed that the glyoxal is very acidic, and
7 therefore, it may cause corrosion. Accordingly, neutralizing the glyoxal till its pH is
8 neutral to basic avoids corrosion of crude oil processing unit, and still improves
9 demulsification efficiency of the demulsifier.

10 In accordance with the present invention, the neutralized glyoxal is obtained by
11 neutralizing the glyoxal with an amine or alkaline medium.

12 As per the present invention, the amine may include (or comprises) triethanol
13 amine (TEA).

14 As per the present invention, the alkaline medium may include (or comprises)
15 sodium hydroxide aqueous solution.

16 In accordance with the present invention, the neutralized glyoxal may also
17 include (or comprise) neutralized derivative of glyoxal. Therefore, in the present
18 invention, the term “neutralized glyoxal” or the term “neutralized derivative of glyoxal”
19 have one and same meaning unless otherwise explicitly described.

20 In accordance with the present invention, the pH neutral to basic includes a pH
21 varying from about 7 to about 12.

22 In accordance with the present invention, the glyoxal derivative may comprise (or
23 include) methanol, ethanol, butanol, or ethylene glycol derivative of glyoxal, or a
24 mixture thereof.

25 In accordance with one of the preferred embodiments of the present invention,
26 the demulsifier is selected from the group comprising oxyalkylated condensation product
27 of:

- 28 i) nonyl phenol and amyl phenol, and formaldehyde;
- 29 ii) nonyl phenol and butyl phenol, and formaldehyde;
- 30 iii) nonyl phenol and formaldehyde;
- 31 iv) amyl phenol and formaldehyde;
- 32 v) butyl phenol and formaldehyde;
- 33 vi) alkyl phenol and formaldehyde; and
- 34 vii) a mixture thereof.

In accordance with another preferred embodiment of the present invention, the demulsifier is selected from the group comprising oxyalkylated condensation product of:

- i) cardanol, nonyl phenol and amyl phenol, and formaldehyde;
- ii) cardanol, nonyl phenol and butyl phenol, and formaldehyde;
- iii) cardanol, nonyl phenol and formaldehyde;
- iv) cardanol, amyl phenol and formaldehyde;
- v) cardanol, butyl phenol and formaldehyde;
- vi) cardanol, alkyl phenol and formaldehyde; and
- vii) a mixture thereof.

In accordance with one of the preferred embodiments of the present invention, the demulsifier is selected from the group comprising:

- i) oxyalkylated nonyl phenol and amyl phenol formaldehyde copolymers;
- ii) oxyalkylated nonyl phenol and butyl phenol formaldehyde copolymers;
- iii) oxyalkylated nonyl phenol formaldehyde polymers;
- iv) oxyalkylated amyl phenol formaldehyde polymers;
- v) oxyalkylated butyl phenol formaldehyde polymers;
- vi) oxyalkylated alkyl phenol formaldehyde polymers; and
- vii) a mixture thereof.

In accordance with one of the preferred embodiments of the present invention, the demulsifier may be selected from a group comprising:

- i) oxyalkylated cardanol, nonyl phenol and amyl phenol, and formaldehyde copolymers;
- ii) oxyalkylated cardanol, nonyl phenol and butyl phenol, and formaldehyde copolymers;
- iii) oxyalkylated cardanol, nonyl phenol and formaldehyde polymers;
- iv) oxyalkylated cardanol, amyl phenol and formaldehyde polymers;
- v) oxyalkylated cardanol, butyl phenol and formaldehyde polymers;
- vi) oxyalkylated cardanol, alkyl phenol and formaldehyde polymers; and
- vii) a mixture thereof.

In accordance with one of the preferred embodiments of the present invention, the oxyalkylated product is an ethylene oxide derivative, propylene oxide derivative, butylene oxide derivative or a mixture thereof. In accordance with one of the preferred embodiments of the present invention, the oxyalkylated product is an oxyalkylated copolymer or an oxyalkylated polymer or an oxyalkylated resin. In accordance with one

of the preferred embodiments of the present invention, the oxyalkylated product is a base catalyzed oxyalkylated copolymer or a base catalyzed oxyalkylated polymer or a base catalyzed oxyalkylated resin of one or more of the said phenolic compound (i.e. cardanol, nonyl phenol, butyl phenol, amyl phenol, alkyl phenol) and formaldehyde. In accordance with one of the preferred embodiments of the present invention, the oxyalkylated product is the oxyalkylated phenol formaldehyde resin, oxyalkylated phenol formaldehyde polymer, or oxyalkylated phenol formaldehyde copolymer.

In accordance with one of the embodiments of the present invention, the phenolic reactants includes alkyl phenols comprising alkyl group. In accordance with one of the embodiments of the present invention, the alkyl group comprises from about 1 to about 20 carbon atoms. In accordance with one of the embodiments of the present invention, the substitution may be of butyl, amyl, nonyl, hexyl, octyl, isooctyl, decyl, or dodecyl group.

It may be noted that term “copolymer” means a polymer made from two different phenols and the term “polymer” means a polymer made from one phenol, and resin is intended to include the polymers and copolymers.

In accordance with the one of the embodiments of the present invention, the reaction of alkyl phenol formaldehyde resin with alkylene oxide forms a high molecular weight oxyalkylated alkyl phenol formaldehyde resin.

In accordance with the one of the embodiments of the present invention, the alkylene oxide comprises ethylene oxide, propylene oxide, butylene oxide or a mixture thereof, preferably the alkylene oxide comprises ethylene oxide, propylene oxide, or a mixture thereof.

In accordance with the one of the preferred embodiments of the present invention, the molecular weight of the demulsifier of the present invention may vary from about 1000 to about 20000 daltons, preferably from about 2000 to about 15000 daltons, more preferably from about 2000 to about 10000 daltons as measured by Gel Permeation Chromatography (GPC) using the tetrahydro furan (THF) as solvent.

In accordance with the one of the embodiments of the present invention, the average molecular weight of the demulsifier of the present invention may vary from about 1000 to about 20000 daltons, preferably from about 2000 to about 15000 daltons, more preferably from about 2000 to about 10000 daltons as measured by Gel Permeation Chromatography (GPC) using the tetrahydro furan (THF) as solvent.

In accordance with the present invention, the composition comprises:

- 1 a) the component (a) in an amount varying from about 99.1 % to about 0.1 %
2 by weight of the total composition;
3 b) the component (b) in an amount varying from about 0.1 % to about 99.1
4 % by weight of the total composition; and
5 c) the component (c) in an amount varying from about 0.1 % to about 99.1 %
6 by weight of the total composition,
7 depending upon the nature of the water-in-oil emulsion to be treated.

8 It may be noted that as per present invention, the additive composition may be
9 added to the crude oil phase or to the desalter wherein wash water is mixed with crude
10 oil and forms a water-in-oil emulsion.

11 It may also be noted that the scope of the present invention is not limited by the
12 crude oil or the wash water.

13 Accordingly, in another embodiment, the present invention relates to a method of
14 demulsification of water-in-oil emulsions, particularly of water-in-oil emulsions formed
15 by mixing of wash water and crude oil, more particularly of water-in-oil emulsions
16 formed by mixing of wash water and crude oil in the desalter unit of the refinery,
17 wherein the water-in-oil emulsion formed due to mixing of wash water in the crude oil is
18 treated with the presently provided demulsification additive composition.

19 Accordingly, in still another embodiment, the present invention also relates to a
20 method of using the presently provided demulsification additive composition for
21 demulsification of water-in-oil emulsions, particularly of water-in-oil emulsions formed
22 by mixing of wash water and crude oil, more particularly of water-in-oil emulsions
23 formed by mixing of wash water and crude oil in the desalter unit of the refinery,
24 wherein the presently provided demulsification additive composition is added to the
25 water-in-oil emulsion formed due to mixing of wash water in the crude oil. It may be
26 noted that the scope of the present invention is not limited by amount of the additive
27 composition of the present invention, which has to be added in an amount sufficient for
28 demulsification of the water-in-oil emulsions.

29 The present invention is now described with the help of following examples,
30 which are not intended to limit scope of the present invention, but have been
31 incorporated for the sake of illustrating the advantages of the present invention over the
32 prior art.

33 **Examples:**

34 The following examples were carried out under the following conditions:

1 PED No 1315
 2 Crude : Raw Crude
 3 API : 28.1
 4 Wash Water : 5% (HMEL, ID 443), pH-8.1
 5 Mixing Temp : 55⁰C
 6 Mixing time : 2 min
 7 Temp : 130⁰C
 8 Voltage : 3KV for 8 min

9 In the following examples, the following compositions have been tested for their
 10 demulsification efficiency.

11 1. Component (a) is demulsifier, which is 50% active nonylphenol
 12 formaldehyde ethoxylate resin (or may be a base catalysed nonylphenol formaldehyde
 13 resin);

14 2. Component (b) of the present invention is glyoxal or neutralized glyoxal,
 15 wherein the glyoxal has been neutralized with triethanol amine (TEA);

16 3. Component (c) of the present invention is phosphoric acid;

17 4. Comparative component may be selected from glycolic acid, glyoxylic
 18 Acid, citric acid, and maleic anhydride. In the following experiments these have been
 19 identified as follows and are taken in 14% by weight of DM (demineralized water):

20 Comparative component (b1) is glycolic acid (40%);

21 Comparative component (b2) is glyoxylic acid (40%);

22 Comparative component (b3) is citric acid (40%);

23 Comparative component (b4) is maleic anhydride (40%).

24 5. Comparative compositions do not comprise the combination of the
 25 component (b) and the component (c) of the present invention.

26 The 'blank' is without any additive.

Table - I

Additive Composition	Dosage (in ppm)	Water Drop, ml						Demulsification / Dehydration (in %)
		20 min 130°C	3KV 8 min	5 min	10 min	15 min	20 min	
Blank	--	Nil	Nil	0.1	0.1	0.15	0.15	3.0
Component (a) (Comparative Composition)	10	Nil	2.0	2.2	2.4	2.6	2.8	56.0
Component (a) + Component (b) (Comparative Composition)	10+3	Nil	2.4	2.8	3.0	3.2	3.7	74.0
Component (a) + Component (c) (Comparative Composition)	10+3	Nil	1.8	2.2	2.4	2.6	2.8	56.0
10 ppm of Component (a) + 3 ppm of [Component (b) + Component (c)] (Present Composition)	10+3	Nil	2.8	3.0	3.5	3.7	4.2	84.0

1 In above Table – I, dosage ‘10+3’ indicates that the additive comprises 10 ppm of
2 Component (a) and 3 ppm of Comparative component (b1), and so on.

3 However, in above Table – I, the ‘Present Composition’ comprises 10 ppm of
4 Component (a) and 3 ppm of [Component (b) + Component (c)], wherein the
5 [Component (b) + Component (c)] comprises the Component (b) which is glyoxal (40%)
6 and the Component (c) which is H₃PO₄ (85%) in DM (demineralized water) water in a
7 weight ratio of 14/0.43/85.57.

8 As can be observed from above Table I, the composition of the present invention
9 demonstrates 84% efficiency as against 56% or 74% efficiency of the comparative
10 compositions.

Table - II

Additive Composition	Dosage (in ppm)	Water Drop, ml						Demulsification / Dehydration (in %)
		20 min 130°C	3KV 8 min	5 min	10 min	15 min	20 min	
Component (a) + Comparative component (b1) (Comparative Composition)	10+3	Nil	2.0	2.2	2.6	2.6	2.8	56.0
Component (a) + with Comparative composition (B) (Comparative Composition)	10+3	Nil	2.2	2.6	2.6	2.8	3.0	60.0
Component (a) + Comparative component (b2) (Comparative Composition)	10+3	Nil	2.0	2.2	2.4	2.6	2.8	56.0
Component (a) + Comparative composition (C) (Comparative Composition)	10+3	Nil	2.2	2.2	2.4	2.6	2.8	56.0
Component (a)+ Comparative component (b3) (Comparative Composition)	10+3	Nil	2.0	2.2	2.4	2.6	2.8	56.0
Component (a) + Comparative composition (D) (Comparative Composition)	10+3	Nil	2.0	2.2	2.4	2.6	2.8	56.0
Component (a)+ Comparative component (b4) (Comparative Composition)	10+3	Nil	1.8	2.2	2.4	2.6	2.8	56.0
Component (a) + Comparative composition (E) (Comparative Composition)	10+3	Nil	2.0	2.2	2.4	2.6	2.8	56.0

- 1 In above Table – II, dosage ‘10+3’ indicates that the additive comprise 10 ppm of
2 Component (a) and 3 ppm of second component, i.e. Comparative component (b1), Comparative
3 composition (B), Comparative component (b2), Comparative composition (C), Comparative

component (b3), Comparative composition (D), Comparative component (b4), Comparative composition (E).

In above Tables I and II, the various components have following composition:

Component (a) is 50% active nonyl phenol formaldehyde ethoxylate resin (oxyalkylated condensation product);

Component (b) comprises glyoxal (40%) in 14% DM water;

Component (c) comprises H_3PO_4 (85%) in 0.43% of DM water;

Present Composition comprises in-addition to the Component (a), the Component (b) which is glyoxal (40%) and the Component (c) which is H_3PO_4 (85%) in DM water in a weight ratio of 14/0.43/85.57;

Comparative component (b1) is glycolic acid (40%) in 14% DM water;

Comparative composition (B) comprises Comparative component (b1) which is glycolic acid (40%) and the component (c) which is H_3PO_4 (85%) in DM water in a weight ratio of 14/0.43/85.57;

Comparative component (b2) is glyoxylic acid (40%) in 14% by weight of DM water;

Comparative composition (C) comprises Comparative component (b2) which is Glyoxylic acid (40%) and component (c) which is H_3PO_4 (85%) in DM water in a weight ratio of 14/0.43/85.57;

Comparative component (b3) is citric acid (40%) in 14% by weight of DM water;

Comparative composition (D) comprises Comparative component (b3) which is Citric acid (40%) and component (c) which is H_3PO_4 (85%) in DM water in a weight ratio of 14/0.43/85.57;

Comparative component (b4) is maleic anhydride (40%) in 14% by weight of DM water;

Comparative composition (E) comprises Comparative component (b4) which is maleic anhydride (40%) and component (c) which is H_3PO_4 (85%) in DM water in a weight ratio of 14/0.43/85.57.

As can be observed from above Table II, all of the comparative compositions only demonstrate 56% or 60% efficiency.

Table - III

Additive Composition	Dosage (in ppm)	Water Drop, ml					Demulsification / Dehydration (in %)
		20 min 130 ⁰ C	3KV 8 min	5 min	10 min	15 min	
Component (a) (Comparative Composition)	15	Nil	2.0	2.2	2.4	2.8	56
Component (a) + Component (b) (Comparative Composition)	15+0.9	Nil	2.6	2.8	3.5	3.7	74
Component (a) + Component (b) + Component (c) (Present Composition)	15+0.9	Nil	3.2	3.5	4.0	4.5	90

1 In Table III, the mixing time was 2 min and mixing temperature was 55⁰C, and
2 the component (b) is 0.9 ppm of glyoxal (40%) in DM water, and the 0.9 ppm of
3 component (c) comprises 0.87 ppm of glyoxal (40%) and 0.03 ppm of H₃PO₄ (85%) in
4 DM [i.e. 97% by weight of glyoxal (40%) and 3% by weight of H₃PO₄ (85%) in DM];
5 and the component (a) is 50% active ethoxylated nonyl phenol cardanol formaldehyde
6 resin, which is ethoxylated condensation product of 90% by weight of nonyl phenol and
7 10% by weight of cardanol.

8 As can be observed from above Table III, the composition of the present
9 invention demonstrates 90% efficiency as against 56% or 74% efficiency of the
10 comparative compositions.

Table - IV

Additive Composition	Dosage (in ppm)	Water Drop, ml						Demulsification / Dehydration (in %)
		20 min 130°C	3KV 8 min	5 min	10 min	15 min	20 min	
Component (a) (Comparative Composition)	15	0	1.8	2.4	2.8	3.0	3.0	60
Component (a) + Component (b) (Comparative Composition)	15+0.9	0	2.4	3.2	3.5	3.7	3.7	74
Component (a) + Component (b) + Component (c) (Present Composition)	15+0.9	0	2.6	3.6	3.8	4.2	4.2	84

In Table IV, the mixing time was again 2 min and mixing temperature was again 55°C, and the component (b) is 0.9 ppm of glyoxal (40%) in DM water, and the 0.9 ppm of component (c) comprises 0.846 ppm of glyoxal (40%) and 0.054 ppm of H₃PO₄ (85%) in DM [i.e. 94% by weight of glyoxal (40%) and 6% by weight of H₃PO₄ (85%) in DM]; and the component (a) is 50% active ethoxylated nonyl phenol para tertiary amyl phenol formaldehyde resin, which is ethoxylated condensation product of 50% by weight of nonyl phenol and 50% by weight of para tertiary amyl phenol.

As can be observed from above Table IV, the composition of the present invention demonstrates 84% efficiency as against 60% or 74% efficiency of the comparative compositions.

Table - V

Additive Composition	Dosage (in ppm)	Water Drop, ml						Demulsification / Dehydration (in %)
		20 min 130 ⁰ C	3KV 8 min	5 min	10 min	15 min	20 min	
Component (a) (Comparative Composition)	15	0.20	2.0	2.2	2.4	2.6	2.8	56
Component (a) + Component (b) (Comparative Composition)	15+1.2	0.25	2.4	2.8	3.2	3.5	3.7	74
Component (a) + Component (b) + Component (c) (Present Composition)	15+1.2	0.25	2.8	3.2	3.7	4.0	4.2	84

1 In Table V, the mixing time was again 2 min and mixing temperature was again
2 55⁰C, and the component (b) is 1.2 ppm of glyoxal (40%) in DM water, and the 1.2 ppm
3 of component (c) comprises 1.164 ppm of glyoxal (40%) and 0.036 ppm of H₃PO₄ (85%)
4 in DM [i.e. 97% by weight of glyoxal (40%) and 3% by weight of H₃PO₄ (85%) in
5 DM]; and the component (a) is 50% active ethoxylated nonyl phenol para tertiary butyl
6 phenol formaldehyde resin, which is ethoxylated condensation product of 90% by weight
7 of nonyl phenol and 10% by weight of para tertiary butyl phenol.

8 As can be observed from above Table IV, the composition of the present
9 invention demonstrates 84% efficiency as against 56% or 74% efficiency of the
10 comparative compositions.

11 In the foregoing examples, the present additive composition and the prior art or
12 comparative additive composition was added to the water-in-oil emulsion of water and
13 crude oil formed after mixing of water and crude oil.

14 The above experimental results confirm the above-discussed surprising and
15 unexpected technical advantages of the present invention. Particularly these experiments
16 confirm that the present additive composition comprising the Component (a), the
17 Component (b) of the present invention and the Component (c) of the present invention
18 demonstrates surprising and unexpected technical advantages.

1 It may be noted that the term “about” as employed herein is not intended to
2 enlarge scope of claimed invention, but has been incorporated only to include
3 permissible experimental errors of the field of the present invention.

4

Claims:

1. A demulsification additive composition, wherein the composition consists of:
 - (a) at least one demulsifier (the component (a)) comprising oxyalkylated alkyl phenol formaldehyde polymer, co-polymer or resin, or oxyalkylated condensation product of at least one alkyl phenol and formaldehyde;
 - 5 (b) a compound selected from the group consisting of glyoxal, neutralized glyoxal, ethylene glycol derivative of glyoxal, and a mixture thereof (the component (b)); and
 - (c) phosphoric acid (the component (c));wherein the demulsifier (component (a)) comprises 50% active nonylphenol
10 formaldehyde ethoxylate resin or a base catalysed nonylphenol formaldehyde resin;
wherein the glyoxal (component (b)) is neutralized with triethanol amine (TEA);
wherein the composition does not comprise:
 - (i) glycolic acid;
 - 15 (ii) glyoxylic Acid;
 - (iii) citric acid; and
 - (iv) maleic anhydride.
2. The demulsification additive composition as claimed in **claim 1**, wherein the neutralized glyoxal is glyoxal having pH neutral to basic varying from about 7 to
20 about 12.
3. The demulsification additive composition as claimed in **claim 1 or 2**, wherein the composition comprises:
 - a) the component (a) in an amount varying from about 99.1 % to about 0.1 % by weight of the total composition;
 - 25 b) the component (b) in an amount varying from about 0.1 % to about 99.1 % by weight of the total composition; and
 - c) the component (c) in an amount varying from about 0.1 % to about 99.1 % by weight of the total composition,depending upon the nature of the water-in-oil emulsion to be treated.
- 30 4. The demulsification additive composition as claimed in any one of **claims 1 to 3**, wherein the molecular weight of the demulsifier varies from about 1000 to about

20000 daltons as measured by Gel Permeation Chromatography (GPC) using the tetrahydro furan (THF) as solvent.

5. A method of demulsification of water-in-oil emulsions comprising a step of treating the water-in-oil emulsion with a demulsification additive composition, wherein the demulsification additive composition comprises:

- (a) at least one demulsifier (the component (a)) comprising oxyalkylated alkyl phenol formaldehyde polymer, or a co-polymer, a resin, or an oxyalkylated condensation product of at least one alkyl phenol and formaldehyde;
- (b) a compound comprising glyoxal, neutralized glyoxal, ethylene glycol derivative of glyoxal, or a mixture thereof (the component (b)); and
- (c) further comprises a phosphoric acid (the component (c)).

6. The method as claimed in **claim 5**, wherein the neutralized glyoxal is glyoxal having pH neutral to basic varying from about 7 to about 12.

7. The method as claimed in **claim 5 or 6**, wherein the demulsifier comprises oxyalkylated condensation product of:

- i) nonyl phenol and amyl phenol, and formaldehyde;
- ii) nonyl phenol and butyl phenol, and formaldehyde;
- iii) nonyl phenol and formaldehyde;
- iv) amyl phenol and formaldehyde;
- v) butyl phenol and formaldehyde;
- vi) alkyl phenol and formaldehyde; or
- vii) a mixture thereof.

8. The method as claimed in any one of **claims 5 to 7**, wherein the demulsifier comprises oxyalkylated condensation product of:

- i) cardanol, nonyl phenol and amyl phenol, and formaldehyde;
- ii) cardanol, nonyl phenol and butyl phenol, and formaldehyde;
- iii) cardanol, nonyl phenol and formaldehyde;
- iv) cardanol, amyl phenol and formaldehyde;
- v) cardanol, butyl phenol and formaldehyde;
- vi) cardanol, alkyl phenol and formaldehyde; or
- vii) a mixture thereof.

9. The method as claimed in any one of **claims 5 to 8**, wherein the said oxyalkylated comprises derivative of ethylene oxide, propylene oxide, or mixture thereof.

10. The method as claimed in any one of **claims 5 to 9**, wherein the demulsifier comprises:
 - i) oxyalkylated nonyl phenol and amyl phenol formaldehyde copolymers;
 - ii) oxyalkylated nonyl phenol and butyl phenol formaldehyde copolymers;
 - 5 iii) oxyalkylated nonyl phenol formaldehyde polymers;
 - iv) oxyalkylated amyl phenol formaldehyde polymers;
 - v) oxyalkylated butyl phenol formaldehyde polymers;
 - vi) oxyalkylated alkyl phenol formaldehyde polymers; or
 - vii) a mixture thereof.
- 10 11. The method as claimed in as claimed in any one of **claims 5 to 10**, wherein the demulsifier comprises:
 - i) oxyalkylated cardanol, nonyl phenol and amyl phenol, and formaldehyde copolymers;
 - ii) oxyalkylated cardanol, nonyl phenol and butyl phenol, and formaldehyde copolymers;
 - 15 iii) oxyalkylated cardanol, nonyl phenol and formaldehyde polymers;
 - iv) oxyalkylated cardanol, amyl phenol and formaldehyde polymers;
 - v) oxyalkylated cardanol, butyl phenol and formaldehyde polymers;
 - vi) oxyalkylated cardanol, alkyl phenol and formaldehyde polymers; or
 - 20 vii) a mixture thereof.
12. The method as claimed in any one of **claims 5 to 11**, wherein the demulsification additive composition added to the water-in-oil emulsion comprises:
 - a) the component (a) in an amount varying from about 99.1 % to about 0.1 % by weight of the total demulsification additive composition;
 - 25 b) the component (b) in an amount varying from about 0.1 % to about 99.1 % by weight of the total demulsification additive composition; and
 - c) the component (c) in an amount varying from about 0.1 % to about 99.1 % by weight of the total demulsification additive composition,
 depending upon the nature of the water-in-oil emulsion to be treated.
- 30 13. The method as claimed in any one of **claims 5 to 12**, wherein the molecular weight of the demulsifier varies from about 1000 to about 20000 daltons as measured by Gel Permeation Chromatography (GPC) using the tetrahydro furan (THF) as solvent.

14. The method as claimed in any one of **claims 5 to 13**, wherein the demulsification additive composition does not comprise:
- (i) glycolic acid;
 - (ii) glyoxylic Acid;
 - 5 (iii) citric acid; and
 - (iv) maleic anhydride.
15. A method of using a demulsification additive composition for demulsification of a water-in-oil emulsion, wherein demulsification additive composition is added to the water-in-oil emulsion for demulsification thereof, and wherein the
- 10 demulsification additive composition comprises:
- (a) at least one demulsifier (the component (a)) comprising oxyalkylated alkyl phenol formaldehyde polymer, or a co-polymer, a resin, or an oxyalkylated condensation product of at least one alkyl phenol and formaldehyde;
 - (b) a compound comprising glyoxal, neutralized glyoxal, ethylene glycol
 - 15 derivative of glyoxal, or a mixture thereof (the component (b)); and
 - (c) further comprises a phosphoric acid (the component (c)).