

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-based 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.

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.

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 muds in which non-polluting 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 non-polluting 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 use of oils of vegetable and/or animal origin 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.

Ester oils of the type in question here do not in fact show the same in-use behavior 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.

Earlier applications P 38 42 659.9 and P 38 42 703.6 (D 8523 "The use of selected ester oils in drilling muds (I)" and D 8524 "The use of selected ester oils in drilling muds (II)") describe the problems which this causes and put forward proposals for solving those problems.

These earlier applications relate to the use of ester oils based on selected monocarboxylic acids or monocarboxylic acid mixtures and monofunctional alcohols containing at least 2 and preferably at least 4 carbon atoms. The earlier applications 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. The alkali reserve is formed by the addition of lime (calcium hydroxide) and/or by the presence of zinc oxide or comparable zinc compounds. However, an additional limitation is appropriate in this regard. 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 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.

The teaching of the invention described in the following broadens the range of ester oils which may be used with advantage in the w/o drilling muds in question.

In a first embodiment, therefore, the present invention relates to the use of esters of C_{6-11} monocarboxylic acids of synthetic and/or natural origin and mono- and/or polyhydric alcohols, which flow at room temperature and have flash points above 80°C , as the oil phase or as part of the oil phase of invert drilling muds which are suitable for the ecologically safe development of, for example, oil and gas occurrences and which, in a continuous oil phase, contain a disperse aqueous phase together with emulsifiers, weighting agents, fluid loss additives and, if desired, other standard additives.

In another embodiment, the invention relates to invert drilling muds of the described type which are characterized

in that the oil phase contains esters of C₆₋₁₁ monocarboxylic acids of synthetic and/or natural origin and mono- and/or polyfunctional alcohols which flow at room temperature and have flash points above 80°C, if desired in admixture with other components from the class of ecologically safe compounds (non-polluting oils).

Alcohol components which are ecologically and toxicologically safe in practical application, even after partial ester cleavage, are preferably used in the ester oils thus defined. In this respect, the invention particularly takes into account the inhalation-toxicological problems involved in handling the oil mud in practice.

The ester oils used in accordance with the invention are described in more detail in the following, subsequent chapters being concerned with possible mixture components and with further particulars of the invention.

The ester oils used in accordance with the invention

On the carboxylic acid side, the ester oils described in accordance with the invention are based on synthetic and/or natural monocarboxylic acids containing 6 to 11 carbon atoms which may be linear and/or branched. Linear and, in general, even-numbered carboxylic acids in this range are derived in particular from oils or fats of natural origin where they form the so-called head-fractionated fatty acids in the C₆₋₁₀ range. Synthetic carboxylic acids of this type are also readily obtainable, for example by oxidation of Ziegler alcohols. Branched carboxylic acids and mixtures of branched and straight-chain carboxylic acids in the range in question are available from numerous petrochemical processes.

Preferred esters of these medium-chain carboxylic acids with monohydric and/or polyhydric alcohols are flowable and pumpable, even at temperatures of 0 to 5°C, for the application according to the invention. The oil

phase is formed in particular by monocarboxylic acid esters of the described type or mixtures thereof with ecologically safe components, the so-called non-polluting oils, which have a Brookfield (RVT) viscosity at 0 to 5°C of not more than 50 mPas and preferably not more than 40 mPas. Esters or ester mixtures of the described type having a viscosity of at most about 30 mPas are particularly suitable.

In addition, the esters preferably used in the drilling mud have solidification values (pour point and setting point) below 0°C, corresponding limits below -5°C and, in particular, below -10°C being particularly suitable. In addition, high flash points are desirable above all for reasons of operational safety, so that corresponding values of at least 90°C and preferably above 100°C are particularly appropriate. Providing the ester-components are suitably selected, the desired combination of properties for the ester oils used in accordance with the invention can be established by the expert in known manner.

The carboxylic acid esters of medium chain length in the carboxylic acid unit, which are used in accordance with the invention, may be divided into two sub-classes, namely: into esters of these acids with monohydric alcohols and into esters of these acids with polyhydric alcohols. The following observations are made on the choice of particularly suitable components.

Esters of the type mentioned based on monohydric alcohols preferably contain at least 6 and, better still, at least 7 carbon atoms in the alcohol component. Through this comparatively high lower limit for the alcohol component, it is possible to ensure that, even after partial ester cleavage, toxicological and, in particular, inhalation toxicological problems occurring in practice can be solved by simple means. It may of course be assumed in this regard that the at least slightly heated drilling fluid is pump-circulated and is freed from any rock cut-

things taken up, above all by sieving. With increasing ageing and the partial hydrolysis which it initiates, problems not only arise from the formation of free fatty acids or their salts, as described in earlier applications D 8523 and D 8524 cited above, the alcohol component released can also present problems in practice. This alcohol content will always have to be taken into account when inhalation problems can be expected from alcohol vapors due to the volatility of the alcohol component and the predetermined operating temperatures. Lower monofunctional alcohols can cause additional problems in this regard which, although controllable, for example, by corresponding design measures, are actually eliminated from the outset in the preferred embodiment of the invention. If monohydric, predominantly aliphatically saturated alcohols of natural and/or synthetic origin are present in the ester oils used in accordance with the invention, corresponding alcohols in the C₈₋₁₅ range are preferably used for forming the esters. Their vapor pressure under the operating conditions encountered in practice is so low that the problems just discussed are eliminated.

However, esters of monohydric alcohols are not confined to this C chain length range. Higher monohydric alcohols of which esters with the carboxylic acids of medium chain length defined in accordance with the invention give rheologically useful oils or oil components may also be used. Mono- and/or polyolefinically unsaturated alcohols which may contain, for example, up to 24 carbon atoms or an even larger number of carbon atoms are particularly suitable in this regard. Alcohols of this type may be obtained in particular by selective reduction of corresponding natural fatty acids, as discussed in the following in connection with further aspects of the invention.

Where esters of polyhydric alcohols are used, inhalation-toxicological problems are generally of no signifi-

cance from the outset. Particularly suitable polyhydric alcohols are dihydric to tetrahydric alcohols, more particularly corresponding lower representatives preferably containing 2 to 6 carbon atoms. Particularly suitable polyhydric alcohols are glycol and/or the propane diols. Accordingly, ethylene glycol, 1,2-propane diol and/or 1,3-propane diol are particularly preferred alcohol components for the formation of the ester oils described in accordance with the invention. Both partial esters and full esters of the type in question are suitable, particular significance being attributed to the fully esterified products, above all on rheological grounds. The esters may be symmetrical and/or asymmetrical esters or ester mixtures providing carboxylic acids having C chain lengths in the range mentioned are at least partly used.

The oil phase of the w/o emulsions may be formed solely of esters of the type described herein although the mixture components described in the following may also be used together with the ester oils defined in accordance with the invention.

Mixture components in the oil phase

Oil components suitable for admixture with the monocarboxylic acid methylesters are the mineral oils typically used in drilling muds and, preferably, substantially non-aromatic aliphatic and/or cycloaliphatic hydrocarbon fractions having the required flow properties. Reference is made in this regard to the relevant prior-art literature and to the commercial products available on the market.

According to the invention, however, particularly important mixture components are environment-friendly ester oils of the type described in particular in the earlier applications cited above (D 8523 and D 8524). To complete the disclosure of the invention, essential characteristics of those esters and ester mixtures are briefly

summarized in the following.

In a first embodiment, esters - flowable and pumpable at 0 to 5°C - of monohydric C₂₋₁₂ and, more particularly, C₆₋₁₂ alcohols and aliphatic saturated C₁₂₋₁₆ monocarboxylic acids or mixtures thereof with at most substantially equal quantities of other monocarboxylic acids are used as the oil phase. Preferred ester oils are those of which at least about 60% by weight, based on the particular 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 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 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 linear and/or branched and of vegetable and/or synthetic origin. They may be derived from corresponding triglycerides, such as coconut oil, palm kernel oil and/or babassu oil. The alcohol radicals of the esters used are derived in particular from linear and/or branched saturated alcohols preferably containing 6 to 10 C atoms. These alcohol components may also be of vegetable and/or animal origin, having been obtained by reductive hydrogenation of corresponding carboxylic acid esters.

Another class of particularly suitable ester oils is derived from mono- and/or polyolefinically unsaturated C₁₆₋₂₄ monocarboxylic acids or mixtures thereof with small quantities of other, in particular saturated monocarboxylic acids and monofunctional C₂₋₁₂ 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 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 C₁₆₋₂₄ carboxylic acids.

In their case, too, the solidification values (pour 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.

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 C₁₆₋₂₄ monocarboxylic acid residues in the ester are derived from di- and polyolefinically unsaturated acids, preferably at least about 60% by weight of the acid residues being mono-olefinically unsaturated. In the second sub-class, more than 45% by weight and preferably more than 55% by weight of the C₁₆₋₂₄ monocarboxylic acids in the ester mixture are derived from di- and/or polyolefinically unsaturated acids. Saturated C_{16/18} carboxylic acids in the ester mixture best make up no more than about 20% by weight and, in particular, no more than about 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 at least 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 herring oil.

Another interesting class of ester oils which may be used as a mixture component in accordance with the present

invention is described in co-pending application (D 8606 "The use of Selected Ester Oils of Lower Carboxylic Acids in Drilling Fluids"). The ester oils in question are based on esters of C_{1-5} monocarboxylic acids and monohydric and/or polyhydric alcohols which are flowable at room temperature and have flash points above 80°C . In a preferred embodiment, these esters are even flowable and pumpable at temperatures of 0 to 5°C . Corresponding esters of these lower carboxylic acids with monohydric alcohols containing at least 8 carbon atoms and/or esters of these acids with dihydric or tetrahydric alcohols preferably containing 2 to 6 carbon atoms are particularly suitable. For practical reasons, acetic acid is a particularly suitable ester-forming acid component of this class. Rheology data and data on the volatility or rather the solidification values of preferred esters of this sub-class correspond to the above-mentioned values and can be found in the co-pending patent application cited above to which express reference is hereby made as part of the disclosure of the present invention.

Suitable mixture components from this sub-class are, in particular, esters of monohydric alcohols of natural and/or synthetic origin of which the chain length may be in the range from C_8 to C_{15} where predominantly aliphatically saturated alcohols are present or may even be longer, for example up to about C_{24} , where mono- and polyolefinically unsaturated alcohols are present.

The invention also encompasses multicomponent mixtures which, together with the ester oils defined in accordance with the invention based on carboxylic acids of medium chain length, may contain several of the mixture components listed in detail in the foregoing. Basically, it is possible in this regard to use any mixtures providing they satisfy the basic rheological requirements for invert drilling muds of the type in question here. Examples of

such multicomponent mixtures are materials based on various types of ester oils or mixtures additionally containing mineral oil.

5 **The mixing ratios in the oil phase**

10 The esters of C₆₋₁₁ monocarboxylic acids of synthetic and/or natural origin and/or polyhydric alcohols defined in accordance with the invention are present as an at least substantial constituent of the oil phase, their percentage content generally making up at least about 20 to 25% by weight of the oil phase. In important embodiments, at least about one third of the oil phase is formed by ester oils of this type, particularly important embodiments of the invention being characterized in that esters of the type described herein form the predominant part of the continuous oil phase.

15 It is pointed out even in earlier application P 38 42 703.6 (D 8524) cited above that limited quantities of esters of so-called head-fractionated fatty acids, i.e. fatty acids in the C₆₋₁₀ range, may be used, particularly where saturated fatty acids of natural origin are used. However, the quantities in which they are used are generally comparatively small quantities which make up at most about 15% by weight, depending on the origin of these saturated fatty acid mixtures. In this respect, therefore, the teaching of the present invention goes beyond the disclosure of the earlier application cited above.

25 **Other mixture components of the invert drilling mud**

30 Other suitable mixture components of the invert drilling mud are any of the constituents typically used for the conditioning and for the practical application of invert drilling muds of the type used at present with mineral oils as the continuous oil phase. In addition to the disperse aqueous phase, emulsifiers, weighting agents, fluid

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loss additives, thickeners and alkali reserves are particularly important in this regard.

5 In one particularly important embodiment of the invention, use is also made here of the further development of such invert drilling muds based on ester oils which is the subject of applicants' earlier application (D 8543 "Oleophilic basic amine compounds as an additive for invert drilling muds").

10 The teaching of this earlier application is based on the concept of introducing into invert drilling muds based on ester oils an additional additive which is capable of keeping the desired rheological data of the drilling mud in the required range, even when increasingly larger quantities of free carboxylic acids are formed in use by partial ester hydrolysis. Not only are these carboxylic acids to be trapped in a harmless form, it is also intended to be possible to convert these free carboxylic acids if desired into useful components having stabilizing or emulsifying properties for the system as a whole. According to the teaching of this earlier application, basic amine compounds of pronounced oleophilic character and at most limited solubility in water, which are capable of forming salts with carboxylic acids, are to be used as an additive in the oil phase. The oleophilic amine compounds may be simultaneously used at least partly as alkali reserve of the invert drilling mud, although they may also be used in combination with conventional alkali reserves, particularly lime. It is particularly preferred to use oleophilic amine compounds which are at least predominantly free from aromatic constituents. 30 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 particularly suitable. In one preferred embodiment, these amine compounds have a solubility in water at room tem- 35

perature of at most about 5% by weight and best below 1% by weight.

Typical examples of such amine compounds are at least substantially water-insoluble primary, secondary, and/or tertiary amines, which may even be alkoxyated to a limited degree and/or substituted by, in particular, hydroxyl groups. Other examples are corresponding aminoamides and/or heterocycles containing nitrogen as a constituent of the ring. Suitable amine compounds of the type in question are, for example, basic amine compounds containing at least one long-chain, preferably C_{8-36} and more preferably C_{10-24} hydrocarbon radical which may even be mono- or polyolefinically unsaturated. The oleophilic basic amine compounds may be added to the drilling mud in quantities of up to about 10 lb/bbl, preferably in quantities of up to about 5 lb/bbl and more preferably in quantities of from about 0.1 to 2 lb/bbl.

It has been found that the use of such oleophilic basic amine compounds can effectively prevent thickening of the drilling mud presumably attributable to a disturbance of the w/o invert system and to the formation of free carboxylic acids by ester hydrolysis.

In one preferred embodiment of the teaching according to the invention, the oil mud does not contain significant quantities of highly hydrophilic inorganic and/or organic bases. In particular, the invention dispenses with the use of 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 to around 2 lb/bbl. A preferred embodiment is characterized by the use of lime in a quantity just below that limit, i.e. for example in a quantity of about 1 to 1.8 lb/bbl (lime/drilling mud). Other known alkali reserves may be used instead of or in addition to lime, including in

particular less basic metal oxides of the zinc oxide type. However, even in cases where acid acceptors such as these are used, it is important to ensure that they are not added in excessive quantities in order to prevent unwanted premature ageing of the drilling mud accompanied by an increase in viscosity and hence a deterioration in the rheological properties. The feature of the teaching according to the invention discussed here prevents the formation of unwanted quantities of highly effective o/w emulsifiers or at least limits it to such an extent that the favorable rheological properties are maintained for sufficiently long periods in practice, even in the event of thermal ageing.

The following observations also apply:

Invert drilling muds of the type in question here typically contain the finely disperse phase, 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. The range from about 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 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 drilling 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 "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 by NL Baroid under the name of "EZ-mul".

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 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.

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.

5 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 amino-amides already mentioned, alkyl benzenesulfonates and imidazoline compounds are mentioned as further examples. Additional information on the relevant prior art can be found
10 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
15 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
20 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
25 of the teaching according to the invention.

Examples

 In the following Examples, invert drilling muds were
30 conventionally produced using the following starting formulation:

230	ml	ester oil
26	ml	water
6	g	organophilic bentonite (Geltone II, a product of 35 NL Baroid)

- 12 g organophilic lignite (Duratone, a product of NL Baroid)
x g lime (x = 1 or 2)
6 g w/o emulsifier (EZ-mul NT, a product of NL Baroid)
5
346 g baryta
9.2 g $\text{CaCl}_2 \cdot 2 \text{H}_2\text{O}$

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

- 10 After a w/o invert drilling mud has been made up in known manner from the particular components used with variation of the ester oil phase, the viscosity values of the material are determined as follows first before and then after ageing:

- 15 Measurement of viscosity at 50°C in an NL Baroid Fann-35 viscosimeter. Plastic viscosity (PV), yield point (YP) and gel strength (lb/100 ft²) after 10 secs. and 10 mins. are determined in known manner.

- 20 The material is aged by treatment in an autoclave (so-called roller oven) for 16 hours at 125°C.

Example 1

- 25 The reaction product of isononanoic acid and isoheptanol - an ester having a flash point of 145°C and a setting point below -10°C - is used as the ester oil. In this Example, the quantity of lime in the basic formulation shown above is 2 g.

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

	Unaged material	Aged material
Plastic viscosity (PV)	26	31
5 Yield point (YP)	14	14
Gel strength (lb/100 ft ²)		
10 secs.	5	6
10 mins.	8	9

10

Example 2

The constituents are the same as in Example 1 although the quantity of lime used in the basic formulation is now 1 g. The characteristic data of the material determined before and after ageing are shown in the following Table:

15

	Unaged material	Aged material
20 Plastic viscosity (PV)	28	31
Yield point (YP)	8	8
Gel strength (lb/100 ft ²)		
10 secs.	5	5
10 mins.	7	7

25

Example 3

The ester oil used in Examples 3 and 4 below is the esterification product of 2-ethyl hexanol and C₆₋₁₀ head-fractionated fatty acids ("Edenor", a product of Henkel KGaA). The ester oil has a flash point of approximately 151°C and a setting point below -10°C.

30

The following Table shows the viscosity values of the material before and after ageing when 2 g lime is added to the basic formulation.

	Unaged material	Aged material
Plastic viscosity (PV)	28	33
5 Yield point (YP)	7	12
Gel strength (lb/100 ft ²)		
10 secs.	5	6
10 mins.	8	16

10 Example 4

The constituents are the same as in Example 3, except that lime is added to the ester oil drilling fluid in a quantity of only 1 g. The viscosity values of the material determined before and after ageing are shown in the following Table:

	Unaged material	Aged material
20 Plastic viscosity (PV)	24	23
Yield point (YP)	12	12
Gel strength (lb/100 ft ²)		
10 secs.	5	5
10 mins.	7	6

25 Example 5

The ester oil from Examples 1 and 2 - ester of isononanoic acid/isoheptanol - is used in another ester drilling fluid with an oil-to-water ratio of 80:20 with simultaneous addition of 2 g of a highly oleophilic amine ("Araphen G2D", a product of Henkel KGaA, the reaction product of an epoxidized C_{12/14} α -olefin and diethanolamine). The basic formulation is as follows:

210 ml ester oil
35 48.2 g water
6 g organophilic bentonite (Omnigel)

- 13 g organophilic lignite (Duratone, a product of NL Baroid)
- 2 g lime
- 8 g w/o emulsifier (EZ-mul Nt, a product of NL Baroid)
- 5
- 270 g Baryta
- 20 g $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$.

The viscosity values of the material determined before and after ageing are shown in the following Table:

10

	Unaged material	Aged material
Plastic viscosity (PV)	35	32
15 Yield point (YP)	31	20
Gel strength (lb/100 ft ²)		
10 secs.	12	7
10 mins.	14	9

20 Examples 6 to 9

The following four esters are used as oil phase in the basic formulation of Examples 1 and 2 (lime being used in a quantity of 1 g as in Example 2) and are rheologically evaluated in accordance with Examples 1 and 2 before and after ageing:

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Example 6: Ester of 2-ethyl hexanol and C_8 acid, flash point 152°C, viscosity 4 to 5 mPas at 20°C and 2 to 3 mPas at 50°C, setting point below -10°C.

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Example 7: Ester of 2-ethyl hexanol and C_{10} acid with a flash point of 166°C, viscosity 4 to 5 mPas at 20°C, 2 to 3 mPas at 50°C, setting point approx. 10°C.

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Example 8: Ester of n-octanol ("Lorol", a product of Henkel KGaA) and C_{10} carboxylic acid ("Edenor", a product of Henkel

KGaA) with a flash point of 171°C, a viscosity of 6 mPas at 20°C and 3 mPas at 50°C and a setting point of +3°C.

5 Example 9: Ester of isononanoic acid and n-octanol ("Lorol", product of Henkel KGaA).

The rheological data determined before and after ageing are as follows:

10 Example 6

	Unaged material	Aged material
15 Plastic viscosity (PV)	21	22
Yield point (YP)	15	11
Gel strength (lb/100 ft ²)		
10 secs.	6	8
10 mins.	8	5

20 Example 7

	Unaged material	Aged material
25 Plastic viscosity (PV)	29	31
Yield point (YP)	8	8
Gel strength (lb/100 ft ²)		
10 secs.	5	5
10 mins.	7	7

Example 8

	Unaged material	Aged material
5		
Plastic viscosity (PV)	26	28
Yield point (YP)	17	14
Gel strength (lb/100 ft ²)		
10 secs.	6	4
10	8	7
10 mins.		

Example 9

	Unaged material	Aged material
15		
Plastic viscosity (PV)	27	29
Yield point (YP)	12	13
Gel strength (lb/100 ft ²)		
20	5	4
10 secs.		
10 mins.	7	7

Examples 10 and 11

25 Another two ester oils in the basic formulation of Example 1 (2 g lime) are made up into drilling fluids of the type mentioned. Their rheological data are determined before and after ageing in a roller oven for 16 hours at 125°C.

Example 10

30 Ester oil of C_{8/10} head-fractionated fatty acids ("V85KR", a product of Henkel KGaA) and isotridecyl alcohol, flash point 183°C, setting point below -10°C.

	Unaged material	Aged material
Plastic viscosity (PV)	44	55
5 Yield point (YP)	13	24
Gel strength (lb/100 ft ²)		
10 secs.	6	7
10 mins.	8	10

10 Example 11

Ester oil based on the C_{8/10} head-fractionated fatty acids mentioned in Example 10 and 2-ethyl hexanol with a flash point of 151°C and a setting point below -10°C.

	Unaged material	Aged material
Plastic viscosity (PV)	24	35
Yield point (YP)	10	15
20 Gel strength (lb/100 ft ²)		
10 secs.	5	5
10 mins.	7	14

Example 12

25 In another series of tests, a highly oleophilic amine ("Araphen G2D", a product of Henkel KGaA) is added as antiager in a quantity of 2 g to an ester oil according to Example 11. Ageing in the roller oven at 125°C is extended to 72 hours. The rheological data of the material deter-
 30 mined before and after ageing are shown in the following Table:

	Unaged material	Aged material
Plastic viscosity (PV)	24	24
5 Yield point (YP)	8	14
Gel strength (lb/100 ft ²)		
10 secs.	4	5
10 mins.	6	7

10 The antiager mentioned above is added in the quantity shown to the formulation of Example 10 and the oil mud based on this mixture is aged in a roller oven for 72 hours at 125°C. The rheological data of the material determined before and after ageing are shown in the following Table:

15

	Unaged material	Aged material
Plastic viscosity (PV)	43	66
20 Yield point (YP)	14	24
Gel strength (lb/100 ft ²)		
10 secs.	7	9
10 mins.	9	13

**CLAIMS**

1. The use of esters of C_{6-11} monocarboxylic acids of synthetic and/or natural origin and mono- and/or polyhydric alcohols, which flow at room temperature and have flash points above 80°C , as the oil phase or as part of the oil phase of invert drilling muds which are suitable for the ecologically safe development of, for example, oil and gas occurrences and which, in a continuous oil phase, contain a disperse aqueous phase together with emulsifiers, weighting agents, fluid loss additives and, if desired, other standard additives.
2. The use claimed in claim 1, characterized in that esters or ester mixtures which are flowable and pumpable even at temperatures of 0 to 5°C are used.
3. The use claimed in claims 1 and 2, characterized in that the oil phase is formed by monocarboxylic acid esters of the type mentioned or mixtures thereof with ecologically safe components (non-polluting oils) which have a Brookfield (RVT) viscosity at 0 to 5°C of not more than 50 mPas, preferably not more than 40 mPas and at most about 30 mPas.
4. The use claimed in claims 1 to 3, characterized in that the esters of the C_{6-11} carboxylic acids used in the drilling mud have solidification values (pour point and setting point) below 0°C , preferably below -5°C and, more preferably, below -10°C for flash points of at least 90°C and preferably above 100°C .
5. The use claimed in claims 1 to 4, characterized in that alcohol components which are ecologically and toxicologically - above all inhalation-toxicologically - safe, even after partial ester cleavage in practical application, are used in the ester oils.
6. The use claimed in claims 1 to 5, characterized in that carboxylic acid esters with monohydric alcohols containing at least 7 and preferably at least 8 C atoms and/or esters of polyhydric alcohols, more particularly



alcohols containing 2 to 6 C atoms, are used.

7. The use claimed in claims 1 to 6, characterized in that esters of monohydric alcohols of natural and/or synthetic origin, which have a chain length in the range from C₈ to C₁₅ where predominantly aliphatically saturated alcohols are present or an even greater chain length, for example up to C₂₄, where mono- and/or polyolefinically unsaturated alcohols are present, are used.

8. The use claimed in claims 1 to 7, characterized in that esters of glycol and/or a propane diol are used as the esters of polyhydric alcohols.

9. The use claimed in claims 1 to 8, characterized in that ester oils of monohydric C₂₋₁₂ and preferably C₆₋₁₀ alcohols and mono- and/or polyolefinically unsaturated C₁₆₋₂₄ monocarboxylic acids which preferably have solidification values (pour point and setting point) below -10°C and preferably below -15°C for flash points above 100°C are used as mixture components from the class of non-polluting oils.

10. The use claimed in claim 9, characterized in that olefinically unsaturated carboxylic acid esters 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 C₁₆₋₂₄ carboxylic acids and which have a Brookfield (RVT) viscosity of no more than 55 mPas and preferably no more than 45 mPas, more particularly at temperatures of 0 to 5°C, are used as a mixture components.

11. The use claimed in claims 9 and 10, characterized in that no more than 35% by weight of the esters of unsaturated monocarboxylic acids used as mixture components are derived from di- and polyolefinically unsaturated acids, of which at least about 60% by weight are mono-olefinically unsaturated, and/or of which more than 45% by weight and preferably more than 55% by weight are derived from di-



and/or polyolefinically unsaturated acids.

5 12. The use claimed in claims 1 to 8, characterized in that esters of aliphatically saturated C_{1-5} monocarboxylic acids and/or esters of aliphatically saturated C_{12-16} monocarboxylic acids, which are preferably pumpable and flowable at 0 to 5°C and which are ecologically and toxicologically safe, even after partial hydrolysis in use, are used as ester-based mixture components.

10 13. The use claimed in claims 1 to 12, characterized in that the carboxylic acid esters are used in the invert drilling mud together with alkali reserves, lime being a particularly preferred alkali reserve, although limited quantities of metal oxides of the zinc oxide type or related zinc compounds may optionally be present in addition to or instead of lime.

15 14. The use claimed in claims 1 to 13, characterized in that the drilling mud does not contain significant quantities of highly hydrophilic bases, such as alkali metal hydroxide and/or diethanolamine, and any addition of lime present is best limited to a maximum of about 2 lb/bbl drilling fluid.

20 15. The use claimed in claims 1 to 14, characterized in that the carboxylic acid esters are used in the invert drilling muds together with amine compounds of pronounced oleophilic character and at most limited solubility in water which are capable of forming salts with free carboxylic acids.

25 16. The use claimed in claims 1 to 15, characterized in that the esters are used in drilling fluids which, in the invert drilling mud, 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 together with the continuous ester-based oil phase.

30 17. Invert drilling fluids which are suitable for the ecologically safe development of oil and gas occurrences
35



and which, in a continuous oil phase, contain a disperse aqueous phase together with emulsifiers, weighting agents, fluid loss additives and, if desired, other standard additives, characterized in that the oil phase contains esters of C₆₋₁₁ monocarboxylic acids of synthetic and/or natural origin and mono- and/or polyfunctional alcohols which flow at room temperature and have flash points above 80°C, if desired in admixture with other components from the class of ecologically safe compounds (non-polluting oils).

18. An invert drilling fluid as claimed in claim 17, characterized in that it is alkali-conditioned, lime and/or metal oxides of the zinc oxide type preferably being present as the alkali reserve.

19. An invert drilling fluid as claimed in claim 17 and 18, characterized in that it does not contain significant quantities of highly hydrophilic bases, such as alkali metal hydroxides, or highly hydrophilic amines, such as diethanolamine, and in that where lime is added the alkali reserve does not exceed quantities of about 2 lb/bbl (lime/drilling fluid).

20. An invert drilling fluid as claimed in claims 17 to 19, characterized in that it contains amine compounds of pronounced oleophilic character and at most limited solubility in water which are capable of forming salts with carboxylic acids.

21. An invert drilling fluid as claimed in claims 17 to 20, characterized in that it has a plastic viscosity (PV) in the range from about 10 to 60 mPas and a yield point (YP) in the range from about 5 to 40 lb/100 ft², as determined at 50°C.

22. An invert drilling fluid as claimed in claim 17 and 21, characterized in that the esters of the C₆₋₁₁ monocarboxylic acids make up at least about 25% by weight, preferably at least about one third and, more preferably, the



predominant part of the continuous oil phase.

23. An invert drilling fluid as claimed in claims 17 to 22, characterized in that its disperse water content makes up about 5 to 45% by weight and preferably about 10 to 25%
5 by weight and, in particular, contains dissolved salts of the CaCl_2 and/or KCl type.

24. An invert drilling fluid as claimed in claims 17 to 23, characterized in that the oil phase of the invert mud has a Brookfield (RVT) viscosity at 0 to 5°C below 50 mPas
10 and preferably of not more than 40 mPas.