

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 fine-particle 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 42 659.5 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 present invention seeks to avoid these problems through the use in drilling muds of the type mentioned of a class of ester oils which forms unproblematical carboxylic acids or carboxylic acid salts during the limited hydrolysis which the ester always undergoes. The implementation of this concept is based on the choice of ester oils which go back to lower carboxylic acids containing 1 to 5 carbon atoms. Particular significance can be attributed in this regard to corresponding esters of acetic acid. The acetate salts formed during the partial hydrolysis of the ester oil do not have an emulsifier property which could seriously affect the w/o system.

In a first embodiment, therefore, the present invention relates to the use of esters of C_{1-5} monocarboxylic acids 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 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 which are suitable for the stated purpose and which contain a disperse aqueous phase together with the additives mentioned in a continuous oil phase, being characterized in that the oil phase consists at least partly of the above-mentioned esters of C_{1-5} monocarboxylic acids with mono- and/or polyhydric alcohols.

Monocarboxylic acid esters of the type with which the invention is concerned can be controlled in their properties through the choice of the alcohol components used for esterification so that they are suitable for the intended application according to the invention. Corresponding esters or ester mixtures which are flowable and pumpable, even at temperatures of 0 to 5°C, are preferred. The oil phase is preferably formed by C_{1-5} monocarboxylic acid esters or mixtures thereof with ecologically safe components from the class of 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. In a preferred embodiment, the oil phase has a viscosity of at most about 30 mPas.

The C_{1-5} carboxylic acid esters used in the drilling mud have solidification values (pour point and setting point) below 0°C, preferably below -5°C and, in particular, below -10°C. At the same time, the flash points of the esters should be as high as possible, above all for reasons of operational safety, so that preferred limits for the flash point are about 90°C and preferably above 100°C.

The esters of lower carboxylic acids suitable for the

purposes of the invention may be divided into two subclasses. In a first class, the lower monocarboxylic acids are present as reaction products of monofunctional alcohols. In this case, the alcohol contains at least 6 carbon atoms, but preferably more, i.e. at least 8 to 10 carbon atoms. The second subclass of ester oils uses polyhydric alcohols as the ester-forming component. The alcohols in question are, in particular, dihydric to tetrahydric alcohols, lower alcohols of this type preferably containing 2 to 6 carbon atoms being particularly suitable. Typical examples of such polyhydric alcohols are glycol and/or propane diols. Particular significance is attributed both to ethylene glycol and to 1,2-propanediol and/or 1,3-propanediol. In the case described here of esters of polyhydric alcohols, fully esterified reaction products are preferred although the invention is by no means limited to such reaction products, particularly in the case of the higher polyhydric alcohols. In the last-mentioned case in particular, it would even be possible to consider using partial esters of these higher polyhydric alcohols with the lower carboxylic acids mentioned.

The most important esters for the teaching according to the invention are derived from C_{2-4} monocarboxylic acids, outstanding significance being attributed to acetic acid - already mentioned - as the ester-forming component.

An important factor in the choice of the particular alcohols goes back to the following additional considerations: in the practical application of the ester oil, partial saponification of the ester generally cannot be ruled out. The free alcohols are formed in addition to the free carboxylic acids formed or carboxylic acid salts form in conjunction with the alkali reserve. They should be selected in such a way that, even after partial hydrolysis, ecologically and toxicologically safe working conditions are guaranteed, inhalation-toxicological considerations in

particular also having to be taken into account in this regard. The alcohols used for ester formation should in particular have such low volatility that, in their free state, they do not lead to any pollution around the working platform under the working conditions likely to be encountered in practice. In the case of the class of ester oils based on very short chain monocarboxylic acids selected in accordance with the invention, it is necessary from the outset to use comparatively long-chain monohydric alcohols in order sufficiently to reduce the volatility of the ester oil. Accordingly, the considerations discussed here are important in particular in cases where ester oils of the type defined in accordance with the invention are used in conjunction with other mixture components, particularly other carboxylic acid esters. In its preferred embodiment, the present invention as a whole is concerned with ensuring that, even after partial hydrolysis in use, the drilling fluids are ecologically and toxicologically safe, in the present case in particular inhalation-toxicologically safe under working conditions.

Suitable alcohols, more particularly suitable monohydric alcohols, may be of natural and/or synthetic origin. Straight-chain and/or branched-chain alcohols may be used. The chain length of the predominantly aliphatically saturated alcohol is preferably in the range from C_8 to C_{15} . However, monoolefinically and/or polyolefinically unsaturated alcohols of the type obtainable, for example, by selective reduction of natural unsaturated fatty acids or fatty acid mixtures are also suitable. These mono- and/or polyolefinically unsaturated alcohols may thus contain even more carbon atoms in the ester oils according to the invention, for example up to about 24 carbon atoms.

Ester oils of the type mentioned here may form the continuous oil phase of the w/o invert mud as a whole. On the other hand, the carboxylic acid esters defined in

accordance with the invention may make up only one mixture component of the oil phase in accordance with the teaching of the invention. Suitable other oil components are virtually any oil components which are either known and/or have been described for the particular field of application in question. Particularly suitable mixture components are discussed in detail hereinafter.

The ester oils according to the invention may be homogeneously mixed with the mixture components, generally in any ratios. According to the teaching of the invention, at least about 25% and, more particularly, at least about one third of the oil phase is best present in the form of the C_{1-5} ester oils. In important embodiments of the invention, these ester oils form the main part of the oil phase.

Mixture components in the oil phase

Oil components suitable for admixture with the monocarboxylic acid esters of the invention 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 C_{2-12} and, more particularly, C_{6-12} alcohols and aliphatic saturated C_{12-16} 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 C_{12-14} 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 (flow and pour 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 C_{16-24} monocarboxylic acids or mixtures thereof with small quantities of other, in particular saturated monocarboxylic acids and monofunctional C_{2-12} alcohols. These ester oils are also flowable and pumpable at temperatures in the range from 0 to 5°C. Particularly suitable esters of this type are those of which more than 70% by weight, preferably more than 80% by weight and, in particular, more than 90% by

weight are derived from olefinically unsaturated C_{16-24} carboxylic acids.

In their case, too, the solidification values (flow and pour 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 C_{16-24} 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 monoolefinically unsaturated. In the second sub-class, more than 45% by weight and preferably more than 55% by weight of the C_{16-24} monocarboxylic acids in the ester mixture are derived from di- and/or polyolefinically unsaturated acids. Saturated $C_{16/18}$ 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. The carboxylic acid residues present are of 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.

Finally, however, other suitable mixture components are the esters of C_{6-11} monocarboxylic acids of natural and/or synthetic origin and mono- and/or polyhydric alcohols which are described in a co-pending application ... (D 8607 "Esters of Carboxylic Acids of Medium Chain Length as Part of the Oil Phase in Invert Drilling Muds") and which are preferably flowable and pumpable even at temperatures

of 0 to 5°C. To complete the disclosure of the present invention, reference is made in this regard to the cited co-pending application which is hereby included in the present disclosure.

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Other mixture components of the invert drilling mud

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

15 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").

20 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. 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 temperature 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.

If esters of relatively long-chain carboxylic acids

which lead by hydrolysis to fatty acids or fatty acid salts having a pronounced o/w emulsifier effect are used as mixture components in accordance with the invention, the measures regarding the alkali reserve which are described in detail in earlier applications P 38 42 659.5 and P 38 42 703.6 in connection with this problem also have to be taken into consideration in the present invention. The following observations apply to ester mixtures such as these:

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, fine-particle 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.

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

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

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:

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.

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

Isotridecyl acetate having the following rheological characteristics is used as the ester oil: viscosity at 20°C 5 mPas; viscosity at 50°C 2.1 mPas; pour point below -10°C.

In Example 1 below, the quantity of lime used in the starting formulation is 2 g. In Example 2: this quantity is reduced to 1 g.

The characteristic data of the material as determined before and after ageing are set out in the following Tables:

Example 1

	Unaged material	Aged material
Plastic viscosity (PV)	31	33
Yield point (YP)	11	13
Gel strength (lb/100 ft ²)		
10 secs.	6	7
10 mins.	9	9

Example 2

	Unaged material	Aged material
Plastic viscosity (PV)	24	25
Yield point (YP)	14	12
Gel strength (lb/100 ft ²)		
10 secs.	5	5
10 mins.	8	7

The starting formulation of Examples 1 and 2 corresponds to a value of 90:10 for the ratio by weight of oil phase to water. Other tests are carried out with a ratio of ester oil to water of 80:20.

5 In Examples 3 and 4 below, invert drilling muds are produced using the ester oil based on isotridecyl acetate in the following starting formulation:

	210	ml	ester oil
	48.2	g	water
10	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)
15			
	270	g	Baryta
	20	g	CaCl ₂ · 2H ₂ O.

20 As in Examples 1 and 2, the viscosities of the material are determined before and after ageing for 16 hours in a roller oven at 125°C (Example 3).

25 In another test (Example 4), a strongly oleophilic amine ("Araphen G2D", the reaction product of an epoxidized C₁₂₋₁₄ alpha-olefin and diethanolamine; a product of Henkel KGaA) is added to the starting formulation of Example 3 in a quantity of 2 g. The viscosity characteristics of the material are then determined before and after ageing in the same way as described above.

Example 3

		Unaged material	Aged material
5	Plastic viscosity (PV)	34	36
	Yield point (YP)	52	51
	Gel strength (lb/100 ft ²)		
	10 secs.	25	23
	10 mins.	37	35

10

Example 4

		Unaged material	Aged material
15	Plastic viscosity (PV)	31	34
	Yield point (YP)	36	32
	Gel strength (lb/100 ft ²)		
	10 secs.	14	13
	10 mins.	17	15

20

Example 5

25 The ester oil used is an ester mixture of acetic acid and a C₆₋₁₀ alcohol cut ("Lorol technisch", a product of Henkel KGaA) prepared by reduction of the corresponding head-fractionated fatty acid of natural origin. The starting formulation of the ester mud corresponds to the formulation mentioned at the beginning for Example 2).

30 The viscosity data before and after ageing are determined in the same way as in the previous Examples. The following results are obtained.

		Unaged material	Aged material
	Plastic viscosity (PV)	28	29
5	Yield point (YP)	17	20
	Gel strength (lb/100 ft ²)		
	10 secs.	9	9
	10 mins.	24	14

10 Examples 6 to 10

15 In parallel tests, three drilling muds based on isotridecyl acetate are prepared in accordance with the starting formulation of Examples 1 and 2 (oil phase to water 90:10). As in the previous Examples, the rheological data are determined immediately after production and after ageing in a roller oven for 16 hours at 125°C.

20 No lime is added to the first mud (Example 6), 2 g lime are added to a second mud (Example 7) and 2 g lime together with 1 g of the strongly oleophilic amine "Araphen G2D" are used in the third mud (Example 8).

The rheological data determined are as follows:

Example 6

25		Unaged material	Aged material
	Plastic viscosity (PV)	28	30
	Yield point (YP)	15	9
	Gel strength (lb/100 ft ²)		
30	10 secs.	9	7
	10 mins.	10	8

Example 7

		Unaged material	Aged material
5	Plastic viscosity (PV)	30	29
	Yield point (YP)	13	17
	Gel strength (lb/100 ft ²)		
	10 secs.	8	8
	10 mins.	10	12

10

Example 8

		Unaged material	Aged material
15	Plastic viscosity (PV)	25	25
	Yield point (YP)	12	8
	Gel strength (lb/100 ft ²)		
	10 secs.	8	7
	10 mins.	11	9

20

Examples 9 to 11

In another comparative test series, drilling muds based on isotridecyl acetate are prepared as follows using the starting formulation of Examples 6 to 8: Example 9 addition of 1 g lime; Example 10 addition of 2 g lime; Example 11 addition of 2 g lime + 1 g "Araphen G2D".

25

With these drilling muds, however, ageing is carried out in a roller oven over a period of 72 hours at 125°C. The rheological data of the material determined before and after ageing are as follows:

30

Example 9

		Unaged material	Aged material
5	Plastic viscosity (PV)	30	37
	Yield point (YP)	15	16
	Gel strength (lb/100 ft ²)		
	10 secs.	7	7
	10 mins.	11	10

10

Example 10

		Unaged material	Aged material
15	Plastic viscosity (PV)	28	34
	Yield point (YP)	16	13
	Gel strength (lb/100 ft ²)		
	10 secs.	6	6
	10 mins.	10	10

20

Example 11

		Unaged material	Aged material
25	Plastic viscosity (PV)	29	36
	Yield point (YP)	11	14
	Gel strength (lb/100 ft ²)		
	10 secs.	7	6
	10 mins.	10	10

**CLAIMS**

1. The use of esters of C_{1-5} monocarboxylic acids and mono- and/or polyhydric alcohols, which flow at room temperature and have flash points above 80°C , as the oil phase or as
5 part of the oil phase of invert drilling muds which are suitable for the ecologically safe development of 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,
10 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
15 that the oil phase is formed by C_{1-5} monocarboxylic acid esters 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.
- 20 4. The use claimed in claims 1 to 3, characterized in that the esters of the C_{1-5} carboxylic acids used in the drilling mud have solidification values (flow and pour point) below 0°C , preferably below -5°C and, more preferably, below -10°C for flash points of no lower than 90°C and
25 preferably above 100°C .
5. The use claimed in claims 1 to 4, characterized in that C_{1-5} carboxylic acid esters of monohydric alcohols containing at least 6 C atoms, preferably at least 8 C atoms and/or esters of these acids with 2- to 4-hydric
30 alcohols preferably containing 2 to 6 C atoms are used.
6. The use claimed in claims 1 to 5, characterized in that esters of glycol and/or a propanediol are used as the esters of polyhydric alcohols.
7. The use claimed in claims 1 to 6, characterized in
35 that esters of C_{2-4} monocarboxylic acids, more especially



acetic acid esters, are used.

8. The use claimed in claims 1 to 7, characterized in that ester-based mixture components which are ecologically and toxicologically safe, above all inhalation-toxicologically safe under working conditions, even after partial hydrolysis in practical application, are used for mixing with other ester oils.

9. The use claimed in claims 1 to 8, characterized in that esters of monohydric alcohols of natural and/or synthetic origin, which have a chain length in the range from C_8 to C_{15} where predominantly aliphatically saturated alcohols are present or an even greater chain length, for example up to C_{24} , where mono- and/or polyolefinically unsaturated alcohols are present, are used.

10. The use claimed in claims 1 to 9, characterized in that ester oils of monohydric C_{2-12} and preferably C_{6-10} alcohols and mono- and/or polyolefinically unsaturated C_{16-24} monocarboxylic acids which preferably have solidification values (flow and pour point) below -10°C and preferably below -15°C for flash points above 100°C are used as ester-based mixture components in the continuous oil phase.

11. The use claimed in claim 10, 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 C_{16-24} 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 component together with the lower carboxylic acid esters.

12. The use claimed in claims 10 and 11, 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 monoolefinically



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 13. The use claimed in claims 1 to 9, characterized in that esters of aliphatically saturated monocarboxylic acids containing 6 to 16 carbon atoms esterified with mono- and/or polyhydric alcohols are used as mixture components.

10 14. The use claimed in claims 1 to 13, characterized in that the carboxylic acid esters or ester mixtures are used in the invert drilling mud together with alkali reserves, lime being a particularly preferred alkali reserve.

15 15. The use claimed in claims 1 to 14, characterized in that the esters or ester mixtures 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.

20 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.

25 17. Invert drilling fluids which are suitable for the ecologically safe development of 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, characterized in that the oil phase contains
30 esters of C_{1-5} monocarboxylic acids with 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).

35 18. An invert drilling fluid as claimed in claim 17,



characterized in that esters of C_{2-4} monocarboxylic acids, particularly acetic acid esters, and monohydric alcohols containing at least 8 C atoms and/or corresponding esters with, in particular, lower 2- to 4-hydric alcohols are present in the oil phase.

19. An invert drilling fluid as claimed in claims 17 and 18, characterized in that the ester oils of the C_{1-5} carboxylic acids make up at least about 25% by weight, preferably at least about one third and, more preferably, the predominant part of the oil phase.

20. An invert drilling fluid as claimed in claims 17 to 19, characterized in that the oil mud contains an alkali reserve, preferably lime and/or other comparable metal oxides, such as zinc oxide and/or basic amine compounds of pronounced oleophilic character and at most limited solubility in water which are capable of forming salts with carboxylic acids, and in particular does not contain significant quantities of highly hydrophilic bases, such as alkali metal hydroxides, or highly hydrophilic amines, such as diethanolamine.

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 claims 17 to 21, characterized in that its disperse water content makes up about 5 to 45% by weight and preferably about 10 to 25% by weight and, in particular, contains dissolved salts of the $CaCl_2$ and/or KCl type.

23. An invert drilling fluid as claimed in claims 17 to 22, characterized in that the oil phase of the invert mud has a Brookfield (RVT) viscosity at 0 to 5°C below 50 mPas and preferably of not more than 40 mPas.