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(54) **BLENDS OF ESTERS WITH ISOMERIZED  
OLEFINS AND OTHER HYDROCARBONS AS  
BASE OILS FOR INVERT EMULSION OIL  
MUDS**

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(57) **ABSTRACT**

Environmentally acceptable or regulatory compliant oil-based drilling fluids and methods of using same in drilling a wellbore in a subterranean formation are disclosed. The fluids are able to meet environmental regulations while maintaining acceptable oil mud rheology and overall oil mud performance. The fluids are comprised of an invert emulsion. The base or continuous phase of the emulsion is comprised of esters blended with isomerized olefins, and/or other hydrocarbons, such as paraffins, mineral oils or glyceride triesters or combinations thereof. Alternatively, the emulsion has as a base comprising isomerized olefins blended with other hydrocarbons such as linear alpha olefins, paraffins or naphthenes.

# BLEND OF ESTERS WITH ISOMERIZED OLEFINS AND OTHER HYDROCARBONS AS BASE OILS FOR INVERT EMULSION OIL MUDS

## BACKGROUND OF THE INVENTION

### [0001] 1. Field of the Invention

[0002] The present invention relates to compositions and methods for drilling boreholes in subterranean formations, particularly hydrocarbon bearing formations. More particularly, the present invention relates to oil or synthetic based drilling fluids, fluids comprising invert emulsions, and more particularly to drilling fluids utilizing esters which combine high ecological compatibility with good stability and performance properties.

### [0003] 2. Description of Relevant Art

[0004] A drilling fluid or mud is a specially designed fluid that is circulated through a wellbore as the wellbore is being drilled to facilitate the drilling operation. The various functions of a drilling fluid include removing drill cuttings from the wellbore, cooling and lubricating the drill bit, aiding in support of the drill pipe and drill bit, and providing a hydrostatic head to maintain the integrity of the wellbore walls and prevent well blowouts. Specific drilling fluid systems are selected to optimize a drilling operation in accordance with the characteristics of a particular geological formation.

[0005] Oil or synthetic-based muds are normally used to drill swelling or sloughing shales, salt, gypsum, anhydrite or other evaporite formations, hydrogen sulfide-containing formations, and hot (greater than about 300 degrees Fahrenheit) holes, but may be used in other holes penetrating a subterranean formation as well. Unless indicated otherwise, the terms "oil mud" or "oil-based mud or drilling fluid" shall be understood to include synthetic as well as natural or traditional oils, and such oils shall be understood to comprise invert emulsions.

[0006] Oil-based muds used in drilling typically comprise: a base oil (or synthetic) comprising the external phase of an invert emulsion; a saline, aqueous solution (typically a solution comprising about 30% calcium chloride and emulsifiers) comprising the internal phase of the invert emulsion; and other agents or additives for suspension, weight or density, oil-wetting, fluid loss or filtration control, and rheology control. An oil-based drilling fluid may commonly comprise between about 50:50 to about 95:5 by volume oil phase to water phase. An all oil mud simply comprises 100% oil by volume; that is, there is no aqueous internal phase.

[0007] Oil-based muds or drilling fluids comprise a key segment of the drilling fluids industry. However, increasingly oil-based drilling fluids have been subjected to greater environmental restrictions and performance and cost demands. There is consequently an increasing need and industry-wide interest in new low-cost drilling fluids that provide robust rheology at high and low temperatures simultaneously while still affording environmental acceptance.

## SUMMARY OF THE INVENTION

[0008] A drilling fluid comprising an invert emulsion is provided in the present invention that provides significant benefits in terms of environmental acceptance or regulatory

compliance without compromising or reducing oil mud rheology or overall oil mud performance significantly. The invert emulsion of the invention has a base, or continuous phase, comprising esters blended with isomerized, or internal, olefins and/or other hydrocarbons, such as paraffins, mineral oils, glyceride triesters, or combinations thereof (hereinafter "the ester blends"). Alternatively, the invert emulsion has a base comprising isomerized olefins blended with other hydrocarbons such as linear alpha olefins, paraffins, or naphthenes, or combinations thereof (hereinafter "the hydrocarbon blends"). In still another embodiment, these two alternative base fluids may themselves be blended together to comprise the base of an invert emulsion.

[0009] In the ester blends, the ester may be any quantity, but preferably should comprise at least about 10 weight percent to about 99 weight percent of the blend and the olefins or other hydrocarbons should preferably comprise about 1 weight percent to about 99 weight percent of the blend. In the hydrocarbon blends, the isomerized olefins should preferably comprise about 1 weight percent to about 99 weight percent of the blend and the other hydrocarbons should preferably comprise about 1 weight percent to about 99 weight percent of the blend. In the alternative embodiment where the ester blends are blended further with the hydrocarbon blends, the esters may be any quantity, but preferably should comprise at least about 10 weight percent (and less than about 99 weight percent) of the final blend. The esters of the blends of the invention are preferably comprised of fatty acids and alcohols and most preferably about C<sub>6</sub> to about C<sub>14</sub> fatty acids and 2-ethyl hexanol. However, esters made other ways than with fatty acids and alcohols, such as for example, esters made from olefins combined with either fatty acids or alcohols, are also believed effective for use in the blends of the invention.

[0010] A method for preparing and using an environmentally acceptable drilling fluid is also provided by the invention. In the method, a drilling fluid is obtained or prepared comprising as its base or continuous phase the blends of the invention. The fluid is then used in drilling boreholes or wellbores in subterranean formations.

## DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

[0011] The present invention provides blends that comprise the oil base or continuous phase of an invert emulsion for oil-based drilling fluids or muds that are environmentally acceptable and still effective as drilling fluids. The environmental acceptability or compatibility and retained effectiveness of the fluids for use as a drilling fluid are accomplished through the blending or mixing of the fluids.

[0012] In preparing the blends of the invention, preferably the blending or mixing is done, i.e., the blends are made, before the emulsion is formed or before other materials or compounds are added to the fluid.

[0013] The blends of the invention most preferably comprise esters, and also preferably comprise isomerized, or internal, olefins. However, blends of the invention may also or alternatively comprise esters with other hydrocarbons. Alternatively, blends of the invention may comprise isomerized olefins and other hydrocarbons.

[0014] In blends of the invention with esters, the esters may be used in any quantity. Preferably, however, the esters

should comprise at least about 10 weight percent of the blend and may comprise up to about 99 weight percent of the blend. Preferred esters for blending are comprised of about C<sub>6</sub> to about C<sub>4</sub> fatty acids and alcohols, and are particularly or more preferably disclosed in U.S. Pat. No. Re. 36,066, reissued Jan. 25, 1999 as a reissue of U.S. Pat. No. 5,232, 910, assigned to Henkel KGaA of Dusseldorf, Germany, and Baroid Limited of London, England, and in U.S. Pat. No. 5,252,554, issued Oct. 12, 1993, and assigned to Henkel Kommanditgesellschaft auf Aktien of Dusseldorf, Germany and Baroid Limited of Aberdeen, Scotland. Esters disclosed in U.S. Pat. No. 5,106,516, issued Apr. 21, 1992, and U.S. Pat. No. 5,318,954, issued Jun. 7, 1984, both assigned to Henkel Kommanditgesellschaft auf Aktien, of Dusseldorf, Germany, may also preferably be used in the blends of the invention. The most preferred esters for use in the blends of the invention are comprised of about C<sub>12</sub> to about C<sub>14</sub> fatty acids and 2-ethyl hexanol or about C<sub>8</sub> fatty acids and 2-ethyl hexanol. These most preferred esters are available commercially as PETROFREE® and PETROFREE LV™, respectively, from Halliburton Energy Services, Inc. in Houston, Tex.

**[0015]** Isomerized, or internal, olefins for the blends of the invention may be any such olefins, straight chain, branched, or cyclic, preferably having about 10 to about 30 carbon atoms. Isomerized, or internal, olefins having about 40 to about 70 weight percent C<sub>16</sub> and about 20 to about 50 weight percent C<sub>18</sub> are especially preferred for blends of the invention. An example of an isomerized olefin for blends of the invention that is commercially available is SF™ Base, available from Halliburton Energy Services, Inc. in Houston, Tex.

**[0016]** As previously noted for the blends of the invention, esters may be blended with other hydrocarbons, in addition to or instead of with isomerized olefins. Particularly, for example, esters may be blended with paraffins, mineral oil hydrocarbons, and/or glyceride triesters, where such other hydrocarbons comprise from about 1 weight percent to about 99 weight percent of the blend.

**[0017]** Paraffins for the blends of the invention may be linear, branched, poly-branched, cyclic, or isoparaffins, preferably having about 10 to about 30 carbon atoms. When blended with esters of the invention, the paraffins should comprise at least about 1 weight percent to about 99 weight percent of the blend, but preferably less than about 50 weight percent. When blended with other hydrocarbons of the invention, particularly isomerized olefins, linear alpha olefins, or naphthenes as will be discussed further below, the paraffins should comprise at least about 1 weight percent up to about 99 weight percent of the blend, but preferably less than about 50 weight percent of the blend. An example of a paraffin suited for blends of the invention that is commercially available is XP-07™, available from Halliburton Energy Services, Inc. in Houston, Tex. XP-07™ is primarily a C<sub>12-16</sub> linear paraffin.

**[0018]** Examples of glyceride triesters for the ester/hydrocarbon blends of the invention include without limitation materials such as rapeseed oil, olive oil, canola oil, castor oil, coconut oil, corn oil, cottonseed oil, lard oil, linseed oil, neatsfoot oil, palm oil, peanut oil, perilla oil, rice bran oil, safflower oil, sardine oil, sesame oil, soybean oil, and sunflower oil.

**[0019]** Further, the blends of the invention may be prepared from esters of the invention mixed with various combinations of the olefin hydrocarbons, paraffin hydrocarbons, mineral oil hydrocarbons and glyceride triesters, and even with the hydrocarbon blends of the invention (as the term "hydrocarbon blends" has previously been defined herein). In such combination blends, the olefin or other hydrocarbon combinations should preferably comprise about 1 to about 99 weight percent of the blend and the esters of the invention should preferably comprise about 10 to about 99 weight percent of the blend, although any quantity of the esters may be used.

**[0020]** The hydrocarbon blends of the invention comprise isomerized olefins blended with other hydrocarbons such as paraffin hydrocarbons. That is, about 1 weight percent to about 99 weight percent isomerized olefins may be blended with about 1 weight percent to about 99 weight percent linear alpha olefins, naphthenes, paraffins, or other similar hydrocarbons, or combinations thereof.

**[0021]** The paraffin hydrocarbons may be linear, branched, poly-branched, cyclic, or isoparaffins preferably having about 10 to about 30 carbon atoms. The linear alpha olefins and the isomerized olefins preferably have about 10 to about 30 carbon atoms. The isomerized olefins may be internal olefins (either straight chain or branched), cyclic olefins, or olefins with any other structure (preferably other than linear alpha). The naphthenes or naphthenic hydrocarbons may be any saturated, cycloparaffinic compound, composition or material with a chemical formula of C<sub>n</sub>H<sub>2n</sub> where n is a number about 5 to about 30.

**[0022]** These hydrocarbon blends may be further blended with the ester blends of the invention. In such blends, the esters may be any quantity but the esters preferably comprise at least about 10 weight percent and less than about 99 weight percent of the ultimate blend.

**[0023]** The exact proportions of the components comprising the blends of the invention will vary depending on drilling requirements (and characteristics needed for the blends to meet those requirements), supply and availability of the components, cost of the components, and characteristics of the blend necessary to meet environmental regulations or environmental acceptance. The manufacture of the various components of the blends of the invention will be understood by one skilled in the art.

**[0024]** According to the method of the invention, blends of the invention are obtained or prepared and used to comprise the oil (or synthetic) base of an invert emulsion or oil-based drilling fluid. The fluid is used for drilling a borehole or wellbore in a subterranean formation, particularly a formation comprising oil, gas or other hydrocarbons.

**[0025]** The foregoing description of the invention is intended to be a description of preferred embodiments. Various changes in the details of the described blends and method of use can be made without departing from the intended scope of this invention as defined by the appended claims.

We claim:

1. A drilling fluid comprising an invert emulsion wherein said invert emulsion has a base or continuous phase comprising a blend of esters and isomerized olefins.

2. The drilling fluid of claim 1 wherein said isomerized olefins have a straight chain structure.

3. The drilling fluid of claim 1 wherein said isomerized olefins have a branched structure.

4. The drilling fluid of claim 1 wherein said isomerized olefins have a cyclic structure.

5. The drilling fluid of claim 1 wherein said isomerized olefins have about 10 to about 30 carbon atoms.

6. The drilling fluid of claim 1 wherein said isomerized olefins comprise about 1 to about 99 weight percent of said blend.

7. The drilling fluid of claim 1 wherein said esters comprise about 5 to about 99 weight percent of said blend.

8. The drilling fluid of claim 1 wherein said esters are prepared from fatty acids and alcohols.

9. The drilling fluid of claim 1 wherein said esters are prepared from fatty acids having about 6 to about 14 carbon atoms and an alcohol.

10. The drilling fluid of claim 1 wherein said esters are prepared from fatty acids having about 12 to about 14 carbon atoms and 2-ethyl hexanol.

11. The drilling fluid of claim 1 wherein said esters are prepared from fatty acids having about 8 carbon atoms and 2-ethyl hexanol.

12. The drilling fluid of claim 1 wherein said esters are prepared from olefins.

13. The drilling fluid of claim 1 wherein said esters are prepared from olefins and fatty acids or alcohols.

14. A drilling fluid comprising an invert emulsion wherein said invert emulsion has a base or continuous phase comprising a blend of esters and olefin hydrocarbons.

15. The drilling fluid of claim 14 wherein said olefin hydrocarbons are selected from the group comprising branched olefins, poly-branched olefins, and mixtures thereof.

16. The drilling fluid of claim 15 wherein at least one double bond site is either internal the molecule or at the alpha position of the molecule.

17. The drilling fluid of claim 14 wherein said olefin hydrocarbons comprise linear olefins where the double bond site or sites are internal the molecule.

18. The drilling fluid of claim 14 wherein said olefin hydrocarbons comprise about 10 to about 30 carbon atoms.

19. The drilling fluid of claim 14 wherein said olefin hydrocarbons comprise about 1 to about 99 weight percent of said blend.

20. The drilling fluid of claim 14 wherein said esters comprise about 10 to about 99 weight percent of said blend.

21. The drilling fluid of claim 14 wherein said esters are prepared from fatty acids and alcohols.

22. The drilling fluid of claim 14 wherein said esters are prepared from fatty acids having about 6 to about 14 carbon atoms and an alcohol.

23. The drilling fluid of claim 14 wherein said esters are prepared from fatty acids having about 12 to about 14 carbon atoms and 2-ethyl hexanol.

24. The drilling fluid of claim 14 wherein said esters are prepared from fatty acids having about 8 carbon atoms and 2-ethyl hexanol.

25. The drilling fluid of claim 14 wherein said esters are prepared from olefins.

26. The drilling fluid of claim 14 wherein said esters are prepared from olefins and fatty acids or alcohols.

27. A drilling fluid comprising an invert emulsion wherein said invert emulsion has a base or continuous phase comprising a blend of esters and paraffin hydrocarbons.

28. The drilling fluid of claim 27 wherein said paraffin hydrocarbons are selected from the group comprising linear paraffins, branched paraffins, poly-branched paraffins, cyclic paraffins, isoparaffins, and mixtures thereof.

29. The drilling fluid of claim 27 wherein said paraffin hydrocarbons have about 10 to about 30 carbon atoms.

30. The drilling fluid of claim 27 wherein said paraffin hydrocarbons comprise about 1 to about 99 weight percent of said blend.

31. The drilling fluid of claim 27 wherein said esters comprise about 10 to about 99 weight percent of said blend.

32. The drilling fluid of claim 27 wherein said esters are prepared from fatty acids and alcohols.

33. The drilling fluid of claim 27 wherein said esters are prepared from fatty acids having about 6 to about 14 carbon atoms and an alcohol.

34. The drilling fluid of claim 27 wherein said esters are prepared from fatty acids having about 12 to about 14 carbon atoms and 2-ethyl hexanol.

35. The drilling fluid of claim 27 wherein said esters are prepared from fatty acids having about 8 carbon atoms and 2-ethyl hexanol.

36. The drilling fluid of claim 27 wherein said esters are prepared from olefins.

37. The drilling fluid of claim 27 wherein said esters are prepared from olefins and fatty acids or alcohols.

38. A drilling fluid comprising an invert emulsion wherein said invert emulsion has a base or continuous phase comprising a blend of esters and mineral oil hydrocarbons.

39. The drilling fluid of claim 38 wherein said mineral oil hydrocarbons comprise less than about 1 weight percent aromatics.

40. The drilling fluid of claim 38 wherein said mineral oil hydrocarbons are selected from the group comprising linear paraffins, isoparaffins, cycloparaffins, branched paraffins, cyclic paraffins, and mixtures thereof, having about 10 to about 30 carbon atoms.

41. The drilling fluid of claim 38 wherein said mineral oil hydrocarbons comprise olefins, having about 10 to about 30 carbon atoms.

42. The drilling fluid of claim 41 wherein said olefins have chemical structures similar to paraffins, isoparaffins, cycloparaffins, or branched paraffins.

43. The drilling fluid of claim 38 wherein said esters comprise at least about 10 to about 99 weight percent of said blend.

44. The drilling fluid of claim 38 wherein said esters are prepared from fatty acids and alcohols.

45. The drilling fluid of claim 38 wherein said esters are prepared from fatty acids having about 6 to about 14 carbon atoms and 2-ethyl hexanol.

46. The drilling fluid of claim 44 wherein said esters are prepared from fatty acids having about 12 to about 14 carbon atoms and 2-ethyl hexanol.

47. The drilling fluid of claim 44 wherein said esters are prepared from fatty acids having about 8 carbon atoms and 2-ethyl hexanol.

48. The drilling fluid of claim 38 wherein said esters are prepared from olefins.

49. The drilling fluid of claim 38 wherein said esters are prepared from olefins and fatty acids or alcohols.

50. A drilling fluid comprising an invert emulsion wherein said invert emulsion has a base or continuous phase comprising a blend of esters and glyceride triesters.

51. The drilling fluid of claim 50 wherein said glyceride triesters comprise about 1 to about 99 weight percent of said blend.

52. The drilling fluid of claim 50 wherein said glyceride triesters are obtained or derived from an oil selected from the group comprising: rapeseed oil, olive oil, canola oil, castor oil, coconut oil, corn oil, cottonseed oil, lard oil, linseed oil, neatsfoot oil, palm oil, peanut oil, perilla oil, rice bran oil, safflower oil, sardine oil, sesame oil, soybean oil, sunflower oil, and mixtures thereof.

53. The drilling fluid of claim 50 wherein said esters comprise about 10 to about 99 weight percent of said blend.

54. The drilling fluid of claim 50 wherein said esters are prepared from fatty acids and alcohols.

55. The drilling fluid of claim 54 wherein said esters are prepared from fatty acids having about 12 to about 14 carbon atoms and 2-ethyl hexanol.

56. The drilling fluid of claim 54 wherein said esters are prepared from fatty acids and alcohols having about 8 carbon atoms and 2-ethyl hexanol.

57. The drilling fluid of claim 50 wherein said esters are prepared from olefins.

58. The drilling fluid of claim 50 wherein said esters are prepared from olefins and fatty acids or alcohols.

59. A drilling fluid comprising an invert emulsion wherein said invert emulsion has a base or continuous phase comprising a blend of linear alpha olefins and paraffin hydrocarbons.

60. The drilling fluid of claim 59 wherein said paraffin hydrocarbons are selected from the group comprising linear paraffins, branched paraffins, poly-branched paraffins, cyclic paraffins, isoparaffins, and mixtures thereof.

61. The drilling fluid of claim 59 wherein said paraffin hydrocarbons have about 10 to about 30 carbon atoms.

62. The drilling fluid of claim 59 wherein said paraffin hydrocarbons comprise about 1 to about 99 weight percent of said blend.

63. The drilling fluid of claim 59 wherein said paraffin hydrocarbons comprise less than about 50 weight percent of the blend.

64. The drilling fluid of claim 59 wherein said linear alpha olefins comprise about 1 to about 99 weight percent of said drilling fluid.

65. The drilling fluid of claim 59 wherein said linear alpha olefins comprise about 10 to about 30 carbon atoms.

66. A drilling fluid comprising an invert emulsion where said invert emulsion has a base or continuous phase comprising isomerized olefins and paraffin hydrocarbons.

67. The drilling fluid of claim 66 wherein said paraffin hydrocarbons are selected from the group comprising linear paraffins, branched paraffins, poly-branched paraffins, cyclic paraffins, isoparaffins, or mixtures thereof.

68. The drilling fluid of claim 66 wherein said paraffin hydrocarbons have about 10 to about 30 carbon atoms.

69. The drilling fluid of claim 66 wherein said paraffin hydrocarbons comprise about 1 to about 99 weight percent of said blend.

70. The drilling fluid of claim 66 wherein said isomerized olefins comprise about 1 to about 99 weight percent of said drilling fluid.

71. The drilling fluid of claim 66 wherein said isomerized olefins have about 10 to about 30 carbon atoms.

72. The drilling fluid of claim 56 wherein said isomerized olefins are selected from the group comprising internal olefins, cyclic olefins, and mixtures thereof.

73. The drilling fluid of claim 72 wherein said internal olefins may be straight chain or branched chain.

74. A drilling fluid comprising an invert emulsion wherein said invert emulsion has a base or continuous phase comprising a blend of naphthenic hydrocarbons and other paraffin hydrocarbons.

75. The drilling fluid of claim 74 wherein said paraffin hydrocarbons are selected from the group comprising linear paraffins, branched paraffins, poly-branched paraffins, isoparaffins, or mixtures thereof.

76. The drilling fluid of claim 74 wherein said paraffin hydrocarbons have about 10 to about 30 carbon atoms.

77. The drilling fluid of claim 74 wherein said paraffin hydrocarbons comprise about 1 to about 99 weight percent of said blend.

78. The drilling fluid of claim 74 wherein said naphthenic hydrocarbons comprise about 1 to about 99 weight percent of said drilling fluid.

79. The drilling fluid of claim 74 wherein said naphthenic hydrocarbons comprise a saturated, cycloparaffinic material having a chemical formula:



where n is about 5 to about 30.

80. A drilling fluid comprising an invert emulsion wherein said invert emulsion has a base or continuous phase comprising isomerized olefins and other hydrocarbons.

81. A method of drilling a wellbore in a subterranean formation, said method comprising obtaining or preparing the drilling fluid of claim 1 and circulating same in said wellbore during said drilling.

82. A method of drilling a wellbore in a subterranean formation, said method comprising obtaining or preparing the drilling fluid of claim 14 and circulating same in said wellbore during said drilling.

83. A method of drilling a wellbore in a subterranean formation, said method comprising obtaining or preparing the drilling fluid of claim 27 and circulating same in said wellbore during said drilling.

84. A method of drilling a wellbore in a subterranean formation, said method comprising obtaining or preparing the drilling fluid of claim 38 and circulating same in said wellbore during said drilling.

85. A method of drilling a wellbore in a subterranean formation, said method comprising obtaining or preparing the drilling fluid of claim 50 and circulating same in said wellbore during said drilling.

86. A method of drilling a wellbore in a subterranean formation, said method comprising obtaining or preparing the drilling fluid of claim 59 and circulating same in said wellbore during said drilling.

87. A method of drilling a wellbore in a subterranean formation, said method comprising obtaining or preparing the drilling fluid of claim 66 and circulating same in said wellbore during said drilling.

88. A method of drilling a wellbore in a subterranean formation, said method comprising obtaining or preparing the drilling fluid of claim 74 and circulating same in said wellbore during said drilling.

89. A method of drilling a wellbore in a subterranean formation, said method comprising obtaining or preparing the drilling fluid of claim 80 and circulating same in said wellbore during said drilling.

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