

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 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Oil-based drilling fluids were originally made from diesel oil fractions containing aromatic constituents.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 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 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 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 oil-based drilling fluids 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 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 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 rheological 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 monofunctional 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 based on ester oils of high environmental compatibility which correspond in their storage and in-use behaviour to the best of the hitherto known oil-based invert drilling fluids, but have the additional advantage of increased environmental compatibility. Two key observations in this regard 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 alcohols 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 behaviour as the mineral oil fractions used hitherto based purely on hydrocarbons. 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 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 having chain lengths of up to about C_{24} , more especially the relatively long-chain acids in the range from about C_{16} to C_{22} , commonly encountered in fats and oils of natural origin are known to be compounds having comparatively 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 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 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 C_{2-12} , more especially C_{4-12} alcohols and

aliphatically saturated C_{12-16} monocarboxylic acids as the oil phase or at least a predominant part of the oil phase of invert drilling muds which contain in a continuous oil phase a disperse aqueous phase together with emulsifiers, weighting agents, fluid loss additives, thickeners and, if desired, other standard additives.

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, 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 C_{2-12} alcohols and aliphatically saturated C_{12-16} monocarboxylic acids. According to one preferred element of the invention, the ester oils of the continuous oil phase have a Brookfield (RVT) viscosity of no more than 50 mPa.s at a temperature in the range from 0 to 5°C.

In one particularly preferred embodiment of the two embodiments of the invention as described here, at least the predominant part, i.e. at least about 50 to 51%, of the ester oils used is based on aliphatic C_{12-14} monocarboxylic acids, ester oils of which at least about 60% by weight, based on the particular carboxylic acid mixture present, are esters of such aliphatic C_{12-14} monocarboxylic acids being particularly suitable.

In one important embodiment, the ester oil contains only saturated aliphatic monocarboxylic acids of the broader C_{12-16} range mentioned, but more especially of the C_{12-14} range. However, the invention is by no means confined to this range. It can be of advantage to use esters of other carboxylic acids in at most substantially the same quantity and preferably in small quantities. In this case, relatively short-chain aliphatic monocarboxylic acids or

esters thereof and/or esters of relatively long-chain carboxylic acids may be considered. However, in cases where esters of relatively long-chain carboxylic acids are used, it is preferred at least partly to use corresponding
5 mono- and/or polyolefinically unsaturated, relatively long-chain carboxylic acid derivatives. In this embodiment, suitable mixture components are, above all, mono- and/or polyolefinically unsaturated C₁₆₋₂₄ and more especially C₁₈₋₂₂ monocarboxylic acid esters.

10 In another important and preferred embodiment of the invention which is discussed in more detail hereinafter, significant quantities of strong hydrophilic bases, such as alkali metal hydroxide and/or diethanolamine, are not used in the invert drilling mud where the ester oils defined
15 herein are present.

It is known that state-of-the-art invert drilling muds incorporating a continuous oil phase always contain an alkali reserve, particularly for protection against in-rushes of CO₂ and/or H₂S into the drilling mud and hence
20 for protecting metal parts of the drill pipe against corrosion. A useful alkali reserve in the context of the teaching of the invention comprises the addition of lime (calcium hydroxide) or the co-use of more weakly basic metal oxides, for example of the zinc oxide type and/or
25 other zinc compounds. Further particulars of these elements of the teaching of the invention are given herein-after. 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 the
30 predominant part thereof are discussed first in the following.

The ester oils used in accordance with the invention of monofunctional alcohols and selected monocarboxylic acids may be derived from unbranched or branched hydro-
35 carbon chains. Particular significance is attributed to

the esters of corresponding straight-chain acids. Saturated C_{12-16} and more especially C_{12-14} monocarboxylic acids and monofunctional alcohols having the C chain lengths defined in accordance with the invention can form ester oils which show adequate rheological properties, even down to temperatures in the range from 0 to 5°C, and in particular are flowable and pumpable in that temperature range. In the context of the invention, preferred esters for the oil phase of drilling muds are saturated components which have a Brookfield (RVT) viscosity at a temperature of 0 to 5°C of no more than 50 mPa.s and preferably of no more than 40 mPa.s. By selecting suitable components for the ester-forming reaction, it is possible to adjust the viscosity at temperatures in the above-mentioned range of 0 to 5°C to values of at most about 30 mPa.s, for example in the range from about 10 to 20 mPa.s. It is clear that this affords important advantages for offshore drilling where the surrounding water can have very low temperatures.

In the preferred embodiment, the ester oils used in accordance with the invention based on selected individual components or on ester mixtures have solidification values (pour point and setting point) below -10°C and more especially below -15°C. Despite this high mobility at low temperatures, the molecular size of the ester oil prescribed in accordance with the invention ensures that the flash points of the ester oils are sufficiently high, being at least 80°C, but generally exceeding a temperature limit of about 100°C. Ester oils having flash points above 150-160°C are preferred. It is possible to produce ester oils of the described type which have flash points of 185°C or higher.

In another important embodiment, the ester oils of the range required in accordance with the invention for the saturated C_{12-16} monocarboxylic acids are derived from materials of predominantly vegetable origin. Carboxylic

acids or carboxylic acid mixtures predominantly containing saturated monocarboxylic acids within the stated range may be obtained, for example, from renewable triglycerides, such as coconut oil, palm kernel oil and/or babassu oil.

5 Fatty acid mixtures of this origin normally contain a limited quantity of lower fatty acids (C_{6-10}) of generally at most about 15%. Their content of C_{12-14} acids is by far predominant, generally making up at least 50% and normally 60% or more of the carboxylic acid mixture. The small
10 remainder consists of higher fatty acids, unsaturated components playing a considerable role in this range. Accordingly, carboxylic acid mixtures of this type, by virtue of their natural structure, readily lead to materials having satisfactory rheological properties.

15 In one embodiment of the invention, suitable mixture components likewise of natural origin are, in particular, monofunctional ester oils of the type described in EP-A1-0 374 671. In the context of the teaching of the present invention, however, these mixture components are preferably
20 used in small quantities (at most about 49%, based on the ester oil mixture). To complete the disclosure of the invention, this class of possible mixture components is briefly discussed in the following. Further particulars can be found in the parallel application.

25 These possible mixture components are esters of monofunctional C_{2-12} alcohols and mono- and/or polyolefinically unsaturated C_{16-24} monocarboxylic acids. In this case, too, the carboxylic acids may be derived from unbranched or branched hydrocarbon chains, particular significance again
30 being attributed the straight-chain acids. Esters of the higher chain lengths in question here are flowable and pumpable down to temperatures of 0 to 5°C providing an adequate level of olefinically unsaturated ester constituents is guaranteed. In the preferred embodiment of the
35 invention, therefore, esters of this type, of which more

than 70% by weight and preferably more than 80% by weight are derived from olefinically unsaturated C₁₆₋₂₄ carboxylic acids are used. Important natural starting materials are 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.

These esters of unsaturated, relatively long-chain monocarboxylic acids used as mixture component preferably have solidification values (pour point and setting point) below -10°C and more especially below -15°C. By virtue of the size of their molecule, these mixture components also have flash points in the desired range, i.e. at least above 80°C, preferably above 100°C and more especially above 160°C. In the preferred embodiment, mixture components of this type are intended to have Brookfield (RVT) viscosities at 0 to 5°C of no more than 55 mPa.s and preferably of at most 45 mPa.s.

Among these highly unsaturated mixture components, 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% 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 carboxylic acid residues are monoolefinically unsaturated.

In contrast to the first sub-class described above, the second sub-class of ester oils of practical signifi-

cance is derived from C_{16-24} monocarboxylic acid mixtures of which more than 45% by weight and preferably more than 55% by weight are derived from diolefinically and/or polyolefinically unsaturated acids within the C chain length range mentioned.

The most important monoethylenically unsaturated carboxylic acids within the range in question here are hexadecenoic acid (palmitoleic acid (C_{16}), oleic acid (C_{18}), the related ricinoleic acid (C_{18}) and erucic acid (C_{22}). The most important di-unsaturated carboxylic acid within the range in question here is linoleic acid (C_{18}) while the most important triethylenically unsaturated carboxylic acid is linolenic acid (C_{18}).

Selected individuals of the ester type formed from an unsaturated monocarboxylic acid and a monoalcohol may be used as mixture component. One example of such esters are the esters of oleic acid, for example of the oleic acid isobutyl ester type. So far as the rheology of the system is concerned and/or for reasons of availability, it is frequently desirable to use acid mixtures.

Vegetable oils of natural origin, of which the hydrolysis or transesterification gives mixtures of carboxylic acids or carboxylic acid esters of the first sub-class mentioned above 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 types of reduced erucic acid content and increased oleic acid content.

Carboxylic acid mixtures of the second sub-class mentioned above are also widely available from natural fats of vegetable and/or animal 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 carboxylic acids are cottonseed oil, soybean oil, sunflower oil and

linseed oil. The tall oil fatty acids isolated during the recovery of cellulose also fall within this range. A typical example of an animal starting material for the production of corresponding carboxylic acid mixtures is fish oil, particularly herring oil.

Another factor to be taken into consideration in the choice of the saturated ester oils used in accordance with the invention, particularly the mixtures of ester oils just mentioned, is that saturated carboxylic acid esters containing 16 and more C atoms can have comparatively high boiling points and hence readily give rise to rheological difficulties. According to the invention, therefore, saturated carboxylic acids containing 16-18 or more C atoms 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 saturated carboxylic acids containing less than 12 carbon atoms is more acceptable. On the contrary, they can be valuable mixture components for the ester oil phases selected in accordance with the invention. Their esters are as invulnerable to oxidation under practical in-use conditions as the saturated principal components envisaged in accordance with the invention, particularly in the C_{12-14} range. The rheological properties of the lower fatty acid esters promote the objective of the invention, namely to replace the pure hydrocarbon oils hitherto solely used in practice at least partly, preferably predominantly or even completely 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 4 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.

5 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
10 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
15 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
20 degradable.

 However, another important aspect of using ester oils of the type in question as sole or predominant constituent in invert oil muds of the type in question has to be taken into consideration. This concerns the difficulty mentioned
25 at the beginning that, in principle, the carboxylic acid esters are vulnerable to hydrolysis and, accordingly, have to behave differently from the pure hydrolysis-stable hydrocarbon oils hitherto used.

 Invert drilling muds of the type in question contain
30 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
35 phase. This precondition from the constitution of conven-

tional 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 in this regard to the alkali metal 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, calcium hydroxide (lime) or even more weakly basic metal oxides, especially zinc oxide and other 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.

The use of ester-based oil muds of the type described here may require 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.

Thus, in the preferred embodiment of the invention, no significant quantities of highly hydrophilic, inorganic and/or organic bases are used in the oil mud. In particular, the invention does not use alkali metal 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 and preferably, 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. 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 increase in viscosity and hence a deterioration in the rheological 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 favourable rheological 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 saturated C₁₂₋₁₆ 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 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 the compounds described in the parallel EP-A1-0 374 671. The invention also encompasses mixtures with such other selected ester oils.

The following rheological 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, BAROID DRILLING FLUIDS, INC., 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, BAROID DRILLING FLUIDS, INC. Emulsifiers of the type in question here are marketed in the form of highly concentrated preparations 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.

10 In practice, organophilic 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, organophilic 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 ester 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, 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.

30 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.

35 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 in the following literature references: GB 2,158,437, EP 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 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.

Examples

In Examples 1 and 2 below and the Comparison Examples, distilled lauric acid/n-hexyl ester is used as the ester oil for forming the continuous oil phase. It is a whitish-yellow liquid with a flash point above 165°C, a pour point below -5°C, a density (20°C) of 0.857 to 0.861, an iodine value and an acid value both below 1, a water content below 0.3% and the following viscosity data (Brookfield mPa.s): 22.5 to 25.5 at -5°C; 15 to 18 at +2°C; 15 to 18 at +5°C; approx. 15 at +10°C; 12 to 14 at 20°C.

Example 1

A w/o invert drilling mud is prepared in known manner

from the components listed below, after which the viscosity data of the material before and after ageing are determined as follows:

5 Measurement of viscosity at 50°C in a Fann 35 viscosimeter of BAROID DRILLING FLUIDS, INC. Plastic viscosity (PV), yield point (YP) and gel strength (lb/100 ft²) after 10 secs. and 10 mins. are determined in known manner.

10 The measurements are carried out before and after ageing of the material, ageing being obtained by treatment in an autoclave - in a so-called roller oven - for 16 h at 125°C. The following composition is selected for the drilling mud:

230	ml ester oil
15 26	ml water
6	g organophilic bentonite (Geltone, a product of BAROID DRILLING FLUIDS, INC.)
6	g organophilic lignite (Duratone, a product of BAROID DRILLING FLUIDS, INC.)
20 1	g lime
6	g w/o emulsifier (EZ-mul, a product of BAROID DRILLING FLUIDS, INC.)
346	g baryta
9.2	g CaCl ₂ x 2H ₂ O

25

In this formulation, approximately 1.35 kg. lime correspond to the limit of 2 lb/bbl.

30 The characteristic data determined on the material before and after ageing as described above are shown in the following Table:

		Unaged material	Aged material
5	Plastic viscosity (PV)	28	28
	Yield point (YP)	11	14
	Gel strength (lb/100 ft ²)		
10	10 seconds	5	6
	10 minutes	7	8

Comparison Example 1

15 The invert drilling mud of Example 1 is prepared using the same quantities except that, on this occasion, the quantity of lime is increased to three times (3 g).

 The characteristic data determined before and after ageing of the material are shown in the following Table:

20

		Unaged material	Aged material
25	Plastic viscosity (PV)	31	72
	Yield point (YP)	8	59
30	Gel strength (lb/100 ft ²)		
	10 seconds	5	13
	10 minutes	7	74

35

Example 2

 A particularly heavily weighted invert drilling mud is prepared in accordance with the following formulation:

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184	ml ester oil
10	ml water
2	g organophilic bentonite (Geltone, a product of BAROID DRILLING FLUIDS, INC.)

20 g organophilic lignite (Duratone, a product
of BAROID DRILLING FLUIDS, INC.)
1 g lime
10 g w/o emulsifier (EZ-mul, a product of BAROID
5 DRILLING FLUIDS, INC.)
568 g baryta
4.8 g $\text{CaCl}_2 \times 2 \text{H}_2\text{O}$

10 The characteristic data of the material are determined
before and after ageing as in Example 1. The values
obtained are shown in the following Table:

	Unaged material	Aged material
15 Plastic viscosity (PV)	20	81
20 Yield point (YP)	12	16
Gel strength (lb/100 ft ²)		
10 seconds	8	8
10 minutes	10	11

25 In this Example, approximately 1.04 g lime correspond
to the limit of 2 lb/bbl.

Comparison Example 2

30 The heavily weighted formulation of Example 2 is
repeated. On this occasion, however, the lime content is
doubled (2 g).

35 The characteristic data of the material before and
after ageing are again determined and are shown in the
following Table:

		Unaged material	Aged material
5	Plastic viscosity (PV)	78	73
	Yield point (YP)	37	59
	Gel strength (lb/100 ft ²)		
10	10 seconds	12	18
	10 minutes	16	27

The ester oil used to form the continuous oil phase in Examples 3 and 4 below is an ester mixture of substantially saturated fatty acids based on palm kernel oil and 2-ethyl hexanol, of which by far the predominant part is made up of C₁₂₋₁₄ fatty acids and which corresponds to the following specification:

C₈ : 3.5 to 4.5% by weight
 C₁₀: 3.5 to 4.5% by weight
 C₁₂: 65 to 70 % by weight
 C₁₄: 20 to 24 % by weight
 C₁₆: approx. 2 % by weight
 C₁₈: 0.3 to 1 % by weight

The ester mixture is present in the form of a light yellow liquid with a flash point above 165°C, a pour point below -10°C, a density (20°C) of 0.86 and an acid value below 0.3. In the low-temperature range, the ester mixture shows the following viscosity data (Brookfield, mPas):
 -5°C 20 to 22; 0°C 16 to 18; +5°C 13 to 15; +10°C approx. 11; 20°C 7 to 9.

Example 3

As in the preceding Examples, a w/o invert drilling mud is prepared from the following components. The viscosity data of the material are determined before and after

ageing.

The following composition is selected for the drilling mud:

5	230	ml ester oil
	6	g emulsifier 1 (INVERMUL NT, a product of the joint applicant, Baroid)
	26	g water
	6	g organophilic bentonite (GELTONE)
10	12	g organophilic lignite (DURATONE)
	1.5	g lime
	6	g emulsifier 2 (EZ-MUL)
	346	g baryta
	9.2	g $\text{CaCl}_2 \times 2\text{H}_2\text{O}$

15

The characteristic data determined on the material before and after ageing are shown in the following Table:

20		Unaged material	Aged material
	Plastic viscosity (PV)	37	30
25	Yield point (YP)	16	14
	Gel strength (lb/100 ft ²)		
	10 seconds	7	5
	10 minutes	10	9

30

Example 4

A 40% water-containing w/o invert drilling mud having the following composition is prepared using the ester oil described just before the preceding Example.

35

350	ml ester oil
20	g emulsifier (EZ-MUL)

8 g organophilic lignite (DURATONE)
4 g lime
6 g organophilic bentonite (GELTONE)
234 ml water
5 99 g $\text{CaCl}_2 \times 2\text{H}_2\text{O}$
150 g baryta

The material shows the following plastic viscosity and yield point values before and after ageing:

10

	Unaged material	Aged material
15 Plastic viscosity (PV)	33	32
Yield point (YP)	77	56

**CLAIMS**

1. The use of selected esters - flowable and pumpable at temperatures in the range from 0 to 5°C - of monofunctional C₂₋₁₂, more especially C₄₋₁₂ alcohols and aliphatically saturated C₁₂₋₁₆ monocarboxylic acids as the oil phase or at least a predominant part of the oil phase of invert drilling muds which are suitable for the ecologically safe development of oil and gas occurrences and which contain in a continuous oil phase a disperse aqueous phase together with emulsifiers, weighting agents, fluid loss additives, thickeners and, if desired, other standard additives.
2. The use claimed in claim 1, characterized in that ester oils are used of which at least about 60% by weight, based on the carboxylic acid mixture, are esters of aliphatic C₁₂₋₁₄ monocarboxylic acids, the rest - if desired - consisting of esters of relatively short-chain aliphatic and/or relatively long-chain monocarboxylic acids, more especially, mono- and/or polyolefinically unsaturated monocarboxylic acids.
3. The use claimed in claims 1 and 2, characterized in that ester oils are used in alkalized drilling muds with an alkali reserve, lime and/or metal oxides of the zinc oxide type being present as the alkali reserve.
4. The use claimed in claims 1 to 3, characterized in that the ester oils are used in drilling muds which contain lime in a quantity of no more than about 2 lb/bbl (lime/drilling mud) as the alkali reserve.
5. The use claimed in claims 1 to 4, characterized in that esters having a Brookfield (RVT) viscosity at 0 to 5°C of no more than 50 mPa.s, preferably no more than 40 mPa.s and, in particular, at most about 30 mPa.s are used in the oil phase of drilling muds.
6. The use claimed in claims 1 to 5, characterized in that the esters used in the drilling mud have solidification values (pour point and setting point) below -10°C and



preferably below -15°C and flash points above 100°C and preferably above 150°C .

5 7. The use claimed in claims 1 to 6, characterized in that the carboxylic acids present in the ester or ester mixture are at least predominantly linear and are preferably of vegetable origin, being derived in particular from corresponding triglycerides, such as coconut oil, palm kernel oil and/or babassu oil.

10 8. The use claimed in claims 1 to 7, characterized in that the esters are used in drilling muds which contain the finely disperse aqueous phase in quantities of from about 5 to 45% by weight and preferably in quantities of from about 5 to 25% by weight in the invert drilling mud together with the continuous ester-based oil phase.

15 9. The use claimed in claims 1 to 8, characterized in that the alcohol radicals of the esters used are derived from linear and/or branched saturated alcohols preferably containing 4 to 10 C atoms.

20 10. The use claimed in claims 1 to 9, characterized in that the alcohol components of the ester oils used are of vegetable and/or animal origin and have been obtained by reductive hydrogenation of corresponding carboxylic acid esters.

25 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
30 predominantly of esters of monofunctional alcohols containing 2 to 12 C atoms and aliphatically saturated monocarboxylic acids containing 12 to 16 C atoms, these esters of the oil phase having a Brookfield (RVT) viscosity at 0 to
35 5°C of no more than 50 mPa.s.



12. A drilling fluid as claimed in claim 11, characterized in that the invert drilling fluid is mildly alkalized and contains an alkali reserve, but preferably not strongly hydrophilic bases, such as alkali metal hydroxide, or
5 strongly hydrophilic amines, such as diethanolamine.

13. A drilling fluid as claimed in claims 11 and 12, characterized in that lime and/or metal oxides of the zinc oxide type are present as the alkali reserve, lime additions of up to about 2 lb/bbl (lime/drilling fluid) being
10 preferred.

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

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