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(54) **Titre : ADDITIFS UTILES POUR STABILISER L'HUILE BRUTE**
(54) **Title: ADDITIVE USEFUL FOR STABILIZING CRUDE OIL**

(57) **Abrégé/Abstract:**

Crude oils, especially heavy crude oils that are subject to instability on storage or during transportation can be treated with additives in order to stabilize the crude oil in regard to precipitating contaminants such as asphaltenes. Alkylphenol resins with at least a second component selected from the group consisting of a fatty acid amides, mannich resins and mixtures thereof are effective additives for stabilizing crude oils.



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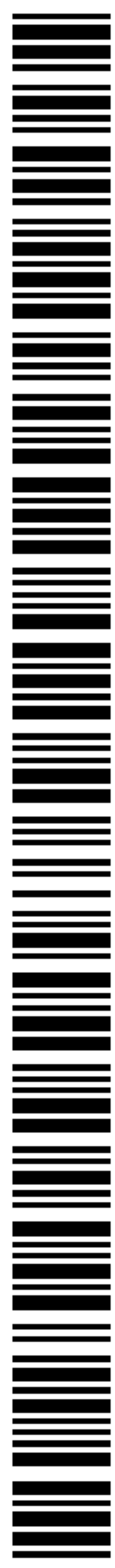
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(54) **Title**: ADDITIVE USEFUL FOR STABILIZING CRUDE OIL

(57) **Abstract**: Crude oils, especially heavy crude oils that are subject to instability on storage or during transportation can be treated with additives in order to stabilize the crude oil in regard to precipitating contaminants such as asphaltenes. Alkylphenol resins with at least a second component selected from the group consisting of a fatty acid amides, mannich resins and mixtures thereof are effective additives for stabilizing crude oils.



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ADDITIVE USEFUL FOR STABILIZING CRUDE OIL

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BACKGROUND OF THE INVENTION

1. Field of the Invention

[0002] The present invention relates to crude oil additives. The present invention particularly relates to crude oil additives useful for stabilizing crude oils.

2. Background of the Art

[0003] Many formation fluids such as petroleum fluids contain a large number of components with a very complex composition. Some of the components present in production fluid, for example wax and asphaltenes, can form or contain solids under ambient conditions, particularly at ambient temperatures and pressures. Asphaltenes are typically dark brown to black-colored amorphous solids with complex structures and relatively high molecular weight. In addition to carbon and hydrogen, asphaltenes also can contain nitrogen, oxygen and sulfur species. Typical asphaltenes are known to have some solubility in the production fluid itself or in certain solvents like carbon disulfide, but are usually insoluble in solvents like light naphthas. Asphaltenes exist as colloidal solids in the oil dispersed by other components in the oil, keeping them suspended and dispersed in the oil.

[0004] When the formation fluid from a subsurface formation comes into contact with a pipe, a valve or other production equipment of a wellbore or when there is a change in temperature, pressure, or change of other conditions, asphaltenes may precipitate or separate out of a well stream or the formation fluid while flowing into and through the wellbore to the wellhead. While any asphaltene

separation or precipitation is undesirable in and by itself, it is much worse to allow the asphaltene precipitants to accumulate by sticking to the equipment in the wellbore. Any asphaltene precipitants sticking to the wellbore surfaces may narrow pipes; and clog wellbore perforations, various flow valves, and other
5 wellsite and downhole equipment.

[0005] For purposes of the present invention, the term "crude oil" means the petroleum fluids produced from an oil well. Typically, the crude oil produced from an oil well is treated to remove excess water and inorganic solids such as salt and then collected and stored for shipment to a refinery. Often, the crude oil from
10 several fields can be accumulated at a central point for shipping through a pipeline or transported by vessel.

[0006] Precipitations and accumulations of asphaltenes in a pipeline for transferring crude oil could result in loss of oil flow and/or equipment failure. Crude oil storage facilities could have maintenance or capacity problems if
15 asphaltene precipitations occur during shipping of crude oil. Precipitation of asphaltene during shipping is clearly just as undesirable as during production. Unstable asphaltenes will have negative impact on refinery operations when oil is received by the refinery resulting in lost production and decreased economic output.

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Summary of the Invention

[0007] In one aspect, the invention is an additive useful for stabilizing crude oils comprising at least a first component which is an alkylphenol resin and further comprising a second component selected from the group consisting of a fatty
25 acid amide, a mannich resin and mixtures thereof.

[0008] In still another aspect, the invention is a method for stabilizing crude oils comprising admixing a crude oil with an additive useful for stabilizing crude oils comprising at least a first component which is an alkylphenol resin and further comprising a second component selected from the group consisting of a fatty
30 acid amide, a mannich resin and mixtures thereof.

[0008a] In accordance with an aspect of the present invention there is provided an additive for stabilizing crude oils comprising a first component which is an alkylphenol resin and a second component selected from the group consisting of a fatty acid amide, a mannich resin and mixtures thereof.

[0008b] In accordance with a further aspect of the present invention there is provided a method for stabilizing crude oils comprising admixing a crude oil with an additive for stabilizing crude oils comprising a first component which is an alkylphenol resin and a second component selected from the group consisting of a fatty acid amide, a mannich resin and mixtures thereof.

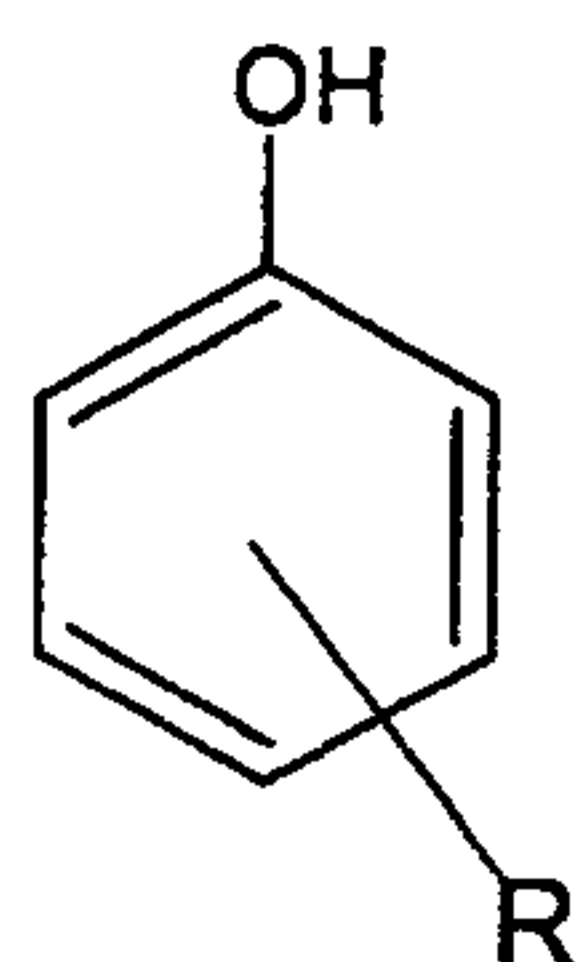
[0008c] In accordance with a further aspect of the present invention there is provided a composition comprising an admixture of the additive as previously described and crude oil.

[0008d] In accordance with a further aspect of the present invention there is provided use of the composition as previously described for stabilizing crude oil.

[0008e] In accordance with a further aspect of the present invention there is provided use of an additive for stabilizing crude oils, wherein the additive comprises a first component which is an alkylphenol resin and a second component selected from the group consisting of a fatty acid amide, a mannich resin and mixtures thereof.

Description of the Preferred Embodiments

[0009] In one embodiment, the present invention is an additive useful for stabilizing crude oils comprising at least a first component which is an alkylphenol resin. The alkyl phenol resins useful as the first component of the additives of the invention include those prepared by reacting an alkyl phenol with an aldehyde. The alkyl phenol may be nonyl phenol but other alkyl phenols may be used. Exemplary alkyl phenols useful for preparing the alkyl phenol resin of the invention include those having the general formula:



10

wherein R is an alkyl group having from 4 to 18 carbons.

[0010] The alkyl phenol resin may be prepared by reacting the alkyl phenol with an aldehyde. Aldehydes useful for preparing the alkyl phenol resins include formaldehyde, but higher aldehydes may also be used. Higher aldehydes which may be used to prepare the alkyl phenol resins include those aldehydes having from 2 to about 5 carbons.

[0011] The alkyl phenol resins may have a molecular weight (M_w) of from about two thousand to about twenty five thousand Daltons. In one embodiment, the alkyl phenol resin has a molecular weight of from about four to about twenty thousand Daltons. In still another embodiment, the alkyl phenol resin has a molecular weight of from about five to about ten thousand Daltons. While the structure of the alkyl phenol resins useful with the invention has been described as the reaction product certain starting materials, the alkyl phenol resins may be prepared by any means known to those skilled in art to be useful for preparing such resins.

[0012] In another embodiment, the additives of the invention may also include second component selected from the group consisting of fatty acid amides,

mannich resins and mixtures thereof. The fatty acid amides useful with the invention include those prepared using a fatty acid having from 8 to about 26 carbons. The amides may be prepared using a hydroxyl alkyl amine such as 2-(2-amino ethylamine)ethanol, diethanolamine, or aminoethyl ethanolamine or
5 other hydroxyl alkyl amine having from about 4 to about 8 carbons. While the structure of the fatty acid amides useful with the invention has been described as the reaction product certain starting materials, the fatty acid amides may be prepared by any means known to those skilled in art to be useful for preparing such resins.

10 **[0013]** Mannich resins useful with the invention include those which may be prepared using an alkyl phenol, an aldehyde and a polyamine. The alkyl phenols useful in preparing the Mannich resins include those already described above, namely those phenols also having an alkyl group on the aromatic ring having from about 4 to about 8 carbons. For example dodecyl phenol may be
15 used to prepare the Mannich resins useful with the invention.

[0014] Similarly the Mannich resins useful with the invention include those made with formaldehyde but may also include those prepared with higher aldehydes. Higher aldehydes which may be used to prepare the Mannich resins include those aldehydes having from 2 to about 5 carbons.

20 **[0015]** The polyamines useful for preparing the mannich resins include ethylene diamine, but other amines may also be used. Any amine having at least two amino groups and from 2 to 22 carbons may be used to prepare the Mannich resins.

[0016] The Mannich resins may have a molecular weight M_w of from about two
25 thousand to about twenty five thousand Daltons. In one embodiment, the Mannich resin has a molecular weight of from about four to about twenty thousand Daltons. In still another embodiment, the Mannich resin has a molecular weight of from about five to about ten thousand Daltons. While the structure of the Mannich resins useful with the invention has been described as
30 the reaction product certain starting materials, the Mannich resins may be prepared by any means known to those skilled in art to be useful for preparing such resins.

[0017] The invention is, in one embodiment, a method stabilizing crude oils comprising admixing a crude oil with an additive useful for stabilizing crude oils. The additives are admixed with the crude oils using any method known by those of ordinary skill in the art to be useful. For example, in one embodiment, the additives are admixed with the crude oils when the crude oils are being prepared by admixing oils of varying viscosity to achieve a target viscosity. In another embodiment, the additives are admixed when the crude oils being subjected to treatment using the additives are being metered into a truck, ship or other vessel.

[0018] The actual means of admixing a crude oil with an additive of the invention may include any apparatus useful for same. Exemplary apparatus include static mixers, blade mixers, stirred vessels, vessels having recycle lines incorporating static or blade mixers, and the like. Any apparatus for mixing known to be useful to those of ordinary skill in the art may be used with the method of the invention.

Passive admixing may be accomplished where the additives are introduced into a vessel or transfer line or pipeline and admixing is effected by means of turbulence.

[0019] The additives of the present invention may be admixed with crude oil from any source and at any point during production, transportation, and refining of crude oil. Exemplary of locations where the additives of the invention may be added include but are not limited to: 1) downhole, 2) phase separators, 3) collection points for pipelines, pipelines, storage vessels, transfer lines, heat exchangers, thermal cracking units, and the like.

[0020] The concentration of the additives needed to stabilize a given crude oil will vary depending upon the properties of the subject crude oil. For example, a crude oil that is comparatively low in destabilizing contaminants such as asphaltenes will require less additive than a crude oil that has a comparatively high amount of asphaltenes. Still, in at least one embodiment, the method of the invention may be practiced by admixing sufficient additive to achieve a concentration of from 5 to about 3000 ppm (by weight) of additive in the crude oil being treated. In other embodiments, the concentration is from about 10 to 2000

ppm. In still other embodiments, the concentration is from about 50 to about 1000 ppm.

[0021] The additives of the invention may be used with any crude oil. The crude oils which are most likely to need the additives of the invention are those
5 characterized as heavy crude oils.

EXAMPLES

[0022] The following examples are provided to illustrate the invention. The examples are not intended to limit the scope of the invention and they should not
10 be so interpreted. Amounts are in weight parts or weight percentages unless otherwise indicated.

Hypothetical Example 1

[0023] An additive is prepared using the components shown in the Table. The
15 alkyl phenol resin is an alkyl phenol resin prepared using nonyl phenol and formaldehyde and has a molecular weight (M_w) of 2000 to 5000 g/mole done using a GPC and polystyrene standard. The Mannich resin is prepared using dodecyl phenol, formaldehyde and ethylene diamine. It has a molecular weight similar to that of the alkyl phenol resin. The fatty acid amide is prepared using a
20 C18 fatty acid and aminoethyl ethanol amine. The additive is admixed with a crude oil and subjected to a storage study. The symbol + means a small amount of precipitation. The symbol ++ means a medium amount of precipitation. And the symbol +++ means a comparatively large amount of precipitation.

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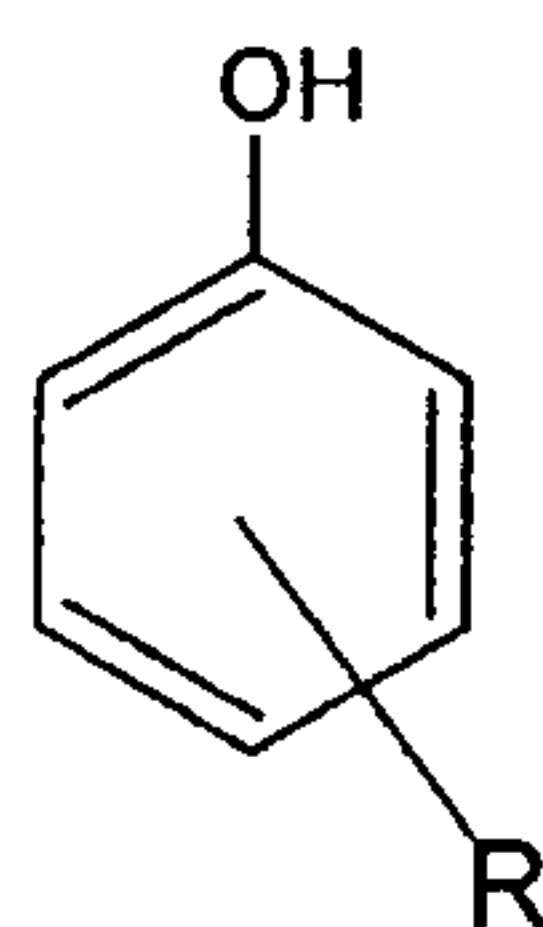
Table

Sample #	Precipitation	Alkylphenol Resin [%]	Mannich Resin [%]	Fatty Acid Amide [%]
1-1*	+++	0	0	0
1-2*	++	100	0	0
1-3	+	60	40	0
1-4	+	60	0	40
1-5	+	60	20	20
1-6*	++	0	100	0
1-7*	++	0	0	100

* Not an example of the invention

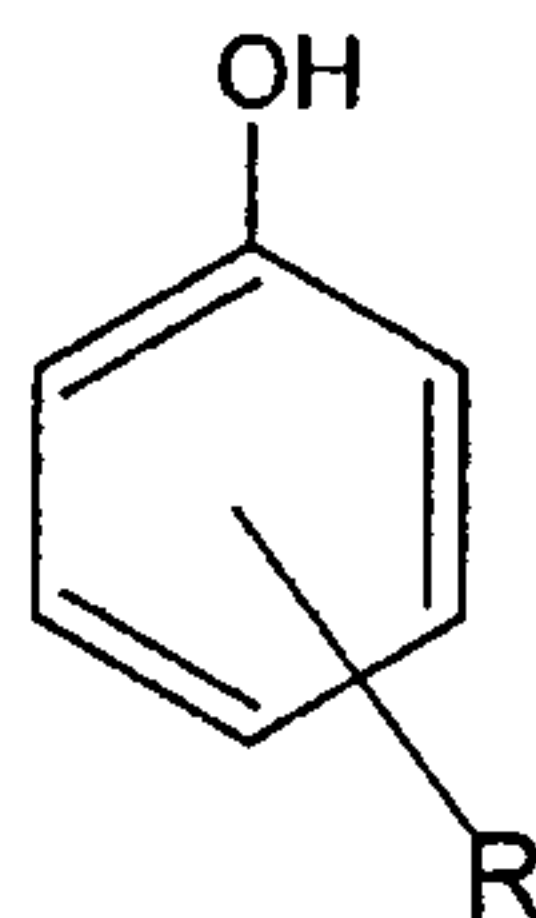
The embodiments of the present invention in which an exclusive property or privilege is claimed are defined as follows:

1. An additive for stabilizing crude oils comprising a first component which is an alkylphenol resin and a second component selected from the group consisting of a fatty acid amide, a mannich resin and mixtures thereof.
2. The additive of claim 1, wherein the alkylphenol resin is prepared using an alkylphenol having a general formula:



wherein R is an alkyl group having from 4 to 18 carbons.

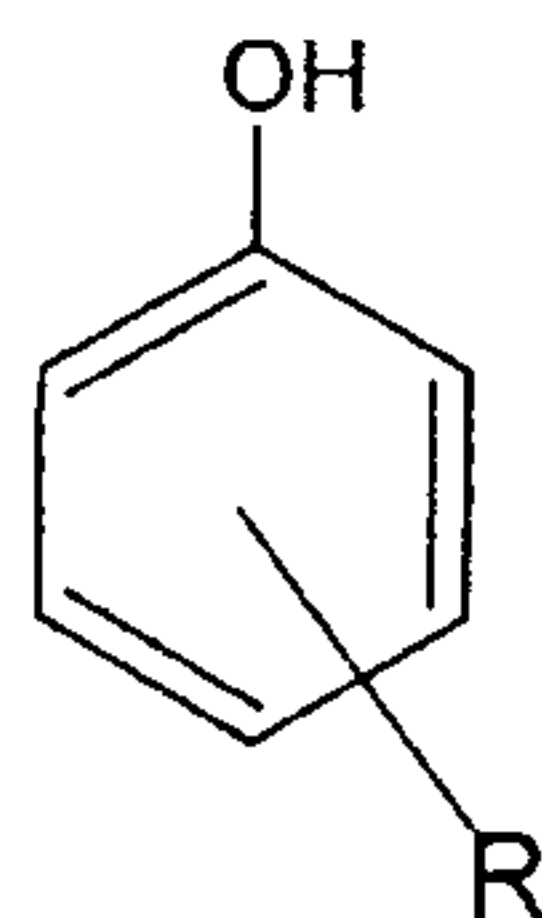
3. The additive of claim 2, wherein the alkylphenol is reacted with formaldehyde to form the alkylphenol resin.
4. The additive of any one of claims 1 to 3, wherein the alkylphenol resin has a molecular weight (M_w) of from about 2,000 to about 20,000 Daltons.
5. The additive of any one of claims 1 to 4, wherein the second component is a fatty acid amide having from 8 to 26 carbons.
6. The additive of any one of claims 1 to 5, wherein the fatty acid amide is prepared using a compound selected from the group consisting of 2-(2-amino ethylamine)ethanol, diethanolamine, aminoethyl ethanolamine and mixtures thereof.
7. The additive of any one of claims 1 to 4, wherein the second component is a mannich resin prepared from a formulation including an alkylphenol, an aldehyde and a polyamine.
8. The additive of claim 7, wherein the alkylphenol has a general formula:



wherein R is an alkyl group having from 4 to 18 carbons.

9. The additive of claim 7 or 8, wherein the alkylphenol is dodecyl phenol.
10. The additive of any one of claims 7 to 9, wherein the aldehyde is formaldehyde.
11. The additive of any one of claims 7 to 10, wherein the polyamine has from 2 to 22 carbons.
12. The additive of any one of claims 7 to 11, wherein the polyamine is ethylene diamine.
13. The additive of any one of claims 1 to 4 or 7 to 12, wherein the second component is a mannich resin having a molecular weight (M_w) of from about 2,000 to about 25,000 Daltons.
14. The additive of any one of claims 1 to 4 or 7 to 13, wherein the second component is a mannich resin having a molecular weight (M_w) of from about 4,000 to about 20,000 Daltons.
15. The additive of any one of claims 1 to 4 or 7 to 14, wherein the second component is a mannich resin having a molecular weight (M_w) of from about 5,000 to about 10,000 Daltons.
16. A method for stabilizing crude oils comprising admixing a crude oil with an additive for stabilizing crude oils comprising a first component which is an alkylphenol resin and a second component selected from the group consisting of a fatty acid amide, a mannich resin and mixtures thereof.

17. The method of claim 16, wherein the additive is admixed with the crude oil at a concentration of from about 5 to about 3,000 ppm.
18. The method of claim 16 or 17, wherein the additive is admixed with the crude oil at a concentration of from about 50 to about 1,000 ppm.
19. The method of any one of claims 16 to 18, wherein the additive is introduced into a vessel, transfer line, or pipeline containing crude oil.
20. A composition comprising an admixture of the additive of any one of claims 1 to 19 and crude oil.
21. Use of an additive for stabilizing crude oils, wherein the additive comprises a first component which is an alkylphenol resin and a second component selected from the group consisting of a fatty acid amide, a mannich resin and mixtures thereof.
22. The use of claim 21, wherein the alkyl phenol resin is prepared using an alkylphenol having a general formula:



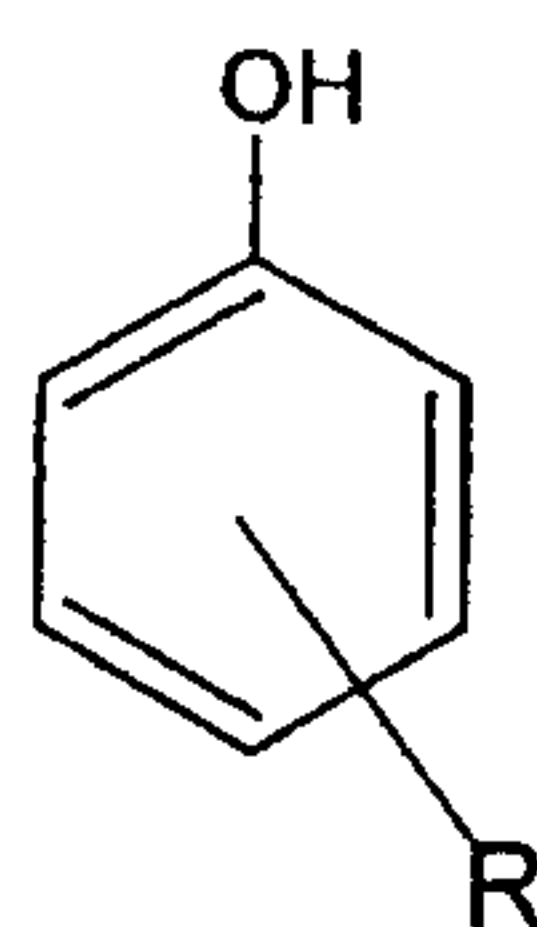
wherein R is an alkyl group having from 4 to 18 carbons.

23. The use of claim 22, wherein the alkylphenol is reacted with formaldehyde to form the alkylphenol resin.
24. The use of any one of claims 21 to 23, wherein the alkylphenol resin has a molecular weight (M_w) of from about 2,000 to about 20,000 Daltons.
25. The use of any one of claims 21 to 24, wherein the second component is a fatty acid amide having from 8 to 26 carbons.

26. The use of any one of claims 21 to 25, wherein the fatty acid amide is prepared using a compound selected from the group consisting of 2-(2-amino ethylamine)ethanol, diethanolamine, aminoethyl ethanolamine and mixtures thereof.

27. The use of any one of claims 21 to 24, wherein the second component is a mannich resin prepared from a formulation including an alkylphenol, an aldehyde and a polyamine.

28. The use of Claim 27 wherein the alkylphenol has a general formula:



wherein R is an alkyl group having from 4 to 18 carbons.

29. The use of Claim 27 or 28, wherein the alkylphenol is dodecyl phenol.

30. The use of any one of claims 27 to 29, wherein the aldehyde is formaldehyde.

31. The use of any one of claims 27 to 30, wherein the polyamine has from 2 to 22 carbons.

32. The use of any one of claims 27 to 31, wherein the polyamine is ethylene diamine.

33. The use of any one of claims 21 to 24 or 27 to 32, wherein the second component is a mannich resin having a molecular weight (M_w) of from about 2,000 to about 25,000 Daltons.

34. The use of any one of claims 21 to 24 or 27 to 33, wherein the second component is a mannich resin having a molecular weight (M_w) of from about 4,000 to about 20,000 Daltons.

35. The use of any one of claims 21 to 24 or 27 to 34, wherein the second component is a mannich resin having a molecular weight (M_w) of from about 5,000 to about 10,000 Daltons.
36. The use of any one of claims 21 to 35, wherein the additive is admixed with the crude oil at a concentration of from about 5 to about 3,000 ppm.
37. The use of any one of claims 21 to 36, wherein the additive is admixed with the crude oil at a concentration of from about 50 to about 1,000 ppm.
38. The use of any one of claims 21 to 37, wherein the additive is introduced into a vessel, transfer line, or pipeline containing crude oil.
39. Use of the composition of claim 19 for stabilizing crude oil.