

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 sources, 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Oil-based drilling fluids were originally made from diesel oil fractions containing aromatic constituents.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 sources because the marine ecosystem
20 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 oil-based drilling fluids in which nonpolluting oils
25 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 teaching of US-PS 4,631,136 also seeks to provide ecologically safe oil-based drilling fluids based on triglycerides of vegetable origin. According to the document in question, glyceride oils with a minimum content of di- and tri-ethylenically unsaturated carboxylic acid residues are preferably used. In addition, known antioxidants and corresponding synergists for enhancing the effect of the antioxidants are used in the ester oils. This measure is claimed to prevent thickening of the system by polymerization or crosslinking reactions initiated by oxidation.

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.

In its general descriptive part, US-PS 4,481,121 mentions not only triglycerides, but also a commercial product "Arizona 208" of the Arizona Chemical Company, Wayne, N.J., which is a purified isooctyl-monoalcohol ester of high-purity tall oil fatty acids. An ester of a monofunctional alcohol and monofunctional carboxylic acids, mentioned for the first time here, is described as equivalent to triglycerides of natural origin and/or de-aromatized hydrocarbon fractions.

The cited US patent does not contain any copyable Examples relating to the use of such an ester of monofunc-

tional components.

The teaching of the present invention is based on the observation that it is in fact possible to produce oil-based invert drilling fluids of the type in question here
5 based on ester oils of high environmental compatibility which correspond in their storage and in-use behavior to the best of the hitherto known oil-based drilling fluids, but have the additional advantage of increased environmental compatibility. Two key observations in this regard
10 dominate the teaching according to the invention:

The triglycerides accumulating in the form of natural oils are not suitable for the production of mineral-oil-free oil-based invert drilling fluids, whereas the esters of monofunctional carboxylic acids with monofunctional al-
15 cohols derived from those oils or fats are suitable for the production of such drilling fluids. The second key observation is that ester oils of the type in question here do not in fact show the same in-use behavior as the mineral oil fractions used hitherto based purely on hydrocarbons.
20 In practical application, the ester oils of monofunctional components in question here undergo partial hydrolysis, resulting in the formation of free fatty acids. These free fatty acids react in turn with the alkaline constituents always present in drilling fluids of the type in question
25 here, for example with the alkali reserve used to prevent corrosion, to form the corresponding salts. However, salts of highly hydrophilic bases and the acids in the range from about C_{16} to C_{24} commonly encountered in fats and oils of natural origin are known to be compounds having compara-
30 tively high HLB values which lead in particular to the formation and stabilization of o/w emulsions. Use is made of this to a very considerable extent in the field of detergents and cleaning preparations. However, the formation of undesirably large quantities of such o/w emulsifier systems
35 must interfere with the w/o emulsions required for solving

the problem addressed by the invention and, hence, lead to problems. The teaching of the present invention as described in the following shows how invert drilling fluids based on ester oils can be effectively used in practice
5 despite these difficulties inherent in the system.

In a first embodiment, therefore, the present invention relates to the use of selected esters - flowable and pumpable at temperatures in the range from 0 to 5°C - of monofunctional C₂₋₁₂ alcohols and olefinically mono- and/or
10 polyunsaturated C₁₆₋₂₄ monocarboxylic acids as the oil phase or at least the predominant part of the oil phase of invert drilling muds which contain in a continuous oil phase a disperse aqueous phase and also emulsifiers, weighting agents, fluid loss additives, thickeners and, if desired,
15 other standard additives together with an alkali reserve, with the proviso that strong hydrophilic bases, such as alkali metal hydroxide and/or diethanolamine, are not used. Lime (calcium hydroxide) is often added as the alkali reserve, more especially for protection against intrushes of
20 CO₂ and/or H₂S into the drilling fluid and hence for protection against corrosion. An addition of lime such as this may be used as the alkali reserve in accordance with the invention. However, it is important to ensure that only comparatively small quantities of this alkaline
25 component are incorporated. In the preferred embodiment of the invention, the maximum addition of lime is of the order of 2 lb/bbl (lime/oil mud) and is thus distinctly below the quantities typically used in practice in oil-based invert drilling fluids.

30 In another embodiment, the invention relates to mineral-oil-free invert drilling fluids which are suitable for the offshore development of oil and gas occurrences and, in a continuous oil phase based on ester oils, contain a disperse aqueous phase together with emulsifiers, thickeners,
35 weighting agents, fluid loss additives and, if desired,

other standard additives. The new drilling fluids are characterized in that the oil phase consists at least predominantly of esters of monofunctional C_{2-12} alcohols and olefinically mono- and/or polyunsaturated C_{16-24} monocarboxylic acids and in that the w/o emulsion is mildly alkalized and, where lime is added, this alkali reserve does not exceed quantities of about 2 lb/bbl (lime/oil mud). The lime content is preferably slightly below this limit.

10 The ester oils selected in accordance with the invention which are intended to form the entire continuous oil phase of the invert drilling muds or at least a substantial part thereof are discussed first in the following.

As already stated, an important criterion lies in the
15 choice of esters which may be assigned to the class of reaction products of monofunctional carboxylic acids with monofunctional alcohols. In addition, however, it is intended in accordance with the invention exclusively or at least predominantly to use $C_{16}-C_{24}$ carboxylic acids within
20 this class. The carboxylic acids may be derived from unbranched or branched hydrocarbon chains, particular significance being attributed to the linear chains. Monocarboxylic acids of this type and of the C_{16} to C_{24} range in question here and esters thereof are unsuitable as predominantly saturated hydrocarbon compounds on account of their
25 comparatively high solidification points. Even then, however, esters of the type in question here are flowable and pumpable down to temperatures of 0 to 5°C providing an adequate level of olefinically unsaturated ester constituents
30 is guaranteed. In the preferred embodiment of the invention, therefore, esters of the described type of which more than 70% by weight and preferably more than 80% by weight are derived from olefinically unsaturated C_{16-24} carboxylic acids are used. Important natural starting materials are
35 carboxylic acid mixtures which contain at least 90% by

weight olefinically unsaturated carboxylic acids in the C range mentioned here. The unsaturated carboxylic acids may be mono- and/or polyolefinically unsaturated. Where carboxylic acids or carboxylic acid mixtures of natural origin are used, the double ethylenic double bond in particular and, to a lesser extent, even a triple ethylenic double bond per carboxylic acid molecule plays a certain part in addition to a single ethylenic double bond in the molecule. Particulars of this are given in the following.

10 In conjunction with the choice of esters of monofunctional reactants in accordance with the invention, the choice of such a comparatively highly unsaturated carboxylic acid component in the ester oils ensures that the ester oils and, ultimately, the final invert emulsions show
15 the rheologic properties required in practice, particularly at relatively low temperatures. The comparatively highly unsaturated ester oils containing 16 to 24 C atoms in the monocarboxylic acid component, which are used in accordance with the invention, have solidification points (pour point
20 and setting point) below -10°C and more especially below -15°C in the preferred embodiment. Despite this high mobility at low temperatures, the molecular size of the ester oil prescribed in accordance with the invention ensures that the flashpoints of the ester oils are sufficiently
25 high, being at least 80°C , but generally exceeding a temperature limit of approximately 100°C . Ester oils having flashpoints above 160°C are preferred. Ester oils of the described type showing high mobility, even at low temperatures, and having flashpoints of 185°C or higher may be
30 produced without difficulty.

In conjunction with these high flashpoints determined by the size of the molecule, it is possible at the same time to ensure that the viscosity values are within the required limits. Thus, preferred ester oils of the described type show a Brookfield (RVT) viscosity at a temper-

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ature of 0 to 5°C of not more than 55 mPa.s and preferably of at most 45 mPa.s or lower. It is possible to adjust values of 30 or even higher, for example in the range from 20 to 25 mPa.s, at temperatures in the range indicated.

5 Among the unsaturated ester oils suitable for use in accordance with the invention, there are two sub-classes of particular importance.

 The first of these sub-classes is based on unsaturated C₁₆₋₂₄ monocarboxylic acids of which no more than about 35%
10 by weight are diolefinically and, optionally, polyolefinically unsaturated. In their case, therefore, the content of polyunsaturated carboxylic acid residues in the ester oil is comparatively limited. Within this sub-class, however, it is preferred that at least about 60% by weight of the
15 carboxylic acid residues are monoolefinically unsaturated.

 In contrast to the first sub-class described above, the second sub-class of ester oils of practical significance is derived from C₁₆₋₂₄ monocarboxylic acid mixtures of which more than 45% by weight and preferably more than 55%
20 by weight are derived from diolefinically and/or polyolefinically unsaturated acids within the C range mentioned.

 The most important monoethylenically unsaturated carboxylic acids within the range in question here are hexadecenoic acid (palmitoleic acid (C₁₆), oleic acid (C₁₈), the
25 related ricinoleic acid (C₁₈) and erucic acid (C₂₂). The most important di-unsaturated carboxylic acid within the range in question here is linoleic acid (C₁₈) while the most important triethylenically unsaturated carboxylic acid is linolenic acid (C₁₈).

30 Selected individuals of the ester type formed from an unsaturated monocarboxylic acid and a monoalcohol may be used as the ester oil in accordance with the invention. One example of such esters are the esters of oleic acid, for example of the oleic acid isobutyl ester type. So far
35 as the rheology of the system is concerned and/or for

reasons of availability, it is frequently desirable to use acid mixtures. This is of importance so far as meeting the above-stated specifications of the two sub-classes for preferred ester oils is concerned.

5 As already mentioned, the first of these two sub-classes is distinguished by the fact that its content of di-unsaturated and polyunsaturated acids is limited and does not exceed about 35% by weight. Vegetable oils of natural origin, of which the hydrolysis or transesterifi-
10 cation gives mixtures of carboxylic acids or carboxylic acid esters of the type required here, are for example palm oil, peanut oil, castor oil and, in particular, rapeseed oil. Suitable rapeseed oils are both traditional types of high erucic acid content and also the more modern
15 types of reduced erucic acid content and increased oleic acid content.

 Ester oils of the first sub-class which correspond to this definition are particularly important for the simple reason that problems possibly arising in their case from
20 the lack of stability to oxidation are reduced. In practice, the drilling fluid is of course continuously pump-circulated and, in the process, is brought constantly into contact with atmospheric oxygen, often over a large area and at at least slightly elevated temperatures, for the
25 purpose of separating out the rock cuttings brought up, for example by sieving.

 However, carboxylic acid mixtures of the second subclass mentioned above are also of considerable practical significance for use in accordance with the invention.
30 This is attributable not least to their broad accessibility from natural fats of animal and/or vegetable origin. Classic examples of oils which have a high content of C_{16-18} or C_{16-22} carboxylic acids and which, at the same time, contain at least about 45% of at least diethylenically unsaturated
35 carboxylic acids are cottonseed oil, soybean oil, sunflower

oil and linseed oil. The tall oil acids isolated during the recovery of cellulose also fall within this range. However, starting materials of the last type are generally distinguished by more or less large additional contents of resin constituents. A typical animal starting material for the production of corresponding carboxylic acid mixtures is fish oil, particularly herring oil.

As already mentioned, the ester oils used in accordance with the invention may be certain selected individual esters corresponding to the above definition. However, mixtures of esters of corresponding monocarboxylic acids and monoalcohols will normally be present. In this regard, the scope of the invention encompasses above all those mixtures which, on the one hand, meet the viscosity requirement according to the invention and of which, on the other hand, at least 50 to 51% comprise the monofunctional esters of the olefinically mono- and/or polyunsaturated C_{16-24} carboxylic acids. Ester constituents and, in particular, carboxylic acid esters of monofunctional alcohols and monofunctional carboxylic acids of different constitution may be present as minor constituents of the mixture providing the mixture has the required property profile. This is important where carboxylic acid mixtures of natural origin are used. Natural starting materials such as these generally also contain more or less large proportions of saturated carboxylic acids, often including linear C_{16-18} carboxylic acids. Saturated fatty acids of this type and their esters readily give rise to rheologic difficulties on account of their comparatively high melting points. According to the invention, therefore, saturated C_{16-18} carboxylic acids preferably make up no more than about 20% by weight and, in particular, no more than about 10% by weight of the ester oils.

By contrast, the presence of, in particular, saturated carboxylic acids containing less than 16 carbon atoms and,

more especially, from 12 to 14 carbon atoms is more acceptable. In small quantities, the contents of such lower, fully saturated fatty acids often present in natural starting materials are frequently valuable mixture components in the context of the problem addressed by the invention. Their esters are not vulnerable to oxidation under practical in-use conditions and their rheologic properties promote the objective of the invention, namely to replace the pure hydrocarbon oils hitherto solely used in practice by ester oils or ester oil fractions.

The alcohol radicals of the esters or ester mixtures according to the invention are preferably derived from straight-chain and/or branched-chain saturated alcohols, particular significance being attributed to alcohols containing at least 3 C atoms and, more especially, to alcohols containing up to about 10 C atoms. The alcohols may also be of natural origin, in which case they have normally been obtained from the corresponding carboxylic acids or their esters by hydrogenating reduction. However, the invention is by no means limited to starting materials of natural origin. Both on the monoalcohol side and on the monocarboxylic acid side, the starting materials of natural origin may be partly or completely replaced by corresponding components of synthetic origin. Typical examples of alcohols are the corresponding oxo alcohols (branched alcohols) and the linear alcohols obtained by the Ziegler process. Similarly, monocarboxylic acid components present in particular in carboxylic acid mixtures may be derived from petrochemical synthesis. However, the advantages of starting materials of natural origin lie in particular in their proven lower toxicological values, their ready degradability and their ready accessibility. The natural destruction of the used oil mud ultimately required presupposes that ester oils of the type described herein be both aerobically and anaerobically degradable.

However, one important limitation is associated with the use of these ester oils in invert oil muds of the type in question. This limitation arises out of the difficulty mentioned at the beginning that, in principle, the carboxylic acid esters are vulnerable to hydrolysis and, accordingly, have to behave differently than the pure hydrocarbon oils hitherto used.

Invert drilling muds of the type in question contain the finely disperse aqueous phase, normally together with the continuous oil phase, in quantities of from about 5 to 45% by weight and preferably in quantities of from about 5 to 25% by weight. Particular significance is attributed to the range of about 10 to 25% by weight of disperse aqueous phase. This precondition from the constitution of conventional drilling muds also applies to the ester-based invert drilling muds in question here. It is clear that, in continuous practical operation, disturbances of the equilibrium can occur in the multiphase system as a result of partial ester hydrolysis.

The situation is complicated by the fact that, in practice, drilling muds of the type in question here always contain an alkali reserve. This alkali reserve is particularly important in affording protection against corrosion caused by unexpected intrushes of acidic gases, particularly CO_2 and/or H_2S . The danger of corrosion to the drill pipe requires the safe establishment of pH values at least in the mildly alkaline range, for example in the range from pH 8.5 to 9 and higher.

In oil muds based on pure hydrocarbon fractions as the oil phase, strongly alkaline and, at the same time, highly hydrophilic inorganic or organic additives are generally used in practice without any difficulty. Particular significance can be attributed to the alkali hydroxides and, in particular, to sodium hydroxide on the one hand or to highly hydrophilic organic bases, diethanolamine and/or

triethanolamine being particularly typical additives for binding impurities of H_2S . In addition to and/or instead of the highly hydrophilic inorganic and organic bases mentioned here, lime or even more weakly basic metal oxides, especially zinc oxide or comparable zinc compounds, are particularly important as the alkali reserve. Lime in particular is widely used as an inexpensive alkalizing agent. It may safely be used in comparatively high quantities of, for example, from 5 to 10 lb/bbl (lime/oil mud) or even higher.

10 The use of ester-based oil muds of the type described here requires a departure from standard practice so far as these variables are concerned. It is of course necessary in this case, too, to ensure that the pH value of the drilling mud is kept at least in the mildly alkaline range and that a sufficient quantity of alkali reserve is available for unexpected intrushes of, in particular, acidic gases. At the same time, however, the ester hydrolysis should not be undesirably promoted and/or accelerated by such an alkali content.

20 Thus, according to the invention, no highly hydrophilic, inorganic and/or organic bases are used in the oil mud. In particular, the invention does not use alkali hydroxides or highly hydrophilic amines of the diethanolamine and/or triethanolamine type. Lime may be effectively used as the alkali reserve. In that case, however, it is best to limit the maximum quantity of lime used in the drilling mud to around 2 lb/bbl or slightly lower, for example to between about 1 and 1.8 lb/bbl (lime/drilling mud). In addition to or instead of lime, it is also possible to use other known alkali reserves, including in particular the less basic metal oxides of the zinc oxide type and other comparable zinc compounds. However, even where acid-binding agents such as these are used, it is important not to use excessive amounts to prevent unwanted premature ageing of the drilling mud accompanied by an

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increase in viscosity and hence a deterioration in the rheologic properties. The particular aspect of the teaching according to the invention in question here prevents or at least limits the formation of unwanted quantities of highly active o/w emulsifiers to such an extent that the favorable rheologic properties are maintained for sufficiently long periods in operation, even in the event of thermal ageing. In relation to the recommendations of the prior art which have hitherto remained in the realm of theoretical considerations, this represents a significant surplus which actually enables the low toxic properties of ester oils of the type in question to be utilized in practice for the first time.

The esters based on olefinically unsaturated C_{16-24} monocarboxylic acids defined in accordance with the invention, which flow and can be pumped at temperatures in the range from 0 to 5°C, generally make up at least about half the continuous oil phase of the drilling mud. However, preferred oil phases are those in which esters or ester mixtures of the type according to the invention are very much predominantly present. In one particularly important embodiment of the invention, the oil phase consists almost entirely of such ester oils. Components suitable for mixing with the ester oils defined in accordance with the invention are, in particular, selected other ester oil fractions which are described in the parallel EP-A1-0 374 672. The invention also encompasses mixtures with such other selected ester oils.

The following rheologic data apply to the rheology of preferred invert drilling muds according to the invention: plastic viscosity (PV) in the range from about 10 to 60 mPa.s and preferably in the range from about 15 to 40 mPa.s, yield point (YP) in the range from about 5 to 40 lb/100 ft² and preferably in the range from about 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 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 one of the joint Applicants, NL-Baroid, cf. in particular the Chapter entitled "Mud Testing - Tools and Techniques" and "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. Selected oleophilic fatty acid salts, for example those based on amidoamine compounds, are particularly suitable, examples being described in the already cited US-PS 4,374, 737 and the literature cited therein. One particularly suitable type of emulsifier is the product marketed under the name of "EZ-mul" by the joint Applicant, NL Baroid.

Emulsifiers of the type in question here are marketed in the form of concentrates and may be used, for example, in quantities of from about 2.5 to 5% by weight and more especially in quantities of from about 3 to 4% by weight, based in each case on the 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. Suitable quantities are, for example, in the range from about 15 to 20 lb/bbl or in the range from about 5 to 7% by weight, based on the ester oil phase.

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 from about 8 to 10 lb/bbl or in the range from about 2 to 4% by weight, based on the es-

ter oil phase. The weighting agent normally used in practice to establish the necessary pressure equalization is baryta which is added in quantities adapted to the particular conditions to be expected in the well. For example,
5 it is possible by addition of baryta to increase the specific gravity of the drilling mud to values of up to about 2.5 and preferably in the range from about 1.3 to 1.6.

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
10 aqueous phase preferably being saturated with the soluble salt at room temperature.

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 imidazole compounds are mentioned as further examples. Additional information on the relevant prior art can be found in the following literature references: GB 2,158,437, EP
15 229 912 and DE 32 47 123.

In addition to the advantages already mentioned, the drilling fluids based in accordance with the invention on the co-use of ester oils of the described type are also distinguished by distinctly improved lubricity. This is
25 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
30 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 have been used for
35 converting units of measurement typically used in the field

in question which do not correspond to the metric system and which have been used in this typical form in the specification and Examples:

5 1 lb - 0.454 kg; 1 bbl = 159 l;

1 lb/bbl = 2.85 kg/m³, particularly in conjunction with the quantity of alkali reserve added;

10 1 lb/100 ft² = 0.4788 Pa, particularly in conjunction with the determination of yield point (YP) and gel strength.

Examples

15 Example 1

An invert drilling mud is prepared using an undistilled isobutyl rapeseed oil ester as continuous oil phase. This rapeseed oil ester is based on a mixture of predominantly unsaturated, straight-chain carboxylic acids which correspond substantially to the following distribution: 60% oleic acid, 20% linoleic acid, 9 to 10% linolenic acid, olefinically unsaturated C₂₀₋₂₂ monocarboxylic acids approximately 4%, remainder saturated monocarboxylic acids predominantly in the C₁₆₋₁₈ range.

25 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; no aromatic compounds.

30 An invert drilling mud is conventionally prepared using the following mixture constituents:

230 ml rapeseed oil fatty acid ester

26 ml water

6 g organophilic bentonite (GELTONE, a product of BAROID DRILLING FLUIDS, INC.)

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- 0.2 g lime
 6 g w/o emulsifier ("EZ-MUL", a product of BAROID DRILLING FLUIDS, INC.)
 340 g baryta
 5 9.2 g $\text{CaCl}_2 \times 2\text{H}_2\text{O}$
 20 g organophilic lignite ("DURATONE", a product of BAROID DRILLING FLUIDS, INC.)

Plastic viscosity (PV), yield point (YP) and gel strength after 10 seconds and 10 minutes are first determined on the material before ageing by viscosity measurement at 50°C.

The invert drilling mud is then aged for 16 h at 125°C in an autoclave in a so-called "roller oven" to determine the effect of temperature on the stability of the emulsion.
 15 The viscosity values are then redetermined at 50°C.

The following results are obtained:

	Unaged material	Aged material
20 Plastic viscosity (PV)	35	62
Yield point (YP)	21	24
25 Gel strength (lb/100 ft ²)		
10 seconds	12	12
10 minutes	14	15

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Comparison Example 1

Another invert drilling mud is prepared in the same way as in Example 1, except that on this occasion the quantity of lime is increased to 4 g, i.e. drastically beyond
 35 the limit of approximately 2 lb/bbl.

Once again, the viscosity values and gel strength of the material are determined before and after ageing. The following results are obtained:

		Unaged material	Aged material
5	Plastic viscosity (PV)	41	cannot be meas- ured
10	Yield point (YP)	22	cannot be meas- ured
	Gel strength (lb/100 ft ²)		
	10 seconds	11	74
15	10 minutes	17	72

Example 2

20 Another invert drilling mud is prepared with a continuous oil phase. The oil phase consists of distilled oleic acid isobutyl ester which has the following characteristic data: density (20°C) 0.86 g/cm³; viscosity (20°C) 8 to 10 mPa.s; pour point below -25°C; flash point (DIN 51584) 25 above 185°C; acid value (DGF-C-V 2) below 1; no aromatic compounds.

A drilling mud of the following composition is prepared:

210	ml	isobutyl oleate
30	6	g fatty-acid-based emulsifier (INVERMUL, a product of BAROID DRILLING FLUIDS, INC.)
	6	g organophilic bentonite (GELTONE, a product of BAROID DRILLING FLUIDS, INC.)
35	13	g organophilic lignite (DURATONE, a product of BAROID DRILLING FLUIDS, INC.)
	1	g lime
	3	g w/o emulsifier (EZ-MUL, a product of BAROID DRILLING FLUIDS, INC.)
	270	g baryta
40	58.2	g saturated aqueous CaCl ₂ solution

Plastic viscosity, yield point and gel strength after 10 seconds and 10 minutes are determined before and after ageing (16 h at 125°C in a roller oven) in the same way as in Example 1. The results obtained are shown below. In the formulation used here, 1.2 kg lime substantially corresponds to the limit of 2 lb/bbl.

	Unaged material	Aged material
Plastic viscosity (PV)	46	41
Yield point (YP)	35	32
Gel strength (lb/100 ft ²)		
10 seconds	17	18
10 minutes	21	29

Compatison Example 2

Another invert drilling oil emulsion is prepared using the formulation of Example 2, except that the addition of lime is increased to 2 g and hence to clearly beyond the limit of 2 lb/bbl. The plastic viscosity, yield point and gel strength of the material before and after ageing are shown in the following:

	Unaged material	Aged material
Plastic viscosity (PV)	53	46
Yield point (YP)	61	45
Gel strength (lb/100 ft ²)		
10 seconds	33	24
10 minutes	40	29

**CLAIMS**

1. The use of selected esters - flowable and pumpable at temperatures in the range from 0 to 5°C - of monofunctional C₂₋₁₂ alcohols and olefinically mono- and/or polyunsaturated
5 C₁₆₋₂₄ monocarboxylic acids as the oil phase or at least the predominant part of the oil phase of invert drilling muds which are suitable for the ecologically safe offshore development of oil and gas occurrences and which, in a continuous oil phase, contain a disperse aqueous phase and
10 also emulsifiers, weighting agents, fluid loss additives, thickeners and, if desired, other standard additives together with an alkali reserve, with the proviso that strong hydrophilic bases, such as alkali metal hydroxide and/or diethanolamine, are not used and any addition of
15 lime present is limited to a maximum of about 2 lb/bbl oil mud.
2. The use claimed in claim 1, characterized in that esters of which more than 70% by weight, preferably more than 80% by weight and, more preferably, more than 90% by weight
20 are derived from olefinically unsaturated C₁₆₋₂₄ carboxylic acids are used.
3. The use claimed in claims 1 and 2, characterized in that the esters used in the drilling mud have solidification points (pour point and setting point) below -10°C,
25 preferably below -15°C, and flash points above 100°C and preferably above 160°C.
4. The use claimed in claims 1 to 3, characterized in that 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
30 preferably of no more than 45 mPa.s.
5. The use claimed in claims 1 to 4, characterized in that no more than 35% by weight of the unsaturated C₁₆₋₂₄ monocarboxylic acids present in the ester are derived from di- and polyolefinically unsaturated acids and at least
35 about 60% by weight are preferably monoolefinically un-



saturated.

6. The use claimed in claims 1 to 4, characterized in that more than 45% by weight and preferably more than 55% by weight of the C₁₆₋₂₄ monocarboxylic acids present in the ester mixture are derived from di- and/or polyolefinically unsaturated acids.

7. The use claimed in claims 1 to 6, characterized in that residues of saturated C₁₆₋₁₈ carboxylic acids present in the ester mixture make up no more than 20% by weight and, in particular, no more than 10% by weight, but preferably contain fewer carbon atoms, preferably 12 to 14 carbon atoms.

8. The use claimed in claims 1 to 7, characterized in that the carboxylic acid residues present in the ester or ester mixture are at least predominantly linear and are preferably of vegetable and/or animal origin, being derived in particular from triglycerides of vegetable origin and/or fish oils and fats.

9. The use claimed in claims 1 to 8, characterized in that the esters are used in drilling fluids which, in the invert drilling mud, contain the finely disperse aqueous phase together with the continuous ester-based oil phase in quantities of 5 to 45% by weight and preferably in quantities of 5 to 25% by weight.

10. The use claimed in claims 1 to 9, characterized in that the alcohol radicals of the esters used are derived from straight-chain and/or branched, saturated alcohols preferably containing from 4 to 10 C atoms.

11. Mineral-oil-free invert drilling fluids which are suitable for the offshore development of oil and gas occurrences and which, in a continuous oil phase based on ester oils, contain a disperse aqueous phase together with emulsifiers, thickeners, weighting agents, fluid loss additives and, if desired, other standard additives, characterized in that the oil phase consists at least



predominantly of esters of monofunctional alcohols containing 2 to 12 C atoms and olefinically mono- and/or polyunsaturated monocarboxylic acids containing 16 to 24 C atoms and in that the w/o emulsion is mildly alkalized and, where
5 lime is added as alkali reserve, the quantity added should not exceed about 2 lb/bbl (lime/oil mud) and is preferably slightly smaller.

12. An invert drilling fluid as claimed in claim 11, characterized in that the oil mud does not contain highly
10 hydrophilic bases, such as alkali hydroxides, or highly hydrophilic amines, such as diethanolamine, and in that limited quantities of metal oxides of the zinc oxide type are optionally present as alkali reserve in addition to or instead of lime.

15 13. Drilling fluids as claimed in claims 11 and 12, characterized in that they have a plastic viscosity (PV) in the range from 10 to 60 mPa.s and a yield point (YP) in the range from 5 to 40 lb/100 ft², as measured at 50°C.

14. Drilling fluids as claimed in claims 11 to 13, characterized in that their disperse water content is from 5 to
20 45% by weight and preferably from 10 to 25% by weight and, in particular, contains dissolved salts of the CaCl₂ and/or KCl type.

15. Drilling fluids as claimed in claims 11 to 14, characterized in that the oil phase of the invert mud has a
25 Brookfield (RVT) viscosity at 0 to 5°C of below 50 mPa.s and preferably not exceeding 40 mPa.s.