

This invention relates to new drilling fluids based on ester oils and to invert drilling muds based thereon which combine high ecological compatibility with good stability and performance properties. One important application for the new drilling fluids is in offshore drilling for the development of oil and/or gas occurrences, the particular object of the invention in this regard being to provide technically useful drilling fluids of high ecological compatibility. The use of the new drilling fluids is of particular importance in, but is not limited to, the offshore sector. The new drilling fluids may also be used quite generally for land-supported drilling, including for example geothermal drilling, water drilling, geoscientific drilling and mine drilling. In this case, too, the ester-based drilling fluids selected in accordance with the invention basically simplify ecotoxic problems to a considerable extent.

It is known that liquid drilling fluids for sinking bores in rock and bringing up the rock cuttings are slightly thickened, water-based or oil-based fluid systems. Oil-based systems are being increasingly used in practice, particularly in offshore drilling or in the penetration of water-sensitive layers.

Oil-based drilling fluids are generally used in the form of so-called invert emulsion muds which consist of a three-phase system, namely: oil, water and finely divided solids. The emulsions in question are of the w/o emulsion type, i.e. the aqueous phase is present in the continuous oil phase in heterogeneous fine dispersion. There are a whole range of additives, including in particular emulsifiers and emulsifier systems, weighting agents, fluid loss additives, alkali reserves, viscosity regulators and the like, for stabilizing the system as a whole and for establishing the desired performance properties. Full particulars can be found, for example, in the Article by P. A

Boyd et al. entitled "New Base Oil Used in Low-Toxicity Oil Muds" in Journal of Petroleum Technology, 1985, 137 to 142 and in the Article by R.B. Bennet entitled "New Drilling Fluid Technology - Mineral Oil Mud" in Journal of Petroleum
5 Technology, 1984, 975 to 981 and the literature cited therein.

Oil-based drilling muds were originally made from diesel oil fractions containing aromatic constituents. For the purposes of detoxification and reducing the ecological
10 problems thus created, it was then proposed to use hydrocarbon fractions substantially free from aromatic compounds - now also known as "nonpolluting oils" - as the continuous oil phase, cf. the literature cited above. Although certain advances were achieved in this way through elimination
15 of the aromatic compounds, a further reduction in the environmental problems caused by drilling fluids of the type in question here seems to be urgently required. This applies in particular to the sinking of offshore wells for the development of oil and gas occurrences because the marine
20 ecosystem is particularly sensitive to the introduction of toxic and non-readily degradable substances.

The relevant technology has for some time recognized the significance of ester-based oil phases for solving these problems. Thus, US-PSS 4,374,737 and 4,481,121 describe
25 oil-based drilling muds in which nonpolluting oils are said to be used. Non-aromatic mineral oil fractions and vegetable oils of the peanut oil, soybean oil, linseed oil, corn oil and rice oil type, and even oils of animal origin, such as whale oil, are mentioned alongside one
30 another as nonpolluting oils of equivalent rank. The ester oils of vegetable and animal origin mentioned here are all triglycerides of natural fatty acids which are known to be environmentally safe and which, ecologically, are distinctly superior to hydrocarbon fractions, even where they have
35 been de-aromaticized.

Interestingly, however, not one of the Examples in the US patents cited above mentions the use of such natural ester oils in invert drilling muds of the type in question here. Mineral oil fractions are used throughout as the continuous oil phase.

The investigations on which the present invention is based have shown that the use of readily degradable oils of vegetable and/or animal origin, which was considered in the prior art, is not feasible for practical reasons. The rheologic properties of such oil phases cannot be controlled for the wide temperature range required in practice of 0 to 5°C on the one hand up to 250°C and higher on the other hand.

Ester oils of the type in question here do not in fact show the same in-use behaviour as the pure hydrocarbon-based mineral oil fractions used hitherto. In practice, ester oils irrespective of their constitution undergo partial hydrolysis precisely in the w/o invert drilling muds, resulting in the formation of free carboxylic acids. These free carboxylic acids in turn react with the alkaline constituents always present in the drilling mud systems of the type in question here, for example with the alkali reserve used for corrosion prevention, to form the corresponding salts. However, salts of highly hydrophilic bases and the acids having carbon chain lengths of about C12 to C24 predominantly encountered in oils of natural origin are known to be compounds having comparatively high HLB values which, in particular, lead to the formation and stabilization of o/w emulsions. Use is made of this on a very wide scale in the field of detergents and cleaning preparations. However, the formation of even limited quantities of such o/w emulsifier systems must interfere with the w/o emulsions required for solving the problem addressed by the invention and, hence, must lead to problems.

Earlier applications EP-A1-374 671 and EP-A1-374 672 relate to the use of ester oils based on selected monocarboxylic acids or monocarboxylic acid mixtures and associated monofunctional alcohols. The earlier applications
5 show that it is possible with the disclosed esters or ester mixtures of monofunctional reactants not only to establish satisfactory rheological properties in the fresh drilling mud, but also to work with selected known alkali reserves in the drilling mud and thus to prevent unwanted corrosion.
10 According to the teaching of these earlier applications, it is crucial so far as the alkali reserve is concerned that no hydrophilic bases, such as alkali metal hydroxide and/or diethanolamine, are present. The alkali reserve is formed by the addition of lime (calcium hydroxide) and/or by the
15 presence of zinc oxide or comparable zinc compounds.

However, an additional limitation is necessary in this regard also. If unwanted thickening of the oil-based invert drilling mud is to be prevented in practice, the quantity of alkalizing additive and, in particular, the
20 quantity of lime have to be limited. According to the disclosure of the earlier applications mentioned, the maximum addition envisaged is put at about 2 lb/bbl oil mud.

By contrast, the teaching of the present invention is
25 based on deeper considerations and realizations hitherto unknown in the field of the invert drilling muds in question here with their continuous oil phase. The teaching according to the invention takes into account the fact that, in practice, drilling muds of the type in question
30 containing ester oils undergo limited partial hydrolysis so that free carboxylic acids are unavoidably formed to an increasing extent as a hydrolysis product and, sooner or later, reach a critical or at least endangered state of ageing reflected in unwanted thickening of the drilling
35 mud. The teaching according to the invention is based on

the concept of using an additional additive in invert drilling muds of the type in question here which is capable of keeping the desired rheological data of the drilling mud within the required limits, even when increasingly more and
5 more or even excessive quantities of free carboxylic acids are formed by partial ester hydrolysis. In this regard, the teaching of the invention seeks not only to trap the free carboxylic acids formed in a harmless form, but also to convert them, if desired, into valuable components
10 having stabilizing or emulsifying properties for the system as a whole.

In a first embodiment, therefore, the present invention relates to the use of basic amine compounds of pronounced oleophilic character and limited solubility in
15 water, which are capable of forming salts with carboxylic acids, as an additive for w/o invert drilling muds which contain in the continuous oil phase ester oils of monobasic C_{6-24} carboxylic acids and monohydric alcohols and, together with the disperse aqueous phase, emulsifiers, viscosity
20 generators, weighting agents, fluid loss additives and, if desired, other additives for protecting the drilling muds against unwanted thickening in use and/or for improving their flow properties.

In another embodiment, the invention relates to w/o
25 invert drilling muds which are suitable for the offshore development of oil and gas occurrences and, in a continuous oil phase containing ester oils of the type mentioned, contain a disperse aqueous phase together with emulsifiers, viscosity generators, weighting agents, fluid loss additives and, if desired, other typical additives. In this
30 embodiment, the invention is characterized in that the drilling muds contain as an additional additive basic amine compounds of pronounced oleophilic character and correspondingly limited solubility in water which are capable of
35 forming salts with carboxylic acids. The addition of the

additives according to the invention affords the drilling muds protection against unwanted thickening in use and, overall, is suitable for improving their flow properties.

Finally, in another embodiment, the invention relates to additive mixtures which are suitable for the stated purpose in drilling muds containing ester oils of the type mentioned and which contain the basic amine compounds of pronounced oleophilic character and limited solubility in water, which are capable of forming salts with carboxylic acids, in a solvent miscible with the oil phase. Preferred solvents are so-called nonpolluting oils, particular significance again being attributed in this regard to the ester oils described above. In mixtures of the type just mentioned, the antiagers based on the oleophilic basic amine compounds are best present in concentrations of at least 20% by weight and preferably in concentrations of at least 50% by weight.

The essence of the teaching according to the invention in all its embodiments is the observation that, where the antiagers according to the invention based on oleophilic basic amine compounds are used, the carboxylic acids unavoidably formed in practice through partial hydrolysis of the ester oils are trapped without the rheological properties of the invert mud having to be adversely affected. By selecting suitable amine compounds, it is even possible to form valuable stabilizing and/or emulsifying mixture constituents in situ through the salt formation which now occurs. The oleophilic basic amine compounds may be added to the drilling mud systems from the outset and/or may be added to them in use. It has been found that it is even possible by adding or using the basic oleophilic amine compounds according to the invention to regenerate aged and undesirably thickened drilling muds of the type in question here to such an extent that their rheology is reduced to the range required for pumpability and free flow, even at

low temperatures.

The use of the additives according to the invention has revealed another important simplification in the composition of w/o drilling muds, namely: the alkalization of the drilling mud required for corrosion prevention and, in particular, the creation of an adequate alkali reserve, particularly against intrushes of acidic gases, such as CO₂ and/or H₂S, becomes unproblematical. The basic amine compounds of pronounced oleophilic character proposed as additives in accordance with the invention spontaneously form a basicity buffer which may be used as an alkali reserve. Of greater importance is the surprising observation that the use of conventional alkali reserves and, in particular, the use of lime, which is particularly inexpensive, becomes largely unproblematical if the antiaging additives according to the invention are simultaneously present in the drilling mud. In general, the above-mentioned limit of 2 lb/bbl (lime/oil mud) for drilling muds based on ester oils, which is disclosed in the earlier applications cited above, may be safely exceeded providing the basic amine compounds of pronounced oleophilic character according to the invention are present in the oil mud. Even if unwanted thickening has occurred through the use of conventional, highly hydrophilic alkali reserves, it may be eliminated by incorporation of the additive component according to the invention in the system as a whole.

The basic amine compounds of pronounced oleophilic character selected in accordance with the invention are discussed in more detail in the following.

Basic amine compounds containing relatively short carbon chains are known to be highly soluble in water and, optionally, miscible with water in any quantitative ratios. By contrast, the amine compounds selected in accordance with the invention are characterized by distinctly limited solubility in water with simultaneous development of their

oleophilic character. Their solubility in water at room temperature is below 10% by weight and, in the preferred embodiment, does not exceed a value of 5% by weight. Of importance above all are oleophilic amine compounds which have very small limits for their solubility in water at room temperature. An important limit is at 1% by weight and preferably at less than 0.1% by weight. Particularly important basic amines for the purposes of the invention may be regarded as substantially insoluble in water.

10 Oleophilic amines of the described type may generally be used providing they are capable of forming salts with the carboxylic acids released during the ester hydrolysis and, preferably, are soluble in the oil phase. In the context of the intention according to the invention of causing
15 minimal toxic environmental pollution, preference is attributed to ecologically comparatively safe representatives of this wide range of basically suitable amine compounds. From these considerations, it follows that aromatic amines are generally less suitable so that another
20 preferred embodiment of the invention is characterized by the use of oleophilic amine compounds which are substantially free from aromatic constituents. Suitable compounds for carrying out the teaching according to the invention may generally be assigned to the groups of aliphatic,
25 cycloaliphatic and/or heterocyclic amines. The particular representatives may contain one or even more N groups capable of forming salts with carboxylic acids. Amine compounds of the described type may be nitrogen-containing saturated hydrocarbon compounds, although amine hydrocarbons containing one or more olefinically unsaturated groups
30 in at least one of their hydrocarbon members are also suitable.

There is considerable freedom of choice in regard to the particular constitution of the amine components used in
35 accordance with the invention. Economic considerations

largely dictate the choice of the particular components. In general, particularly suitable representatives may be assigned to the following classes:

Primary, secondary and/or tertiary amines substantially insoluble in water, corresponding aminoamides and/or heterocycles containing nitrogen as a ring constituent. Amine bases containing at least one long-chain hydrocarbon radical preferably bearing 8 to 36 carbon atoms and, more preferably, 10 to 24 carbon atoms in the molecule can be particularly suitable. These hydrocarbon radicals may be directly attached to the nitrogen atom. However, they may also be attached to an N-containing part of the molecule through a functional group, as in the case of the aminoamides for example. In this case, it is important to ensure that at least one basic N atom capable of forming a salt with the carboxylic acids released by ester hydrolysis is present in the molecule as a whole. Typical examples of the various classes mentioned here are discussed in more detail in the following.

A first group comprises primary, secondary and tertiary amines containing one or more N atoms, the ratio of hydrocarbon groups to amine groups in the particular compound being selected so that the conditions stated above with regard to limited solubility in water and pronounced oleophilic character are fulfilled. In simple unsubstituted compounds of the type in question, the C:N ratio is at least about 5 or, better yet, 6, but preferably higher. In amines of the type in question readily obtainable on an industrial scale, 1 or 2 comparatively long-chain hydrocarbon radicals and, for the rest, methyl groups are often present at the aminonitrogen. Typical examples of the type in question here contain 1 nitrogen atom per molecule. Comparable compounds derived from polyfunctional amines, particularly lower diamines, for example ethylenediamine or propylenediamine, are also readily obtainable on an in-

dustrial scale. Lower polyamines of the type in question here are highly soluble in water. However, if one or more long-chain hydrocarbon radicals of the above-mentioned type are introduced into their molecule, suitable additives
5 according to the invention are formed providing at least one nitrogen atom is capable of salt formation with the carboxylic acids. Suitable representatives of this type are, for example, compounds corresponding to the general formula $R-NH-(CH_2)_n-NH_2$ where R is, for example, a hydrocar-
10 bon radical containing 8 to 22 C atoms and n is a low number of up to 6 and, more preferably, from 2 to 4.

Primary and possibly even secondary amines in which parts of the molecule are of pronounced oleophilic character may be suitable for the purposes of the invention even
15 when oligo-alkoxide groups are introduced at the NH groups present by alkoxylation with, for example, ethylene oxide and/or propylene oxide or higher homologs, for example butylene oxide. For example, long-chain primary and/or secondary amines are sufficiently oleophilic, even where up
20 to 8 to 10 EO and/or PO groups are introduced, so that they may be considered for use in accordance with the invention.

Industrially readily obtainable amine compounds for use in accordance with the invention are derived from the epoxidation of olefinically unsaturated hydrocarbon com-
25 pounds with subsequent introduction of the N function by addition to the epoxide group. The reaction of the epoxidized intermediate components with primary and/or secondary amines to form the corresponding alkanolamines is of particular significance in this regard. Polyamines, particular-
30 ly lower polyamines of the corresponding alkylenediamine type, are also suitable for opening of the epoxide ring.

Another important class of the oleophilic amine compounds for the purposes of the invention are aminoamides derived from preferably long-chain carboxylic acids and
35 polyfunctional, particularly lower, amines of the above-

mentioned type. The key factor in their case is that at least one of the amino functions is not bound in amide form, but remains intact as a potentially salt-forming basic amino group. Both in this case and in all the cases
5 discussed in the foregoing, the basic amino groups, where they are formed as secondary or tertiary amino groups, may contain hydroxyalkyl substituents and, in particular, lower hydroxyalkyl substituents containing up to 5 and preferably up to 3 C atoms in addition to the oleophilic part of the
10 molecule. Suitable N-basic starting components for the preparation of such adducts containing long-chain oleophilic molecule constituents are monoethanolamine and/or diethanolamine. Thus, in one preferred embodiment, suitable additives according to the invention are reaction
15 products from the epoxidation of long-chain olefins containing, for example, 8 to 36 and, in particular, 10 to 18 C atoms and mono- and/or diethanolamine. α -Olefins of the type mentioned may be particularly important as starting material for the epoxidation and the subsequent reaction to
20 the secondary and/or tertiary amine containing hydroxyalkyl groups at the N atom.

An important class of heterocyclic additives for regulating the flow properties of the drilling muds according to the invention are the imidazoline compounds. Other
25 important members of this heterocyclic group are alkylpyridines.

The additives based on oleophilic basic amine compounds according to the invention are preferably added to the drilling muds in quantities of no more than 10 lb/bbl
30 and, more preferably, in quantities of no more than 5 lb/bbl. The quantity used may be determined inter alia by the form of application envisaged in practice. Many variants are possible in this regard and may even be combined with one another.

35 In a first embodiment, the flow-control additive is

added to the drilling mud in a considerable quantity from the outset and, in this case, may perform a dual function. On the one hand, it forms the alkali reserve of the drilling mud to trap any intrushes of acidic constituents, such as CO_2 and/or H_2S ; on the other hand, the basic amine compound optionally present in a large excess takes up the carboxylic acid components formed by hydrolysis as they are being formed and converts them into the corresponding oil-soluble salts. In the opposite extreme case, the invention initially operates with the drilling mud based on ester oil without the additives according to the invention, for example in accordance with the teaching of the earlier applications EP-A1 374 671 and EP-A1 374 672 cited above. If ageing of the drilling mud occurs, as reflected in an incipient increase in viscosity, the flow-control additive according to the invention is added to the drilling mud continuously or in portions. This may readily be done during drilling. It is clear that any combinations between these two extremes are possible for the introduction of the additive according to the invention before and during the drilling operation or the use of the drilling mud. Providing suitable amine compounds forming effective emulsifier systems are used, it is even possible to save emulsifier in the oil to be subsequently added and, instead, to use the emulsifying amine salts formed in situ to stabilize the system as a whole.

The amine compounds may be added to the invert drilling muds directly or indirectly. Thus, they may be incorporated beforehand in the oil phase containing ester oil or are added to the overall system as such. In one particularly suitable embodiment, additive concentrates are prepared and may then be added to the drilling mud, particularly during drilling. The products in question are solutions of the oleophilic amine compounds in suitable solvents with preferred concentrations of the additive of

at least 20% by weight, but preferably of at least 50% by weight. Suitable solvents are nonpolluting oils which may be homogeneously incorporated in the drilling mud. Ester oils, for example of the type mentioned in the two earlier applications cited, are particularly suitable for this purpose.

As already mentioned, it is an important advantage of the invention that the use of the additives according to the invention to regulate the flowability and pumpability of the drilling muds now opens up the possibility, even in the case of oil phases based on ester oil, of using conventional alkali reserves in the quantities hitherto typically used for drilling muds based on mineral oils as the oil phase. For example, lime may be used in quantities of up to 5 lb/bbl with no risk of lasting damage to the drilling mud in operation. The same applies to the zinc compounds mentioned in the earlier applications, such as zinc oxide, zinc complex compounds and the like. Surprisingly, however, it is even possible to use the strongly hydrophilic bases hitherto typically used for the alkalization of drilling muds. If the alkali reserve is formed as described by conventional means, for example by the use of considerable quantities of lime, the quantity of amine-based additives selected in accordance with the invention may be reduced into the range required during the process as a result of ester saponification. In one important embodiment, only a slight excess of the oleophilic amine base is used and the amount consumed by salt formation is added continuously or in portions during the drilling operation. In this embodiment, the quantity of amine base added may be, for example, in the range from 0.1 to 2 lb/bbl (amine base/drilling mud) or even smaller.

Particularly suitable ester oils are esters of monofunctional carboxylic acids or carboxylic acid mixtures and monofunctional alcohols, more especially the esters de-

scribed in detail in the earlier applications cited above. To complete the disclosure of the invention, essential characteristics of those esters or ester mixtures are briefly summarized in the following.

- 5 In a first embodiment, esters - flowable and pumpable at 0 to 5°C - of monohydric C₂₋₁₂ and, more particularly, C₄₋₁₂ alcohols and aliphatic saturated C₁₂₋₁₆ monocarboxylic acids or mixtures thereof with at most equal quantities of other monocarboxylic acids are used as the oil phase.
- 10 Preferred ester oils are those of which at least 60% by weight, based on carboxylic acid mixture, are esters of aliphatic C₁₂₋₁₄ monocarboxylic acids and optionally, for the rest, small quantities of relatively short-chain aliphatic and/or relatively long-chain, in that case more especially
- 15 mono- and/or polyolefinically unsaturated monocarboxylic acids. Preferred esters are those which have a Brookfield (RVT) viscosity at 0 to 5°C of no more than 50 mPa.s, preferably of no more than 40 mPa.s and, more preferably, of at most 30 mPa.s. The esters used in the drilling mud
- 20 have solidification values (pour point and setting point) below -10°C and preferably below -15°C and, in particular, flash points above 100°C and preferably above 150°C. The carboxylic acids present in the ester or ester mixture are predominantly linear and, preferably, of vegetable origin.
- 25 They may be derived from corresponding triglycerides, such as coconut oil, palm kernel oil and/or babassu oil. The monohydric alcohol radicals of the esters used are derived in particular from linear and/or branched saturated alcohols preferably containing 4 to 10 C atoms. These monohydric
- 30 alcohol components may also be of vegetable and/or animal origin, having been obtained by reductive hydrogenation of corresponding carboxylic acid esters.

The other class of particularly suitable ester oils is derived from mono- and/or polyolefinically unsaturated

- 35 C₁₆₋₂₄ monocarboxylic acids or mixtures thereof with small

quantities of other, in particular saturated monocarboxylic acids and monofunctional C_{2-12} alcohols. These ester oils are also flowable and pumpable at temperatures in the range from 0 to 5°C. Particularly suitable esters of this type
5 are those of which more than 70% by weight, preferably more than 80% by weight and, in particular, more than 90% by weight are derived from olefinically unsaturated C_{16-24} carboxylic acids.

In their case, too, the solidification values (pour
10 point and setting point) are below -10°C and preferably below -15°C while the flash points are above 100°C and preferably above 160°C. The esters used in the drilling mud have a Brookfield (RVT) viscosity at 0 to 5°C of no more than 55 mPa.s and preferably of no more than 45 mPa.s.

15 Ester oils of the type in question here may be divided into two sub-classes. In the first sub-class, no more than 35% by weight of the unsaturated C_{16-24} monocarboxylic acid residues in the ester are derived from di- and polyolefinically unsaturated acids, preferably at least 60% by weight
20 of the acid residues being monoolefinically unsaturated. In the second sub-class, more than 45% by weight and preferably more than 55% by weight of the C_{16-24} monocarboxylic acids in the ester mixture are derived from di- and/or polyolefinically unsaturated acids. Saturated C_{16-18}
25 carboxylic acids in the ester mixture best make up no more than 20% by weight and, in particular, no more than 10% by weight. However, saturated carboxylic acids preferably have relatively low C chain lengths of the acid residues. In this case, too, the carboxylic acid residues present are
30 predominantly linear and are of preferably vegetable and/or animal origin. Vegetable starting materials are, for example, palm oil, peanut oil, castor oil and, in particular, rapeseed oil. Carboxylic acids of animal origin are, in particular, corresponding mixtures of fish oils, such as
35 herring oil.

Invert drilling muds of the type in question here typically contain the finely disperse phase, together with the continuous oil phase, in quantities of 5 to 45% by weight and preferably in quantities of 5 to 25% by weight.

5 The range from 10 to 25% by weight of disperse aqueous phase can be particularly important.

The following rheological data apply to the rheology of preferred invert drilling muds according to the invention: plastic viscosity (PV) in the range from 10 to 60
10 mPa.s and preferably in the range from 15 to 40 mPa.s, yield point (YP) in the range from 5 to 40 lb/100 ft² and preferably in the range from 10 to 25 lb/100 ft², as measured at 50°C. Full information on the determination of these parameters, on the measurement techniques used and on
15 the otherwise standard composition of the invert oil muds described herein can be found in the prior art cited above and, for example, in "Manual of Drilling Fluids Technology" published by NL-Baroid, London, GB, cf. in particular the Chapter entitled "Mud Testing - Tools and Techniques" and
20 "Oil Mud Technology", which is freely available to interested experts. In the interests of fullness of disclosure, the following summary observations may be made:

Emulsifiers suitable for use in practice are systems which are capable of forming the required w/o emulsions.
25 Selected oleophilic fatty acid salts, for example those based on amidoamine compounds, are particularly suitable, examples being described in the already cited US-A-4,374, 737 and the literature cited therein. One particularly suitable type of emulsifier is the product marketed under
30 the name of "EZ-mul" by NL Baroid, London.

Emulsifiers of the type in question here are marketed in the form of concentrates and may be used, for example, in quantities of 2.5 to 5% by weight and more especially in quantities of 3 to 4% by weight, based in each case on the
35 ester oil phase.

In practice, hydrophobicized lignite in particular is used as a fluid-loss additive and, hence, in particular for forming an impervious coating in the form of a substantially water-impermeable film over the walls of the well.

5 Suitable quantities are, for example, in the range from 15 to 20 lb/bbl or in the range from 5 to 7% by weight, based on the ester oil phase.

10 In drilling muds of the type in question here, the thickener normally used to create viscosity is a cationically modified, finely divided bentonite which may be used in particular in quantities of 8 to 10 lb/bbl or in the range from 2 to 4% by weight, based on the ester oil phase. The weighting agent normally used in practice to establish the necessary pressure equalization is baryta which is
15 added in quantities adapted to the particular conditions to be expected in the well. For example, it is possible by addition of baryta to increase the specific gravity of the drilling mud to values of up to 2.5 and preferably in the range from 1.3 to 1.6.

20 In invert drilling muds of the type in question here, the disperse aqueous phase is charged with soluble salts, generally calcium chloride and/or potassium chloride, the aqueous phase preferably being saturated with the soluble salt at room temperature.

25 The emulsifiers or emulsifier systems mentioned above may also be used to improve the oil wettability of the inorganic weighting materials. In addition to the aminoamides already mentioned, alkyl benzenesulfonates and imidazoline compounds are mentioned as further examples. Additional information on the relevant prior art can be found
30 in the following literature references: GB-A 2,158,437, EP-A 229 912 and DE-A 32 47 123.

In addition to the advantages already mentioned, the drilling fluids based in accordance with the invention on
35 the co-use of ester oils of the described type are also

distinguished by distinctly improved lubricity. This is particularly important when the path of the drill pipe and hence the well deviate from the vertical during drilling, for example at considerable depths. In such cases, the rotating drill pipe readily comes into contact with the well wall and embeds itself therein. Ester oils of the type used as oil phase in accordance with the invention have a distinctly better lubricating effect than the mineral oils hitherto used, which is an important advantage of the teaching according to the invention.

The following conversion factors should be used for converting the non-metric units of measurement typically used in the specialist field in question and in the description of the present invention and the following Examples:

1 lb = 0.454 kg; 1 bbl = 159 l;

1 lb/bbl = 2.05 kg/m³, particularly in conjunction with the quantity of alkali reserve added

1 lb/100 ft² = 0.4788 Pa, particularly in conjunction with determination of the yield point (YP) and gel strength

Examples

In the following Examples, two typical ester oils are used as the oil phase of the invert drilling muds. In both cases, the ester oils in question are monocarboxylic acids/monoalcohol esters which may be characterized as follows: Examples 1 to 3: distilled n-hexyl lauric acid ester having the following characteristic data: flash point above 165°C, pour point above -5°C, density (20°C) 0.857 to 0.861, iodine value and acid value below 1, water content below 0.3%

and the following viscosity data (Brookfield mPa.s) in the low-temperature range:

-5°C 22.5 to 25.5; + 2°C 15 to 18; + 5°C 15 to 18; + 10°C approx. 15; 20°C 12 to 14.

- 5 Examples 4 to 10: isobutyl rapeseed oil ester based on a mixture of predominantly unsaturated linear carboxylic acids corresponding to substantially the following distribution: 60% oleic acid, 20% linoleic acid, 9 to 10% linolenic acid, olefinically unsaturated C₂₀₋₂₂ monocarboxylic acids approx. 4%, remainder saturated monocarboxylic acids predominantly in the C₁₆₋₁₈ range.

The rapeseed oil ester used has the following characteristic data: density (20°C) 0.872 g/cm³; pour point below -15°C; flash point (DIN 51584) above 180°C; acid value (DGF-C-V 2) 1.2; viscosity at 0°C 32 mPa.s, viscosity at 5°C 24 mPa.s.

An invert drilling mud is conventionally produced using the following constituents:

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|----|-----|----|---|
| | 230 | ml | ester oil |
| 20 | 26 | ml | water |
| | 6 | g | organophilic bentonite (Geltone II, a product of NL Baroid) |
| | 12 | g | organophilic lignite (Duratone, a product of NL Baroid) |
| 25 | x | g | lime |
| | 6 | g | w/o emulsifier (EZ-mul NT, a product of NL Baroid) |
| | 346 | g | baryta |
| | 9.2 | g | CaCl ₂ x 2 H ₂ O |
| 30 | y | g | oleophilic basic amine |

The plastic viscosity (PV), the yield point (YP) and the gel strength after 10 secs. and 10 mins. of the particular invert drilling mud tested are first determined by measuring the viscosity of the unaged material at 50°C.

- 35 The invert drilling mud is then stored in an autoclave

(so-called roller oven) for 16 hours at 125°C to investigate the effect of temperature on emulsion stability. The viscosities are then remeasured at 50°C.

5 Example 1

The n-hexyl ester of lauric acid is used as the oil phase. Lime is added in a quantity of 2 g to the above starting formulation. There is no addition of a basic amine of pronounced oleophilic character corresponding to the definition according to the invention. The following values are determined on the material before and after ageing:

	Unaged material	Aged material
Plastic viscosity (PV)	19	50
Yield point (YP)	8	36
Gel strength (lb/100 ft ²)		
10 secs.	6	41
10 mins.	7	48

The drilling mud undergoes considerable thickening after ageing for only 16 hours at 125°C. The quantity of lime used is above the threshold value of 2 lb/bbl.

Example 2

0.5 g of a basic amine of pronounced oleophilic character is added to the invert drilling mud of Example 1. The reaction product of an epoxidized C₁₂₋₁₄ α-olefin and diethanolamine (Applicants' "Araphen G2D") is used as the basic amine.

The rheological data of the material before and after ageing are as follows:

	Unaged material	Aged material
Plastic viscosity (PV)	19	36
5 Yield point (YP)	9	18
Gel strength (lb/100 ft ²)		
10 secs.	5	20
10 mins.	7	33

10 Example 3

The same oleophilic basic amine as in Example 2 ("Araphen G2D") is added to the invert drilling mud in a quantity of 1 g. The material shows the following values before and after ageing:

15

	Unaged material	Aged material
Plastic viscosity (PV)	20	21
20 Yield point (YP)	8	6
Gel strength (lb/100 ft ²)		
10 secs.	5	4
10 mins.	6	5

25 Comparison of Examples 1 to 3 with one another clearly shows the stabilizing effect of the addition of an oleophilic basic amine corresponding to the definition according to the invention.

30 Example 4

In this Example and in Examples 5 to 9, the isobutyl rapeseed oil ester defined above is used as continuous oil phase.

35 In Example 4, no lime is added, although 2 g of the oleophilic basic amine ("Araphen G2D") defined above are incorporated in the drilling mud. The material shows the following values before and after ageing:

	Unaged material	Aged material
Plastic viscosity (PV)	28	28
5 Yield point (YP)	11	4
Gel strength (lb/100 ft ²)		
10 secs.	15	6
10 mins.	13	9

10 Example 5

Example 4 is repeated, except that stearyl amine is used in a quantity of 2 g as the oleophilic basic amine. The materials shows the following values before and after ageing:

15

	Unaged material	Aged material
Plastic viscosity (PV)	27	27
20 Yield point (YP)	16	5
Gel strength (lb/100 ft ²)		
10 secs.	12	5
10 mins.	13	7

25 Example 6

For comparison, 1 g lime is added to the isobutyl rapeseed oil ester in the absence of oleophilic basic amine compounds. The quantity of 1 g used in the starting formulation is below the threshold value of 2 lb/bbl which, 30 for the formulation used here, corresponds to an addition of approximately 1.35 g lime.

The rheological data of the material before and after ageing are as follows:

	Unaged material	Aged material
Plastic viscosity (PV)	27	28
5 Yield point (YP)	10	18
Gel strength (lb/100 ft ²)		
10 secs.	6	6
10 mins.	8	8

10 Example 7

2 g of the oleophilic basic amine compound "Araphen G2D" are added to the formulation of Example 6. The drilling mud shows the following rheological values:

15	Unaged material	Aged material
Plastic viscosity (PV)	30	32
Yield point (YP)	10	11
20 Gel strength (lb/100 ft ²)		
10 secs.	8	7
10 mins.	9	7

Example 8

25 An isobutyl rapeseed oil ester is again investigated with addition of 2 kg lime to the starting formulation, but without the addition of the oleophilic basic amine. The rheological data are as follows:

30	Unaged material	Aged material
Plastic viscosity (PV)	27	84
Yield point (YP)	12	22
35 Gel strength (lb/100 ft ²)		
10 secs.	7	21
10 mins.	8	51

Comparison of Example 8 with Example 6 shows the considerable thickening effect which is initiated during ageing when the quantity of lime is increased beyond the threshold value of approximately 2 lb/bbl.

5

Example 9

2 g "Araphen G2D" are added to the invert drilling mud of Example 8. The material shows the following rheological values before and after ageing:

10

	Unaged material	Aged material
Plastic viscosity (PV)	28	32
15 Yield point (YP)	15	12
Gel strength (lb/100 ft ²)		
10 secs.	8	6
10 mins.	8	6

20

Comparison with the rheological data of Example 8 shows the effect of the oleophilic basic amine compound added in accordance with the invention.

Example 10

25

2 g diethylenetriamine, i.e. a strongly hydrophilic base, is added to the invert drilling mud of Example 8. The rheological data of the material are determined before ageing.

This invert drilling mud is then aged for 16 hours at 30 125°C in the same way as described above. It was found that the mud thickened to such an extent that the rheological data could not be measured.

2 g of the oleophilic basic amine compound "Araphen G2D" were added to the thickened mass and the resulting 35 mixture re-aged for 16 hours at 125°C in a roller oven. The thickened mass is liquefied so that its rheological

data can now be measured.

Overall, the following values were determined:

5		Unaged material	1st ageing	2nd ageing after addi- tion of the amine com- pound
10	Plastic viscosity (PV)	31	cannot be measured	45
	Yield point (YP)	24		25
	Gel strength			
15	10 secs.	16		114
	10 mins.	23		120

**CLAIMS**

1. The use of basic amine compounds of pronounced oleophilic character and limited solubility in water, which are capable of forming salts with carboxylic acids, as an additive for w/o invert drilling muds which contain in the continuous oil phase ester oils of monobasic C_{6-24} carboxylic acids and monohydric alcohols and, together with the disperse aqueous phase, emulsifiers, viscosity generators, weighting agents, fluid loss additives and, if desired, other additives for protecting the drilling muds against unwanted thickening in use and/or for improving their flow properties.
2. The use claimed in claim 1, characterized in that the basic oleophilic amine compounds are also used partly as the alkali reserve of the invert drilling mud.
3. The use claimed in claims 1 and 2, characterized in that the oleophilic basic amines are used together with conventional alkali reserves, more especially together with lime.
4. The use claimed in claims 1 to 3, characterized in that oleophilic amine compounds free or substantially free from aromatic constituents are used.
5. The use claimed in claims 1 to 4, characterized in that optionally olefinically unsaturated aliphatic, cycloaliphatic and/or heterocyclic, oleophilic basic amine compounds containing one or even more N groups capable of forming salts with carboxylic acids are used.
6. The use claimed in claims 1 to 5, characterized in that the basic amine compounds used have a solubility in water at room temperature of at most 5% by weight, preferably less than 1% by weight and more preferably less than 0.1% by weight.
7. The use claimed in claims 1 to 6, characterized in that at least substantially water-insoluble primary, secondary and/or tertiary amines, which may even be alkoxy-



lated to a limited degree and/or substituted by, in particular, hydroxyl groups, corresponding aminoamides and/or heterocycles containing N as a constituent of the ring are used.

- 5 8. The use claimed in claims 1 to 7, characterized in that the basic amine compounds used contain at least one long-chain hydrocarbon radical preferably containing from 8 to 36 and, more preferably, from 10 to 24 carbon atoms, which may even be mono- or polyolefinically unsaturated.
- 10 9. The use claimed in claims 1 to 8, characterized in that the oleophilic basic amine compounds are added to the drilling mud in quantities of up to 10 lb/bbl, preferably in quantities of up to 5 lb/bbl and more preferably in quantities of 0.1 to 2 lb/bbl.
- 15 10. The use claimed in claims 1 to 9, characterized in that the oleophilic basic amine compounds are used in drilling muds containing ester oils of monohydric alcohols and monobasic C₆₋₂₄ carboxylic acids of natural origin.
- 20 11. W/o invert drilling muds which are suitable for the offshore development of oil and gas occurrences and, in a continuous oil phase containing ester oils of monobasic C₆₋₂₄ carboxylic acids and monohydric alcohols, contain a disperse aqueous phase together with emulsifiers, viscosity generators, weighting agents, fluid loss additives and, if
- 25 desired, other typical additives, characterized in that the drilling muds additionally contain basic amine compounds of pronounced oleophilic character and correspondingly limited solubility in water which are capable of forming salts with carboxylic acids as an additive for protection against
- 30 unwanted thickening in use and for improving their flow properties.
12. A drilling mud as claimed in claim 11, characterized in that the oleophilic basic amine compounds make up the alkali reserve or a predominant part of the alkali reserve
- 35 of the drilling mud or are present in admixture with



conventional alkali reserves, more especially together with lime.

13. A drilling mud as claimed in claims 11 and 12, characterized in that optionally olefinically unsaturated aliphatic, cycloaliphatic and/or heterocyclic basic amine compounds of oleophilic character containing one or even more N groups capable of forming salts with carboxylic acids are present as an additive for protecting the rheology of the drilling mud.
14. A drilling mud as claimed in claims 11 to 13, characterized in that it contains basic amine compounds having a solubility in water at room temperature of at most 5% by weight and preferably below 1% by weight.
15. A drilling mud as claimed in claims 11 to 14, characterized in that substantially water-insoluble primary, secondary and/or tertiary amines, which may even be alkoxy-
lated to a limited degree and/or substituted by, in particular, hydroxyl groups, corresponding aminoamides and/or heterocycles containing N as a constituent of the ring are present as the rheology-protecting additive.
16. A drilling mud as claimed in claims 11 to 15, characterized in that basic amine compounds containing at least one long-chain hydrocarbon radical preferably containing from 8 to 36 and more preferably from 10 to 24 C atoms, which may even be mono- and/or polyolefinically unsaturated, are present as the additive.
17. A drilling mud as claimed in claims 11 to 16, characterized in that the oleophilic basic amine compounds are present in the drilling mud in quantities of up to 10 lb/bbl and preferably in quantities of no more than 5 lb/bbl.
18. A drilling mud as claimed in claims 11 to 17, characterized in that the ester oil phase contains esters of monobasic C₁₂₋₂₄ carboxylic acids.
19. An additive for improving and, in particular, prevent-



ing the ageing of the flow properties of w/o invert drilling muds based on a continuous oil phase containing ester oils of monobasic C₆₋₂₄ carboxylic acids and monohydric alcohols which, together with the disperse aqueous phase,
5 contains emulsifiers, viscosity generators, weighting agents, fluid loss additives and, if desired, other additives, characterized in that it contains the basic amine compounds of pronounced oleophilic character and correspondingly limited solubility in water, which are capable
10 of forming salts with carboxylic acids, in solution in a solvent miscible with the oil phase based preferably on nonpolluting oils and, more preferably, on ester oil.