

1 **Title of the invention:**

2 Additive composition for demulsification of water-in-oil emulsion, and method
3 of use thereof, and method of demulsification.

4 **Field of the invention:**

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

7 In particular, the present invention relates to additive composition for
8 demulsification of water-in-oil emulsion caused by mixing of wash water and crude oil.

9 More particularly, the present invention relates to additive composition for
10 demulsification of water-in-oil emulsion caused by mixing of wash water and crude oil
11 in the desalter unit of the refinery.

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

- 15 a. a compound selected from the group comprising glyoxal, neutralized
16 glyoxal and mixture thereof; and
17 b. one or more demulsifiers.

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

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

27 **Background of the invention:**

28 The water-in-oil emulsions are formed in various industrial operations, and are
29 responsible for substantial loss of various industrial ingredients including difficulties in
30 separation of oil. Therefore, breaking of water-in-oil emulsions during the processing
31 of oil is the requirement of the industry, particularly of the crude oil refinery industry
32 wherein the wash water gets mixed with crude oil in the desalter unit of the refinery and
33 forms water-in-oil emulsion.

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

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

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

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

11 **Need of the invention:**

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

16 **Problem to be solved by the Invention:**

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

- 19 *i)* effective additive composition for demulsification of water-in-oil
20 emulsions, and
- 21 *ii)* method of using the additive composition for demulsification of water-
22 in-oil emulsions, and
- 23 *iii)* method for demulsification of water-in-oil emulsions by employing the
24 additive composition.

25 **Objects of the invention:**

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

- 27 *i)* an additive composition for demulsification of water-in-oil emulsions,
28 particularly of water-in-oil emulsions caused by mixing of wash water and crude oil,
29 more particularly of water-in-oil emulsions caused by mixing of wash water and crude
30 oil in the desalter unit of the refinery.

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

- 32 *ii)* a method of demulsification of water-in-oil emulsions by employing an
33 additive composition of the present invention, particularly of water-in-oil emulsions
34 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, another object of the present invention is to provide:

iii) a method of using the 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.

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

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

Description and Preferred Embodiments of the Invention:

With aim to overcome above-described industrial problems of the prior art and to achieve above-described objects of the present invention, the inventor has found that when a compound selected from the group comprising glyoxal, neutralized glyoxal, glyoxal derivative and a mixture thereof is added to one or more demulsifiers, the said compound, surprisingly and unexpectedly, results in substantial improvement of demulsification efficiency of the demulsifier, and thereby, results in substantial reduction of requirement of amount of the demulsifier, which results in substantial decrease in cost of processing of crude oil, and associated environmental adverse effects.

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

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

1 a. a compound selected from the group comprising glyoxal, neutralized
2 glyoxal, glyoxal derivative and a mixture thereof; and

3 b. at least one (or one or more) demulsifiers.

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

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

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

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

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

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

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

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

26 i) nonyl phenol and amyl phenol, and formaldehyde;

27 ii) nonyl phenol and butyl phenol, and formaldehyde;

28 iii) nonyl phenol and formaldehyde;

29 iv) amyl phenol and formaldehyde;

30 v) butyl phenol and formaldehyde;

31 vi) alkyl phenol and formaldehyde; and

32 vii) a mixture thereof.

33 In accordance with one of the embodiments of the present invention, the
34 demulsifier is selected from the group comprising condensation product of:

- 1 i) cardanol, nonyl phenol and amyl phenol, and formaldehyde;
- 2 ii) cardanol, nonyl phenol and butyl phenol, and formaldehyde;
- 3 iii) cardanol, nonyl phenol and formaldehyde;
- 4 iv) cardanol, amyl phenol and formaldehyde;
- 5 v) cardanol, butyl phenol and formaldehyde;
- 6 vi) cardanol, alkyl phenol and formaldehyde; and
- 7 vii) a mixture thereof.

8 In accordance with one of the preferred embodiments of the present invention,
9 the above-described condensation product is oxyalkylated.

10 Therefore, in accordance with one of the embodiments of the present invention,
11 the demulsifier is selected from the group comprising oxyalkylated condensation
12 product of:

- 13 i) nonyl phenol and amyl phenol, and formaldehyde;
- 14 ii) nonyl phenol and butyl phenol, and formaldehyde;
- 15 iii) nonyl phenol and formaldehyde;
- 16 iv) amyl phenol and formaldehyde;
- 17 v) butyl phenol and formaldehyde;
- 18 vi) alkyl phenol and formaldehyde; and
- 19 vii) a mixture thereof.

20 Therefore, in accordance with one of the embodiments of the present invention,
21 the demulsifier is selected from the group comprising oxyalkylated condensation
22 product of:

- 23 i) cardanol, nonyl phenol and amyl phenol, and formaldehyde;
- 24 ii) cardanol, nonyl phenol and butyl phenol, and formaldehyde;
- 25 iii) cardanol, nonyl phenol and formaldehyde;
- 26 iv) cardanol, amyl phenol and formaldehyde;
- 27 v) cardanol, butyl phenol and formaldehyde;
- 28 vi) cardanol, alkyl phenol and formaldehyde; and
- 29 vii) a mixture thereof.

30 In accordance with one of the preferred embodiments of the present invention,
31 the above-described condensation products is oxyalkylated with ethylene oxide,
32 propylene oxide, butylene oxide or their mixtures to result in oxyalkylated copolymers
33 or oxyalkylated polymers thereof.

1 Therefore, in accordance with one of the embodiments of the present invention,
2 the demulsifier is selected from the group comprising:

- 3 i) oxyalkylated nonyl phenol and amyl phenol formaldehyde copolymers;
- 4 ii) oxyalkylated nonyl phenol and butyl phenol formaldehyde copolymers;
- 5 iii) oxyalkylated nonyl phenol formaldehyde polymers;
- 6 iv) oxyalkylated amyl phenol formaldehyde polymers;
- 7 v) oxyalkylated butyl phenol formaldehyde polymers;
- 8 vi) oxyalkylated alkyl phenol formaldehyde polymers; and
- 9 vii) a mixture thereof.

10 Therefore, in accordance with one of the embodiments of the present invention,
11 the demulsifier may be selected from a group comprising:

- 12 i) oxyalkylated cardanol, nonyl phenol and amyl phenol, and formaldehyde
13 copolymers;
- 14 ii) oxyalkylated cardanol, nonyl phenol and butyl phenol, and
15 formaldehyde copolymers;
- 16 iii) oxyalkylated cardanol, nonyl phenol and formaldehyde polymers;
- 17 iv) oxyalkylated cardanol, amyl phenol and formaldehyde polymers;
- 18 v) oxyalkylated cardanol, butyl phenol and formaldehyde polymers;
- 19 vi) oxyalkylated cardanol, alkyl phenol and formaldehyde polymers; and
- 20 vii) a mixture thereof.

21 It may be noted that term “copolymer” means a polymer made from two
22 different phenols and the term “polymer” means a polymer made from one phenol.

23 In accordance with the present invention, the molecular weight of the
24 demulsifier of the present invention may vary from about 2000 to about 20000 daltons
25 as measured by Gel Permeation Chromatography using the tetrahydro furan (THF) as
26 solvent.

27 In accordance with the present invention, the composition comprises:

- 28 a) about 0.1 to about 99.1 % by weight of the compound selected from the
29 group comprising glyoxal, neutralized glyoxal, glyoxal derivative and a
30 mixture thereof; and
- 31 b) about 99.1 to about 0.1 % by weight of the one or more demulsifiers.

32 In accordance with one of the preferred embodiments of the present invention,
33 the composition may comprise:

1 a) about 0.1 ppm to about 1000 ppm of the compound selected from the
2 group comprising glyoxal, neutralized glyoxal, glyoxal derivative and a
3 mixture thereof; and

4 b) about 0.5 ppm to about 200 ppm of the one or more demulsifiers,
5 depending upon the nature of the crude oil.

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

9 Accordingly, in one embodiment, the present invention relates to
10 a method of demulsification of water-in-oil emulsions, particularly of water-in-
11 oil emulsions formed by mixing of wash water and crude oil, more particularly of
12 water-in-oil emulsions formed by mixing of wash water and crude oil in the desalter
13 unit of the refinery, wherein the water-in-oil emulsion formed due to mixing of wash
14 water in the crude oil is treated with

15 the present demulsification composition comprising:

16 a. a compound selected from the group comprising glyoxal, neutralized
17 glyoxal, glyoxal derivative and a mixture thereof; and

18 b. at least one demulsifier.

19 Accordingly, in one embodiment, the present invention relates to

20 a method of using the present additive composition for demulsification of water-
21 in-oil emulsions, particularly of water-in-oil emulsions formed by mixing of wash
22 water and crude oil, more particularly of water-in-oil emulsions formed by mixing of
23 wash water and crude oil in the desalter unit of the refinery, wherein the present
24 demulsification composition comprising:

25 a. a compound selected from the group comprising glyoxal, neutralized
26 glyoxal, glyoxal derivative and a mixture thereof; and

27 b. at least one demulsifier,

28 is added to the water-in-oil emulsion formed due to mixing of wash water in the
29 crude oil.

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

34 **Examples:**

- 1 The present compositions have been tested for their demulsification efficiency.
2 In the following examples,
- 3 1. the 'blank' is without any additive;
 - 4 2. compound 'A' is demulsifier, which is base catalysed nonylphenol
5 formaldehyde resin and used for comparison;
 - 6 3. the present compositions comprise
 - 7 i) compound 'A' and glyoxal; or
 - 8 ii) compound 'A' and neutralized glyoxal, wherein the glyoxal has been
9 neutralized with triethanol amine (TEA); and
 - 10 4. the comparative compositions comprise:
 - 11 a) compound 'A', and a compound selected from glycolic acid, glyoxylic
12 acid, DL-malic acid, benzaldehyde, or glutaraldehyde.

13 In the following examples, the compound 'A' (the demulsifier) is 50% active,
14 the glyoxal is 40% active, the neutralized glyoxal comprises 40% active glyoxal
15 neutralized with 100% active triethanol amine (TEA); the glycolic acid, the glyoxylic
16 acid and the DL-malic acid are 40% active.

17 In the following examples, the present additive composition and the prior art or
18 comparative additive composition was added to the water-in-oil emulsion of water and
19 crude oil formed after mixing of water and crude oil.

20 The results confirm that the addition of a compound selected from a group
21 comprising glyoxal, neutralized glyoxal, glyoxal derivative and mixture thereof in one
22 or more of the demulsifiers results in substantial increase of demulsification efficiency
23 of the demulsifier. Accordingly, the present compositions overcome problems of the
24 prior art.

25 In the following examples, the tests were carried out in portable electric desalter
26 (PED) or electrostatic separator at 130°C, with water-in-oil emulsion comprising 5% by
27 vol of wash water (pH of wash water was 6.6), and 95% by vol of crude oil from
28 Western part of India.

29 In the following examples, 100 ml of water-in-oil emulsion of above is taken.

30 The values in the following Table 1 are of % by vol of water separated in PED
31 tubes, i.e. 50% in below table means only 2.5 ml of initial 5 ml of wash water has been
32 separated.

33

1

Table-1

Additive	Dosage of Additive (ppm)	After 5 min	After 10 min	After 15 min	After 20 min
Blank	--	0	0	0	0
Compound 'A' (no additive)	10	52	60	60	64
Compound 'A' + glyoxal (as per the present invention)	10 + 0.4	80	90	90	94
Compound 'A' + glyoxal neutralized with TEA (as per the present invention)	10 + 0.4	80	90	94	94
Compound 'A' + glycolic acid (comparative composition)	10 + 0.4	56	60	60	64
Compound 'A' + glyoxylic acid (comparative composition)	10 + 0.4	56	60	60	60
Compound 'A' + DL-malic acid (comparative composition)	10 + 0.4	60	70	70	74
Compound 'A' + benzaldehyde (comparative composition)	10 + 0.4	52	60	60	60
Compound 'A' + glutaraldehyde (comparative composition)	10 + 0.4	52	60	60	60

2

3 In above **Table – 1**, the expression “10 + 0.4” means that the composition
4 comprises:

- 5 a) 10 ppm of Compound 'A' (the demulsifier); and
6 b) 0.4 ppm of the second component, which is either the glyoxal or the
7 neutralized glyoxal (as per the present invention); or the glycolic acid, the glyoxylic
8 acid; the DL-malic acid; the benzaldehyde; or the glutaraldehyde (for the purpose of
9 comparison).

10 The above Table-1 confirms that the additives of the present invention, for
11 example, glyoxal and the glyoxal neutralized with TEA till pH of glyoxal becomes
12 neutral to basic. i.e. > or = to pH 7 have surprising and unexpected effects in improving
13 the demulsification efficiency of the demulsifier to demulsify the water-in-oil emulsion
14 formed by mixing of wash water in the crude oil.

1 Therefore, above experimental findings confirm synergistic, surprising and
2 unexpected effects, and technical advantages of the present compositions in
3 demulsifying the water-in-oil emulsion formed by mixing of wash water in the crude
4 oil.

5 Furthermore, above experimental findings also confirm that the present
6 compositions have better demulsification efficiency to demulsify the water-in-oil
7 emulsion formed by mixing of wash water in the crude oil.

8 Furthermore, as amount of demulsifier has been substantially reduced to
9 achieve desired demulsification efficiency, the present compositions are more
10 economical and environmental friendly.

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

14

Claims

1. A demulsification composition for demulsification of water-in-oil emulsion caused due to wash water in crude oil, wherein the composition comprises:
 - 5 a. a compound comprising glyoxal, neutralized glyoxal, glyoxal derivative or a mixture thereof; and
 - b. at least one demulsifier,wherein the glyoxal derivative comprises methanol, ethanol, butanol, ethylene glycol derivatives of glyoxal, or a mixture thereof;
- 10 wherein the one or more demulsifier comprises condensation product of formaldehyde with a compound comprising:
 - i) nonyl phenol, amyl phenol, butyl phenol, alkyl phenol, or cardanol;
 - ii) oxyalkylated condensation product of nonyl phenol, amyl phenol, butyl phenol, alkyl phenol, or cardanol;
 - 15 iii) oxyalkylated condensation product of nonyl phenol, amyl phenol, butyl phenol, alkyl phenol, or cardanol obtained by oxyalkylation with ethylene oxide, propylene oxide, butylene oxide or mixtures thereof;
 - iv) oxyalkylated copolymer or oxyalkylated polymer of the condensation product; or
 - 20 v) a mixture thereof.
2. The demulsification composition as claimed in **claim 1**, wherein the neutralized glyoxal is glyoxal having pH neutral to basic.
3. The demulsification composition as claimed in **claim 2**, wherein the pH neutral to basic comprises a pH varying from about 7 to about 12.
- 25 4. The demulsification composition as claimed in any one of the preceding **claims 1 to 3**, wherein the neutralized glyoxal is obtained by neutralizing the glyoxal with an amine or alkaline medium.
5. The demulsification composition as claimed in **claim 4**, wherein the amine comprises triethanol amine (TEA).
- 30 6. The demulsification composition as claimed in **claim 4**, wherein the alkaline medium comprises sodium hydroxide aqueous solution.

7. The demulsification composition as claimed in any one of the preceding **claims 1 to 6**, wherein the neutralized glyoxal comprises neutralized derivative of glyoxal.
8. The demulsification composition as claimed in any one of the preceding **claims 1 to 7**, wherein the one or more demulsifier comprises a condensation product of:
- 5 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;
- 10 vi) alkyl phenol and formaldehyde; or
vii) a mixture thereof.
9. The demulsification composition as claimed in any one of the preceding **claims 1 to 8**, wherein the one or more demulsifier comprises a condensation product of:
- 15 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
- 20 vii) a mixture thereof.
10. The demulsification composition as claimed in **claim 1**, wherein the oxyalkylated condensation product comprises:
- 25 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
- 30 vii) a mixture thereof.
11. The demulsification composition as claimed in **claim 1**, wherein the oxyalkylated condensation product comprises:

- 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;
 - 5 v) cardanol, butyl phenol and formaldehyde;
 - vi) cardanol, alkyl phenol and formaldehyde; or
 - vii) a mixture thereof.
12. The demulsification composition as claimed in **claim 1**, wherein the one or more demulsifier comprises:
- 10 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;
 - 15 vi) oxyalkylated alkyl phenol formaldehyde polymers; or
 - vii) a mixture thereof.
13. The demulsification composition as claimed in **claim 1**, wherein the one or more demulsifier comprises:
- 20 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;
 - 25 v) oxyalkylated cardanol, butyl phenol and formaldehyde polymers;
 - vi) oxyalkylated cardanol, alkyl phenol and formaldehyde polymers; or
 - vii) a mixture thereof.
14. The demulsification composition as claimed in any one of the preceding **claims 1 to 13**, wherein the composition comprises:
- 30 a) about 0.1 to about 99.1 % by weight of the compound comprising glyoxal, neutralized glyoxal, glyoxal derivative or a mixture thereof; and

- b) about 99.1 to about 0.1 % by weight of the one or more demulsifiers.
15. A method of demulsification of water-in-oil emulsions, wherein the water-in-oil emulsion is treated with the demulsification composition as claimed in any one of the preceding **claims 1 to 14**.
- 5 16. A method of using the demulsification composition as claimed in any one of the preceding **claims 1 to 14** for demulsification of water-in-oil emulsion, wherein the demulsification composition is added to the water-in-oil emulsion formed due to mixing of wash water in the crude oil.