

This invention relates to new drilling fluids based on water-based o/w emulsions and to o/w emulsion drilling muds based thereon which combine high ecological compatibility with good stability and performance properties.

5 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
10 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, i.e. for the development of oil and/or gas occurrences. However, they are also new
15 valuable working media, for example for geothermal drilling, water drilling, geoscientific drilling and mine drilling. Basically, the new water-based drilling fluids selected in accordance with the invention simplify ecotoxic problems to a considerable extent.

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Prior art

It is known that drilling fluids for sinking bores in rock and bringing up the rock cuttings are slightly thickened, fluid systems which may be assigned to one of
25 the following three classes:

Water-based drilling fluids, oil-based drilling fluids which are generally used in the form of so-called invert emulsion muds and which represent preparations of the w/o emulsion type in which the aqueous phase is
30 distributed in the continuous oil phase in the form of a fine heterogeneous dispersion. The third class of known drilling fluids is based on aqueous o/w emulsions, i.e. on liquid systems which contain a finely dispersed heterogeneous oil phase in a continuous aqueous phase.
35 The invention is concerned with improved systems of the

last type.

Drilling fluids based on o/w emulsion systems occupy an intermediate position between water-based systems and oil-based invert fluids in terms of their performance properties. The advantages and disadvantages of water-based systems combine with the advantages and disadvantages of hitherto described oil-based invert emulsions. Detailed information can be found in the relevant specialist literature, cf. for example the book by George R. Gray and H.C.H. Darley entitled "Composition and Properties of Oil Well Drilling Fluids", 4th Edition, 1980/81, Gulf Publishing Company, Houston, and the extensive specialist and patent literature cited therein and the handbook entitled "Applied Drilling Engineering" by Adam T. Bourgoyne, Jr. et al., First Printing, Society of Petroleum Engineers, Richardson, Texas (USA).

One of the main weaknesses of water-based drilling fluids lies in the interaction of water-sensitive and, in particular, water-swellable rock and/or salt formations with the aqueous drilling fluid and in the ensuing consequences, more particularly borehole instability and thickening of the drilling fluid. Numerous proposals are concerned with limiting these problems and have led, for example, to the development of so-called inhibitive water-based muds, cf. for example "Applied Drilling Engineering", loc. cit., Chapter 2, Drilling Fluids, 2.4 and Gray and Darley, loc. cit., Chapter 2, more particularly the subchapter on pages 50 to 62 (Muds for "Heaving Shale", Muds for Deep Holes, Non-Dispersed Polymer Mud, Inhibited Mud: Potassium Compounds).

More recently, oil-based drilling fluids in particular have been successfully used to overcome the difficulties described above, consisting of the three-phase system oil, water and fine-particle solids. These oil-based drilling fluids are preparations of the w/o

emulsion type. Oil-based drilling fluids were originally based on diesel oil fractions containing aromatic constituents. Subsequently, it was proposed to use substantially dearomatized hydrocarbon fractions (also known as "non-polluting oils") as the continuous oil phase in the interests of detoxification and reducing the ecological problems involved, see for example the Articles by E.A. Boyd et al. entitled "New Base Oil Used in Low Toxicity Oil Muds", Journal of Petroleum Technology, 1985, 137-143 and by R.B. Bennet entitled "New Drilling Fluid Technology - Mineral Oil Mud", Journal of Petroleum Technology, 1984, 975 - 981 and the literature cited therein.

Hitherto, drilling fluids of the water-based o/w emulsion type have used pure hydrocarbon oils as the dispersed oil phase, see for example Gray, Darley, loc. cit., pages 51/52, Chapter entitled "Oil Emulsion Muds" and the tabular composition on page 25 (Tables 1 to 3) with particulars of water-based emulsion muds of the salt water mud type, the lime mud type, the gyp mud type and the CL-CLS mud type.

It is known in particular in this regard that water-based o/w emulsion fluids represent a substantial improvement over water-based drilling fluids in many respects. In recent years, however, the advantages and disadvantages of such water-based emulsion fluids have also been critically compared with those of oil-based invert systems. The reason for this lies in the ecological objections being made on a significant scale against the oil-based invert fluids in use at the present time.

These ecological objections are concerned with two problem areas:

Apart from the basic constituents, oil and water, all water- and/or oil-based drilling fluids require a large number of additives for establishing the required

performance properties, including for example emulsifiers and emulsifier systems, weighting agents, fluid loss additives, wetting agents, alkali reserves, viscosity controllers, optionally auxiliaries for inhibiting
5 drilled rock characterized by high sensitivity to water, biocides and the like. A comprehensive list can be found, for example, in Gray and Darley, loc. cit., Chapter 11, "Drilling Fluid Components". Although ecologically safe additives have now been developed, there are
10 still some ecologically unsafe or even ecologically undesirable additives.

The second problem area is centred on the oil phase used in such drilling fluids. Even the substantially dearomatized hydrocarbon fractions presently used as
15 "non-polluting oils" are not entirely safe on release into the environment. A further easing of the environmental problems caused by liquid oil phases of the type in question appears to be urgently necessary. This applies in particular to offshore drilling, for example
20 for the development of oil and gas occurrences, because the marine eco system reacts particularly sensitively to the introduction of toxic and non-readily degradable substances.

Some proposals have recently been put forward with
25 a view to easing the problems discussed in the foregoing. Thus, US-PSS 4,374,737 and 4,481,121 describe oil-based invert drilling fluids in which non-polluting oils are said to be used. Dearomatized mineral oil fractions and vegetable oils, such as peanut oil, soybean oil,
30 linseed oil, corn oil, rice oil, or even oils of animal origin, such as whale oil, are mentioned alongside one another as equivalent non-polluting oils. All the ester oils mentioned of vegetable and animal origin are triglycerides of natural fatty acids which are known to show
35 high environmental compatibility and which, ecologically,

are distinctly superior to hydrocarbon fractions, even where they have been dearomatized.

However, in the US patents cited above, there is not a single example which describes the use of such natural ester oils in invert drilling fluids. Mineral oil fractions are used throughout as the continuous oil phase. In fact, oils of vegetable and/or animal origin of the type mentioned are unsuitable for use in invert drilling fluids for practical reasons. The rheological properties of such oil phases are impossible to establish for the broad temperature range required in practice of 0 to 5°C on the one hand and up to 250°C and higher on the other hand.

Applicants' earlier proposals

A number of earlier applications filed by applicants describe the use of readily biodegradable and ecologically safe ester oils as the continuous oil phase of w/o invert drilling fluids, cf. in particular earlier applications DE-A-38 42 659 and DE-A-38 42 703 and the modifications of useful ester oils according to earlier patent applications DE-A-39 07 391 and DE-A-39 07 392.

These earlier applications relate to the use of ester oils based on selected monocarboxylic acids or monocarboxylic acid mixtures and monohydric and optionally polyhydric alcohols as the continuous oil phase of w/o invert systems. According to these earlier applications, not only can satisfactory rheological properties be established in the fresh drilling fluid using the esters or ester mixtures disclosed therein, it is also possible to use selected known alkali reserves in the drilling mud without any danger of unwanted thickening occurring in the event of partial ester hydrolysis.

An important further development of these invert drilling fluids based on ester oils is the subject of

applicants' earlier application DE-A-39 03 785.

5 The teaching of these earlier applications is based on the concept of using in invert drilling fluids based on ester oils an additional additive which is capable of maintaining the required rheological data of the drilling fluid in the required range, even when increasingly larger quantities of free carboxylic acids are formed in use by partial ester hydrolysis. It is proposed to use basic, decidedly oleophilic amine compounds capable of forming salts with carboxylic acids and showing at most limited solubility in water as additive in the oil phase.

10 A modified form of such w/o invert drilling fluids is described in applicants' earlier application DE-A-39 11 238. This application describes the use of

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- a) at least substantially water-insoluble mono- and/or polyhydric alcohols of natural or synthetic origin which flow and can be pumped at temperatures of 0 to 5°C
- 20 or
- b) solutions of at least substantially water-insoluble mono- and/or polyhydric alcohols of natural and/or synthetic origin in ecologically safe water-insoluble oils, which flow and can be pumped at temperatures in the above-mentioned range, as the continuous oil phase of drilling fluids which - in the form of a w/o emulsion - contain a dispersed aqueous phase and optionally other typical additives in the alcohol-containing oil phase. Ester oils of the type described in applicants' earlier applications cited above are at least partly used as ecologically safe water-insoluble oils for mixing with the water-insoluble alcohols.

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35 Finally, applicants' earlier application DE-A-39 11

299 describes the use of water-insoluble ethers of monohydric alcohols of natural and/or synthetic origin containing at least 4 and preferably at least 6 carbon atoms in the alcohol radical, which have flashpoints
5 above 80°C, as the oil phase or as part of the oil phase of invert drilling fluids present as w/o emulsions. In this case, too, the ester oils mentioned above are intended for mixing with the ethers.

10 The problem addressed by the invention and its technical solution

The problem addressed by the present invention was to provide drilling fluids of extremely high and, in this form, hitherto unknown ecological compatibility which, at
15 the same time, would exhibit favourable performance properties and which could be satisfactorily used, even in problem areas. In seeking to solve this problem, the invention would deliberately discard oil-based invert drilling fluids and would return to oil-modified water-based o/w emulsions. At the same time, however, it would
20 use the auxiliaries described in applicants' earlier applications cited above and the resulting ecological advantages even in this class of drilling fluids.

In a first embodiment, the invention seeks to
25 utilize the advantages of o/w emulsion fluids over pure water-based drilling fluids, but at the same time to replace the mineral oil phase at least substantially and preferably completely by ecologically safe ethers of pronounced oleophilic character.

30 In another embodiment, the invention seeks to provide an ecological solution to the second problem of auxiliaries and additives in drilling fluids by at least predominantly and preferably completely selecting ecologically safe auxiliaries from the broad range of known
35 additives.

In a first embodiment, therefore, the present invention relates to the use of at least substantially water-insoluble ethers of mono- and/or polyhydric alcohols of natural and/or synthetic origin, which are liquid and/or at least plastic at the working temperature and have flashpoints of at least 80°C, or of corresponding solutions of such ethers in ecologically safe water-insoluble oils as the dispersed oil phase of water-based o/w emulsion drilling fluids for the ecologically safe development of geological formations which, if desired, contain insoluble fine-particle weighting agents for forming water-based o/w emulsion drilling fluids and/or other additives, such as emulsifiers, fluid loss additives, wetting agents, alkali reserves and/or auxiliaries for inhibiting drilled rock highly sensitive to water.

In another embodiment, the present invention relates to water-based o/w emulsion drilling fluids which, in a homogeneous aqueous phase, contain a stably dispersed oil phase in quantities of around 5 to 50% by weight (based on the sum of the unweighted water and oil phase), optionally together with dissolved and/or dispersed auxiliaries, such as emulsifiers, fluid loss additives, wetting agents, fine-particle weighting agents, salts, alkali reserves and/or biocides, characterized in that at least a substantial part of the dispersed oil phase is formed by water-dispersible ethers of mono- and/or polyhydric alcohols of natural and/or synthetic origin, which are liquid and/or at least plastic at the working temperature and have flashpoints of at least 80°C, or by corresponding solutions of such ethers in ecologically safe water-insoluble oils, more particularly in oleophilic, mono- and/or polyhydric alcohols and/or corresponding ester oils.

The additional preferred feature that ecologically and toxicologically at least substantially safe inorganic

and/or organic auxiliaries and additives are at least substantially used for water-based emulsion drilling fluids or emulsion drilling muds applies to both embodiments of the teaching according to the invention. For
5 example, in the most important embodiments of the invention, no auxiliaries based on soluble toxic heavy metal compounds are used.

The preferred embodiments of the invention

10 The mixing ratios of the ether oil/water phases cover the usual range for known o/w emulsion drilling fluids based on mineral oils. The lower limits for the oil phase are typically at least about 5% by weight or preferably between about 5 and 10% by weight, i.e. for
15 example 7 or 8% by weight, based on the total weight of the liquid phases oil + water in the unweighted state. Minimum quantities of the order indicated ensure that use can be made of the characteristic features of an o/w emulsion fluid. The upper limit to the content of oil is
20 typically around 50% by weight or even slightly higher, for example at most about 65% by weight. However, given a sufficiently uniform droplet size of the dispersed oil phase, the closest packing is achieved even with oil contents of this order, so that the changeover to fluids of
25 the w/o invert fluid type appears logical or appropriate.

The upper limit to the content of dispersed oil phase in the o/w drilling fluids according to the invention is generally determined by cost effectiveness and is, for example, about 45% by weight and preferably
30 lower, for example about 40% by weight.

A quantity of ether of about 10 to 40% by weight (on the same basis as before) and, in particular, quantities of the ether phase of around 15 to 35% by weight enable numerous hitherto unknown and hitherto unreported advantages of such emulsion drilling fluids to be utilized.
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Oil contents of, for example, 20% by weight or, in the most extreme case, 30% by weight establish the basis for high-quality drilling fluids which come at least very close in their function to oil-based invert muds, although they require a very much smaller quantity of ether phase.

The various embodiments of the invention

In a first embodiment, the dispersed oil phase of the water-based o/w drilling fluids is formed solely or by far predominantly by the substantially water-insoluble and preferably decidedly oleophilic ether. The rheology of the ethers used is adapted to the technical requirements of the drilling fluids and any small rheological corrections may be made by using the small amounts of diluents provided for in this embodiment. Dispersed oil phases of which more than 70% by weight, preferably more than 80% by weight and, if desired, 100% by weight are formed by the ethers as such are particularly suitable for the embodiment in question.

The oil mixture components optionally present in small quantities in this embodiment may be pure and, in particular, dearomatized hydrocarbon compounds, but especially selected ester oils and/or oleophilic alcohols of the type mentioned in applicants' earlier applications cited above. This embodiment will be discussed in more detail hereinafter.

A second embodiment of the invention relates to the use of dispersed oil phases in systems of the type in question which contain considerable or even predominant quantities of water-immiscible oils which are not identical with, but are present in admixture with, the oleophilic ethers.

In this embodiment, the content of ethers selected in accordance with the invention in the dispersed oil

phase is in the range from at least about 10% by weight to about 70% by weight, based on the liquid oil phase, the ether preferably making up at least about 35% by weight and, more particularly, about 50% by weight of the oil phase. Preferred mixture components in this second embodiment are, again, ecologically safe ester oils of the type described in detail hereinafter. However, the use of pure hydrocarbon oils is not ruled out.

10 The ethers of decidedly oleophilic character used in accordance with the invention

The use of the ethers as the oil phase or as a smaller or larger part of the oil phase presupposes their adequate insolubility in water. The solubility of suitable ethers in water should be less than 1% by weight and is preferably no more than about 0.5% by weight.

The following general principles apply to the chemical characteristics of the ethers: ethers of monohydric and/or polyhydric alcohols are suitable. Besides the ethers of monohydric alcohols, those of dihydric and monohydric alcohols are particularly suitable. The alcohols themselves should be ecologically safe and, accordingly, preferably contain no aromatic constituents. Linear and/or branched aliphatic or even corresponding unsaturated, more particularly mono- and/or polyolefinically unsaturated, alcohols are the preferred ether-forming compounds. Cycloaliphatic alcohols and ethers may be used.

An important general requirement for the teaching according to the invention is that the alcohols and ethers as such should not only be ecologically safe, they should also not involve any other toxicological, more particularly inhalation-toxicological, risks.

From the basically broad range of suitable ethers preferably based at least partly on decidedly oleophilic

alcohols, ethers of alcohols with a linear and/or branched hydrocarbon structure are particularly suitable. Among the corresponding monohydric alcohols, compounds containing at least 5 and preferably at least 6 or 7 carbon atoms are suitable compounds, corresponding alcohols containing at least 8 carbon atoms in the molecule being particularly suitable. The upper limit to the number of carbon atoms is imposed by technical accessibility and, for example, is around 36 and preferably about 20 to 24. The ether-forming alcohols themselves may be linear and/or branched, aliphatically saturated or even mono- and/or polyolefinically unsaturated.

Basically, ethers of alcohols of natural and/or synthetic origin are suitable. Synthetic alcohols in the C chain range of particular interest here, namely C₈₋₂₄, which may even contain unsaturated components, are often inexpensively available commercial components and may be used for the purposes of the invention.

The ethers themselves should have flashpoints of at least 80°C, preferably of at least 100°C and more preferably of at least 120°C. In addition to the above-mentioned ethers based on monohydric alcohols preferably containing at least 8 carbon atoms, ethers of selected polyols are also suitable. Particularly suitable ether-forming polyols are lower diols, such as ethylene glycol and/or the propylene glycols, and optionally branched diols containing a relatively long oleophilic hydrocarbon chain in the molecule. For example, oleophilic diols containing hydroxyl groups in the alpha,omega-position and/or relatively long-chain diols of which the hydroxyl groups are present at adjacent carbon atoms are suitable. Characteristic examples of compounds of this type are 2,2-dimethylpropane-1,3-diol (neopentyl glycol) or the saponification products of epoxidized olefins.

The mixture components in the dispersed oil phase

Oil components suitable for mixing in accordance with the present invention are the mineral oils used in conventional drilling fluids, preferably substantially
5 dearomatized aliphatic and/or cycloaliphatic hydrocarbon fractions. Reference is made in this regard to the relevant prior art literature and to the commercial products available on the market.

However, particularly important mixture components
10 in the context of the teaching according to the invention are ecologically safe oleophilic alcohols and/or ester oils, the following general considerations applying in this regard:

The alcohols and/or ester oils should be fluid at
15 ambient temperature and also under in-use conditions, although the fluidity range also encompasses materials which are at least plastically deformable at ambient temperature and soften to a fluid state at the elevated working temperatures typically applied. For reasons of
20 easier processability under practical conditions, it is preferred to use alcohols and ester oils having solidification values (flow point and pour point) below 10°C and preferably below 0°C. Corresponding compounds with solidification values no higher than -5°C can be particu-
25 larly suitable. A factor to be taken into consideration in this regard is that the drilling fluids are normally made up on site using seawater, for example, at comparatively low water temperatures.

In the interests of operational safety, the additives
30 should also have flashpoints of at least 80°C, higher flashpoints of at least 100°C and considerably higher, for example above 150 or 160°C, being preferred.

To ensure optimal utilization of the objective of the present invention, it is also important that these
35 alcohols and/or ester oils have a biologically or ecolog-

ically compatible constitution, i.e. in particular are free from unwanted toxic constituents. Accordingly, the preferred embodiment of the invention uses alcohols and/or ester oils which are free from aromatic constituents and, in particular, contain saturated and/or olefinically unsaturated, linear and/or branched hydrocarbon chains. Although components containing cycloaliphatic structural elements are suitable for use from the ecological point of view, they are of little importance in practice for reasons of cost.

As a highly dispersed oil phase in a continuous aqueous phase, carboxylic acid esters of the type in question undergo hydrolytic ester cleavage to a limited extent with release of the ester-forming constituents carboxylic acid and alcohol. So far as the performance properties of the ester oils in the context of the invention are concerned, two factors bearing a limited relationship to one another have to be taken into consideration in this regard, namely the possible inhalation toxicity of any components released, particularly the alcohol components, and variations in the composition of the emulsion drilling fluid and, hence, possible variations in its performance properties.

To enable the teaching according to the invention to be fully understood, these considerations should be separately regarded for the basic ester-forming components - on the one hand the alcohols and on the other hand the carboxylic acids.

According to the invention, suitable ester-forming alcohol components are both monohydric alcohols and polyhydric alcohols. Mixtures of these types may of course also be used. The alcohols may also be differentiated on the basis of their solubility in water. The alcohols may be soluble and/or insoluble in water.

A first group comprises the polyhydric alcohols. Of

these, the readily obtainable, lower polyhydric alcohols containing 2 to 5 and preferably 2 to 4 hydroxyl groups and in particular 2 to 6 carbon atoms which form esters of suitable rheology are particularly preferred.

5 Characteristic representatives are ethylene glycol, the propanediols and, in particular, glycerol.

 Polyhydric alcohols of the type in question are distinguished by high solubility in water and by such low evaporation levels that there is normally no need to take
10 measures to rule out inhalation-toxic risks.

 Lower polyhydric alcohols of the type in question may be used as fully esterified oil components and/or as partial esters with some free hydroxyl groups and/or are formed in the practical application of the emulsion
15 drilling fluid according to the invention. Providing any partial esters formed retain the substantially water-insoluble character of the oil phase, no substantial change occurs in the oil-to-water ratio of the emulsion drilling fluid. The situation only changes when the
20 state of water-soluble hydrolysis products, i.e. in particular the free lower polyhydric alcohols, is reached. However, the changes occurring in practice in such emulsion drilling fluids from this source are insignificant. Above all, comparatively high stability of the ester bond
25 is established under the working conditions according to the invention. It is known that o/w emulsion drilling fluids normally work at pH values in the neutral to moderately alkaline range, for example at pH values of around 7.2 to 11 and, more particularly, at pH values of
30 around 7.5 to 10.5, so that for this reason alone there is no aggressive hydrolytic attack on the ester bond. In addition, however, the following observations above all also apply:

 In the practical application of the drilling fluid
35 and the resulting advance of the drilling operation into

lower layers of the earth, the drilling fluid and, in particular, the oil phase used therein are steadily consumed. Emulsion drilling fluids are known for this purpose and an important aspect of value for their practical application is that the emulsified oil phase is absorbed onto solid surfaces and hence seals the filter layer on the wall of the borehole and impedes or even completely suppresses any interaction between the drilled rock and the aqueous phase. This continuous consumption of drilling fluid and, above all, of oil phase necessitates a continuous supply of drilling fluid. In practical application, therefore, an equilibrium state is rapidly established in the drilling fluid, enabling continuous operation to be carried out over prolonged periods.

The foregoing observations are of course only relevant to the present invention where considerable quantities of the dispersed oil phase are formed by ester oils. The oleophilic ethers and their mixtures with hydrolysis-resistant mixture constituents are not affected by such additional considerations so that even the substantial or complete absence of esters oils represents an important and preferred embodiment of the teaching according to the invention.

Considerations delving further in certain aspects are necessary in regard to the use of monohydric alcohols as the ester-forming component of the ester oils. It is only the lower members of these alcohols which are soluble in water or miscible in limited quantities with water. In addition, the volatility of these alcohols also plays an important part. In the sinking of a borehole, moderately elevated temperatures are quickly established in the circulated drilling fluid, so that the fractions which are exposed during repumping to remove rock cuttings have a temperature of, for example, 50 to

70°C. Accordingly, inhalation toxicological considerations are necessary. Even C₄ alcohols, for example isobutyl alcohol, can be so volatile under the working conditions prevailing on the drilling platform that there
5 is a danger to personnel. According to the invention, therefore, the number 6 is preferably selected as the lower carbon limit for monohydric alcohols where ester oils using monohydric alcohols are used. It is particularly preferred to use esters of monohydric alcohols
10 containing at least 8 carbon atoms.

At the same time, however, the choice and limitation of the carbon number in the ester-forming alcohol leads to the following result regarding the composition of the ester oil phase taking partial hydrolysis into account:
15 the hydrolyzing components of such ester oils change into the free alcohol which remains in the dispersed ester oil phase as a substantially water-insoluble mixture component.

The carboxylic acids formed by partial hydrolysis of
20 the ester oils also require a number of considerations.

There are basically two types (with a fluid transition), depending on the particular constitution of the carboxylic acids used, namely: carboxylic acids which lead to emulsifying carboxylic acid salts and inert
25 salts.

The particular chain length of the carboxylic acid molecule released is particularly critical in this regard. The salt-forming cation normally present through the alkali reserve of the drilling fluid also has to be
30 taken into consideration.

The following rules generally apply in this regard: lower carboxylic acids, for example those containing 1 to 5 carbon atoms, lead to the formation of inert salts, for example to the formation of corresponding acetates or
35 propionates, while fatty acids of longer chain length,

particularly those in the C_{12-24} range, lead to emulsifying compounds.

Accordingly, by suitably selecting the ester oils and, to a certain extent, the salt-forming cations in the emulsion drilling fluid, it is possible selectively to control the secondary products in the drilling fluid which can have a major influence on the quality and effect of the emulsion drilling fluid. However, the foregoing observations also apply in this regard: not only the dispersed organic phase, but also the aqueous phase is continuously consumed in practical application and has to be replaced. Under steady-state conditions, therefore, rapidly controllable equilibrium states are also established in regard to the secondary reaction products based on the ester-forming carboxylic acids under discussion herein.

General definition of ester oils suitable as a mixture component

Preferred ester oils according to the invention are the corresponding reaction products of monocarboxylic acids with monohydric and/or polyhydric alcohols of the type mentioned. However, polybasic carboxylic acids may also be used, although they are of minor importance, particularly for reasons of cost.

The carboxylic acids may be of natural and/or synthetic origin and, as already mentioned, are preferably linear and/or branched and optionally cyclic, but not aromatic. The ester-forming carboxylic acids may be saturated and/or unsaturated, unsaturated compounds being understood in particular to be olefinically unsaturated compounds which may be mono- or even polyolefinically unsaturated. Olefinically unsaturated components may be of particular significance for establishing predetermined rheological data. It is known that olefinic relatively

long-chain compounds are more suitable for the formation of esters of lower melting point than corresponding saturated components.

5 The preferred range for the carbon number of the carboxylic acids extends from 1 to 36 and, more particularly, from 2 to 36. In the interests of ready availability, the upper limit to the carbon value may be 22 to 24. The choice of the particular chain length in the ester-forming carboxylic acid component is made - in
10 consistency with the nature of the alcohol component(s) used - taking into account the many considerations which have already been discussed and which relate not only to the ester per se and/or its rheology, but also to the secondary reaction products formed in particular by
15 partial hydrolysis.

As already mentioned, suitable alcohols are both monohydric alcohols - taking the limitations listed into account - and also polyhydric alcohols, more particularly lower polyhydric alcohols containing 2 to 6 carbon atoms
20 and preferably at most 4 hydroxyl groups.

The alcohol components may also be of natural and/or synthetic origin, are linear or branched and, in the particular case of the monohydric alcohols, are saturated and/or even olefinically unsaturated. Monohydric al-
25 cohols contain in particular up to 36 carbon atoms and preferably up to about 24 carbon atoms. Alcohols of natural and/or synthetic origin containing 6 to 18 carbon atoms and, in particular, 7 to 15 carbon atoms can be particularly important for forming the ester oil phase.

30 Particularly important ester oils in the context of the teaching according to the invention are environmentally safe ester oils of the type described in particular in the earlier applications cited above, DE-A-38 42 659, 38 42 703, 39 07 391 and 39 07 392. To complete the
35 disclosure of the invention, key characteristics of such

ester oils or ester mixtures are briefly summarized in the following.

Accordingly, the dispersed ester oil phase contains carboxylic acid esters of at least one of the following subclasses:

- 10 a) esters of C_{1-5} monocarboxylic acids and monohydric and/or polyhydric alcohols, residues of monohydric alcohols containing at least 6 and preferably at least 8 carbon atoms and the polyhydric alcohols preferably containing 2 to 6 carbon atoms in the molecule,
- 15 b) esters of monocarboxylic acids of synthetic and/or natural origin containing 6 to 16 carbon atoms, more particularly esters of corresponding aliphatically saturated monocarboxylic acids and monohydric and/or polyhydric alcohols of the type mentioned in a),
- 20 c) esters of olefinically mono- and/or polyunsaturated monocarboxylic acids containing at least 16 and, more particularly, 16 to 24 carbon atoms and, more particularly, monohydric linear and/or branched alcohols.

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The last-mentioned esters of mono- and/or poly-olefinically unsaturated monocarboxylic acids containing at least 16 carbon atoms (c) may advantageously be assigned to one of the following subclasses:

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- c1) esters of which more than 45% by weight and preferably more than 55% by weight are derived from di- and/or polyolefinically unsaturated C_{16-24} monocarboxylic acids,

c2) esters of which no more than 35% by weight are derived from di- and polyolefinically unsaturated acids and of which preferably at least about 60% by weight are monoolefinically unsaturated.

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Starting materials for the production of many of the monocarboxylic acids belonging to these subclasses, more particularly with relatively high carbon numbers, are vegetable and/or animal oils, such as coconut oil, palm kernel oil and/or babassu oil, more particularly as starting materials for the production of monocarboxylic acids predominantly containing up to 18 carbon atoms and substantially saturated components. Vegetable ester oils, more particularly for mono- and optionally polyolefinically unsaturated carboxylic acids in the C₁₆₋₂₄ range are, for example, palm oil, peanut oil, castor oil and in particular rapeseed oil. Carboxylic acids of animal origin of this type are in particular corresponding mixtures of fish oils, such as herring oil.

20 The teaching according to the invention also specifically encompasses the use of monocarboxylic acid triglycerides and, in particular, the use of corresponding glyceride oils of natural origin. However, the following factors have to be taken into consideration in this regard: natural oils and fats normally accumulate in a form so heavily contaminated, for example, by free carboxylic acids or other impurities that they cannot be directly processed in o/w emulsion fluids of the type in question. If such natural starting materials are added to water-based drilling fluids in their commercial form, intensive foaming of the drilling fluid occurs almost instantaneously in operation to such an extent that the drilling fluid is seriously affected to the point where it can no longer be used. The situation can take on a different appearance when purified and/or synthetically

obtained, selected triglycerides are used in the dispersed oil phase. In this case, the teaching of the invention can readily be put into practice even in this range. Basically, such esters of relatively high alcohols can
5 always be expected to show a considerable tendency towards foaming. Partial esters of glycerol - the mono- or diglycerides - are known to be effective emulsifier components.

As already mentioned, not only comparatively low-
10 viscosity ester oils corresponding to the disclosure of applicants' earlier applications cited above in the field of invert drilling fluids based on ester oils are suitable for the purposes of the invention, ester oils of comparatively high viscosity may also be used with particular
15 advantage as the dispersed phase of o/w emulsion drilling fluids. For example, they are valuable auxiliaries for sealing very fine pores in the filter cake of the borehole or in the desensitization of swellable rock; the lubricity of such ester oils of comparatively high
20 viscosity, even at elevated temperatures in the borehole, may even be distinctly better than that of comparatively low-viscosity ester oils, particularly where the borehole deviates from the vertical. The drilling technology is not affected by a dispersed ester oil phase of comparatively
25 high-viscosity ester oils, the rheology of the system as a whole being determined by the continuous aqueous phase. It may be preferable in this regard to use ester oils having a Brookfield viscosity of up to about 500,000 mPas, preferably up to 1,000,000 mPas or
30 even higher, for example up to about 2,000,000 mPas (as determined at room temperature), as the dispersed phase. This represents an important broadening in relation to applicants' above-cited earlier applications relating to oil-based invert drilling fluids based on ester oils.

35 In one embodiment of the invention, particular

significance is attributed to branched-chain components and, more particularly, to α -branched alcohols and/or carboxylic acids. It is known that branching of this type can have an influence on rheology, the ester formed normally becoming easier to move as a result of such branching. In addition, however, α -branching can also increase stability to hydrolysis under working conditions which is thus utilized in accordance with the invention.

10 The oleophilic alcohols suitable as a possible mixture component

Oleophilic alcohols of the type described in applicants' earlier application DE-A-39 11 238 cited at the beginning are particularly suitable in this regard. In the most important embodiment, the oleophilic alcohols in question are the oleophilic monohydric alcohols described in the foregoing in connection with the formation of the ether oils. Reference is made to the relevant observations.

20

The aqueous phase

Any type of water may be used for the production of o/w emulsion fluids according to the invention. Accordingly, the emulsion fluids may be based on fresh water and, more particularly, on salt water - especially seawater in the case of offshore drilling.

Additives in the emulsion drilling fluid

Basically, any of the additives typically used for comparable drilling fluids may be used in accordance with the invention, their addition normally being associated with a certain desirable property spectrum of the drilling fluid. The additives may be water-soluble, oil-soluble and/or dispersible in water and oil.

35 Conventional additives of water-based o/w emulsion

- drilling fluids include emulsifiers, fluid-loss additives, soluble and/or insoluble substances which build up pseudoplasticity, alkali reserves, agents for inhibiting the unwanted exchange of water between drilled formations
- 5 - for example water-swellable clays and/or salt layers - and the water-based drilling fluid, wetting agents for improving the absorption of the emulsified oil phase onto solid surfaces, for example for improving the lubricating effect and also for improving the oleophilic sealing of
- 10 exposed rock formations or rock surfaces, biocides, for example for inhibiting bacterial contamination of o/w emulsions of the type in question and the like. Full information can be found in the relevant prior art as represented, for example, by the specialist references
- 15 cited at the beginning, cf. in particular Gray and Darley, loc. cit., Chapter 11, "Drilling Fluid Components". Accordingly, the following extracts are cited purely by way of example:
- 20 Finely dispersed additives for increasing the density of the fluid: barium sulfate (barite) is widely used, although calcium carbonate (calcite) and the mixed carbonate of calcium and magnesium (dolomite) are also used.
- 25 Agents for building pseudoplasticity which also act as fluid loss additives: bentonite is mentioned above all as such an additive, being used in unmodified form in water-based drilling fluids so that it is ecologically safe. Considerable importance is attributed in practice to
- 30 other comparable clays, more particularly attapulgite and sepiolite, for saltwater fluids.

Considerable significance can also be attributed in this regard to the use of organic polymer compounds of natural

35 and/or synthetic origin, including in particular starch

or chemically modified starches, cellulose derivatives, such as carboxymethyl cellulose, guar gum, xanthan gum, or even purely synthetic water-soluble and/or water-dispersible polymer compounds, more particularly of the
5 high molecular weight polyacrylamide compound type with or without anionic or cationic modification.

Diluents for controlling viscosity: the so-called diluents may be organic or inorganic. Examples of organic
10 diluents are tannins and/or quebracho extract. Further examples are lignite and lignite derivatives, more particularly lignosulfonates. As mentioned above, however, the preferred embodiment of the invention does not use any toxic components of this type which include
15 above all the corresponding salts with toxic heavy metals, such as chromium and/or copper. Examples of inorganic diluents are polyphosphate compounds.

Emulsifiers: two special factors in particular have to be
20 taken into account in this regard so far as the teaching according to the invention is concerned. It has been found that ethers, alcohols and optionally ester oils can be stably dispersed very much more easily than pure mineral oils of the type used in the prior art. This
25 represents a first simplification. Another factor to be taken into account is that, where relatively long-chain carboxylic acid esters are used, effective o/w emulsifiers are reformed through partial saponification of the ester oils under the effect of suitable alkali reserves,
30 thus contributing towards stabilization of the system.

Additives which inhibit the unwanted exchange of water, for example with clays: suitable additives of this type are the additives known from the prior art on water-based
35 drilling fluids, more particularly halides and/or car-

bonates of the alkali metals and/or alkaline earth metals, particular significance being attributed to corresponding potassium salts, optionally in combination with lime, cf. for example the corresponding articles in
5 "Petroleum Engineer International", September 1987, 32 - 40 and "World Oil", November 1983, 93-97.

Alkali reserves: suitable alkali reserves are inorganic and/or organic bases adapted to the overall behaviour of
10 the drilling fluid, more particularly corresponding basic salts or hydroxides of alkali metals and/or alkaline earth metals and also organic bases.

In the field of organic bases, a distinction has to
15 be drawn between water-soluble organic bases, for example compounds of the diethanolamine type, and substantially water-insoluble bases of oleophilic character, more particularly basic oleophilic amine compounds of limited solubility in water of the type described in applicants'
20 above-cited earlier application DE-A-39 03 785 as an additive in invert drilling muds based on ester oils. The use of such oil-soluble bases for the purposes of the present invention also falls within the scope of the new teaching. However, oleophilic bases of this type, which
25 are distinguished in particular by at least one relatively long hydrocarbon radical containing for example 8 to 36 carbon atoms, are dissolved in the dispersed oil phase and not in the aqueous phase. These basic components are important in many respects. On the one hand, they may
30 directly act as an alkali reserve. On the other hand, they provide the dispersed oil droplets with a certain positive charge and hence lead to more intensive interaction with negative surface charges as encountered in particular in hydrophilic clays capable of ion exchange.
35 According to the invention, it is thus possible to

influence the hydrolytic cleavage and the oleophilic sealing of water-reactive layers of rock.

Basically, the quantities in which the auxiliaries and additives are used are within the usual limits and, accordingly, may be taken from the relevant literature cited in the foregoing.

Examples

A 6% by weight homogenized bentonite suspension is first prepared from commercial bentonite (non-hydrophobized) using tapwater, a pH value of 9.2 to 9.3 being adjusted with sodium hydroxide solution.

Starting out from this preswollen aqueous bentonite phase, the individual components of the water-based ester oil emulsion are incorporated in successive process steps (each accompanied by intensive mixing) in accordance with the following formulation:

350	g 6% by weight bentonite solution
20	1.5 g technical carboxymethyl cellulose, low viscosity (Relatin U 300 S9)
35	g sodium chloride
70	g ether (corresponding to the following definition)
	1.7 g emulsifier (sulf. castor oil "turkey red oil")
25	219 g barite.

Viscosity measurements are carried out as follows on the o/w emulsion fluids thus prepared:

First, the plastic viscosity (PV), the yield point (YP) and the gel strength after 10 secs. and after 10 mins. of the emulsion fluid are measured at 50°C before ageing.

The emulsion fluid is then aged for 16 h at 125°C in a roller oven to determine the effect of temperature on the stability of the emulsion. The viscosity values are

then remeasured at 50°C. The type of ester oil used, the values measured before and after ageing and, where necessary, general observations are set out in the following Examples.

5

Example 1

Oil phase used: n-C₁₀ dialkylether

	Unaged material	Aged material
10 Plastic viscosity [mPa·s]	10	13
Yield point [Pa]	15.3	9.6
Gel strength [Pa]		
10 secs.	10.5	6.7
15 10 mins.	11.5	9.1

Example 2

Example 1 is repeated without the emulsifier (turkey red oil).

20 The viscosities of the material before and after ageing are as follows:

	Unaged material	Aged material
25 Plastic viscosity [mPa·s]	8	7
Yield point [Pa]	16.2	17.7
Gel strength [Pa]		
10 secs.	17.2	18.2
30 10 mins.	16.8	13.4

Even in the fresh state, a few droplets are formed on the surface.

Example 3

Oil phase used: diisotridecyl ether

The viscosities of the drilling fluid before and after ageing are as follows:

		Unaged material	Aged material
5			
	Plastic viscosity [mPa·s]	15	15
	Yield point [Pa]	11.5	14.4
	Gel strength [Pa]		
10	10 secs.	11.0	13.4
	10 mins.	16.8	12.5

Examples 4 and 5 (Comparison Examples)

For comparison with the ether-based emulsion fluids according to the invention, emulsion fluids (one with and one without turkey red oil as emulsifier) are prepared from a pure hydrocarbon oil using the formulation described above and tested. The commercial product "WP83HF", which is widely used in drilling fluids, is used as the hydrocarbon oil.

The table of values for Example 4 relates to the emulsifier-containing emulsion drilling fluid while the table of values for Example 5 relates to the product used without any emulsifier.

25

Example 4:

		Unaged material	Aged material
30			
	Plastic viscosity [mPa·s]	10	10
	Yield point [Pa]	16.3	9.1
	Gel strength [Pa]		
	10 secs.	10.1	4.8
	10 mins.	11.9	8.6

Example 5

	Unaged material	Aged material
5 Plastic viscosity [mPa·s]	9	8
Yield point [Pa]	16.8	17.7
Gel strength [Pa]		
10 secs.	16.8	17.2
10 mins.	28.7	14.8

CLAIMS

1. The use of at least substantially water-insoluble ethers of mono- and/or polyhydric alcohols of natural and/or synthetic origin, which are liquid and/or at least plastic at the working temperature and have flashpoints of at least 80°C, or of corresponding solutions of such ethers in ecologically safe water-insoluble oils as the dispersed oil phase of water-based o/w emulsion drilling fluids which are suitable for the ecologically safe development of geological formations and which, if desired, contain insoluble fine-particle weighting agents for forming water-based o/w emulsion drilling muds and/or other additives, such as emulsifiers, fluid loss additives, wetting agents, alkali reserves and/or auxiliaries for inhibiting drilled rock highly sensitive to water.
2. The use claimed in claim 1, characterized in that the dispersed ether oil phase is used in quantities of at least about 5% by weight and preferably in quantities of at least about 8% by weight in the o/w drilling fluid (% by weight based on the sum of the unweighted liquid components ether oil/water) and preferably makes up no more than about 50% by weight and, in particular, no more than about 40% by weight (% by weight on the same basis as before).
3. The use claimed in claims 1 and 2, characterized in that the water-insoluble ethers make up an at least substantial part of the continuous oil phase, i.e. form more than 10% by weight, preferably more than 50% by weight and, more preferably, at least by far the predominant part of the continuous oil phase.
4. The use claimed in claims 1 to 3, characterized in that oleophilic ethers of mono- and/or dihydric alcohols, more particularly monohydric alcohols, are used.
5. The use claimed in claims 1 to 4, characterized in that the ethers used are free from aromatic molecule



constituents and are preferably derived from linear and/or branched hydrocarbon chains which may even be olefinically unsaturated.

- 5 6. The use claimed in claims 1 to 5, characterized in that ethers of monohydric alcohols containing at least 4 and preferably at least 6 to 8 carbon atoms, which are linear and/or branched and, if desired, at least partly olefinically unsaturated and, in particular, contain up to 36 carbon atoms, are used.
- 10 7. The use claims in claims 1 to 6, characterized in that ethers, mixed ethers and/or ether mixtures of monohydric alcohols containing up to 24 carbon atoms are used.
- 15 8. The use claimed in claims 1 to 7, characterized in that at least partly water-insoluble polyalkylene glycol (mixed) ethers of, in particular, lower alkylene glycols, for example corresponding mixed ethers of ethylene oxide and/or propylene oxide with alcohols containing at least 4 carbon atoms are used in the continuous oil phase.
- 20 9. The use claimed in claims 1 to 8, characterized in that oleophilic alcohols and/or ester oils of which the ester-forming alcohol components are derived from mono- and/or polyhydric alcohols are at least partly used as ecologically safe water-insoluble oils for mixing with
- 25 the water-insoluble ethers, the alcohols preferably being selected so that their use does not involve any toxicological risks, particularly inhalation-toxicological risks, in the event of partial ester saponification.
- 30 10. The use claimed in claims 1 to 9, characterized in that esters of monohydric alcohols of natural and/or synthetic origin and pronounced oleophilic character preferably containing at least 6 and, more preferably, at least 8 carbon atoms are used as the ester oils.
- 35 11. The use claimed in claims 1 to 10, characterized in that, where ester oils based on polyhydric alcohols are



present, full and/or partial esters of, in particular, lower alcohols containing up to 4 OH groups in the molecule, which may even be present as partial ethers, are used, corresponding mixture components based on water-soluble polyols, more particularly ethylene glycol, propylene glycol and/or glycerol, being preferred.

12. The use claimed in claims 1 to 11, characterized in that oleophilic ethers or mixtures thereof with alcohols and/or ester oils having solidification values (flow point and pour point) below 0°C and preferably below -5°C and flashpoints of at least 100°C are used.

13. The use claimed in claims 1 to 12, characterized in that ethers or mixtures thereof with ecologically safe oils, which have a Brookfield RVT viscosity at 20°C of up to about 2,000,000 mPas and preferably up to about 1,000,000 mPas as a continuous oil phase, are used as the dispersed oil phase.

14 The use claimed in claims 1 to 13, characterized in that the dispersed oil phase contains ethers mixed with carboxylic acid esters from at least one of the following subclasses:

a) esters of C₁₋₅ monocarboxylic acids and monohydric and/or polyhydric alcohols, residues of monohydric alcohols containing at least 6 and preferably at least 8 carbon atoms and the polyhydric alcohols preferably containing 2 to 6 carbon atoms in the molecule;

b) esters of monocarboxylic acids of synthetic and/or natural origin containing 6 to 16 carbon atoms, more particularly esters of corresponding aliphatically saturated monocarboxylic acids and mono- and/or polyhydric alcohols of the type mentioned in a),



- 5 c) esters of olefinically mono- and/or polyunsaturated monocarboxylic acids containing at least 16 and, more particularly, 16 to 24 carbon atoms and, in particular, monohydric linear and/or branched alcohols.

10 15. The use claimed in claims 1 to 14, characterized in that ester oils according to claim 14, c) present in the dispersed phase may be assigned to at least one of the following subclasses:

15 c1) esters of which more than 45% by weight and preferably more than 55% by weight are derived from di- and/or polyolefinically unsaturated C₁₆₋₂₄ monocarboxylic acids,

20 c2) esters of which no more than 35% by weight are derived from di- and polyolefinically unsaturated acids and of which preferably at least about 60% by weight are monoolefinically unsaturated.

25 16. The use claimed in claims 1 to 15, characterized in that basic amine compounds of pronounced oleophilic character and at most limited solubility in water are co-used as an additive in the dispersed oil phase.

30 17. The use claimed in claims 1 to 16, characterized in that oleophilic amine compounds which are at least predominantly free from aromatic constituents and of which the solubility in water at room temperature is no more than about 1% by weight are co-used.

18. The use claimed in claims 1 to 17, characterized in that basic amine compounds containing at least one long-chain, preferably C₈₋₃₆ hydrocarbon radical are used as an additive.

35 19. The use claimed in claims 1 to 18, characterized in



that a dispersed oil phase containing up to 10% by weight and preferably about 0.1 to 2% by weight of oleophilic amine compounds, based on oil phase, is used.

5 20. The use claimed in claims 1 to 19, characterized in that the homogeneous aqueous phase used consists of fresh water or water containing dissolved or suspended salts, more particularly halides and/or carbonates of the alkali and/or alkaline earth metals, which if desired may even be modified seawater.

10 21. The use claimed in claims 1 to 20, characterized in that inorganic and/or organic auxiliaries and additives for water-based emulsion drilling fluids or muds which are at least substantially ecologically and toxicologically safe, for example are free from soluble toxic
15 heavy metal compounds, are used.

22. The use claimed in claims 1 to 21, characterized in that the dispersed ether phase is used together with known inorganic and/or organic auxiliaries for limiting the rock hydration of correspondingly disposed mineral
20 layers.

23. Water-based o/w emulsion drilling fluids for the ecologically safe development of geological formations which, in a homogeneous aqueous phase, contain a stably dispersed oil phase in quantities of 5 to 50% by weight
25 (based on the sum of the unweighted water and oil phase), optionally together with dissolved and/or dispersed auxiliaries, such as emulsifiers, fluid loss additives, wetting agents, fine-particle weighting agents, salts, alkali reserves and/or biocides, characterized in that an
30 at least substantial part of the dispersed oil phase is formed by water-dispersible ethers of mono- and/or polyhydric alcohols of natural and/or synthetic origin, which are liquid and/or at least plastic at the working temperature and have flashpoints of at least 80°C, or by
35 corresponding solutions of such ethers in ecologically



safe water-insoluble oils, more particularly in oleophilic alcohols and/or corresponding ester oils.

24. Emulsion drilling fluids as claimed in claim 23, characterized in that the dispersed oil phase makes up at least about 8% by weight and preferably no more than about 40% by weight, percentage contents of the emulsified oil phase of about 10 to 35% by weight being preferred.

25. Emulsion drilling fluids as claimed in claims 23 and 24, characterized in that the ethers and the oleophilic alcohols and/or ester oils optionally present are free from ecologically unsafe, more particularly aromatic constituents.

26. Emulsion drilling fluids as claimed in claims 23 to 25, characterized in that, together with the ethers, they contain as ecologically safe oils ester oils of at least predominant percentages of monocarboxylic acids and mono- and/or polyhydric alcohols which, preferably, may be at least partly assigned to one of the following classes:

a) esters of C_{1-5} monocarboxylic acids and monohydric and/or polyhydric alcohols, residues of monohydric alcohols containing at least 6 and preferably at least 8 carbon atoms and the polyhydric alcohols preferably containing 2 to 6 carbon atoms in the molecule,

b) esters of monocarboxylic acids of synthetic and/or natural origin containing 6 to 16 carbon atoms, more particularly esters of corresponding aliphatically saturated monocarboxylic acids and monohydric and/or polyhydric alcohols of the type mentioned in a),

c) esters of olefinically mono- and/or polyunsaturated monocarboxylic acids containing at least 16 and,



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more particularly, 16 to 24 carbon atoms and, in particular, monohydric linear and/or branched alcohols.

- 5 27. Emulsion drilling fluids as claimed in claims 23 to 26, characterized in that, where ester oils of subclass c) are present, they may be at least partly assigned to at least one of the following subclasses:
- 10 c1) esters of which more than 45% by weight and preferably more than 55% by weight are derived from di- and/or polyolefinically unsaturated C₁₆₋₂₄ monocarboxylic acids,
- 15 c2) esters of which no more than 35% by weight are derived from di- and polyolefinically unsaturated acids and of which preferably at least about 60% by weight are monoolefinically unsaturated.
- 20 28. Emulsion drilling fluids as claimed in claims 23 to 27, characterized in that, together with free alcohols, ester oils based on monohydric, substantially water-insoluble alcohols of pronounced oleophilic character, which are the same as or different from the free alcohol
- 25 constituent of the dispersed oil phase, are present as mixture component in the oil phase.
29. Emulsion drilling fluids as claimed in claims 23 to 28, characterized in that the monohydric alcohols present in the ester oil are selected so that, in the event of
- 30 partial ester hydrolysis in use, no inhalation-toxicologically unsafe alcohols are formed.
30. Emulsion drilling fluids as claimed in claims 23 to 29, characterized in that basic amine compounds of pronounced oleophilic character and limited solubility in
- 35 water which are free from aromatic constituents and which



* C L M S *

preferably contain at least one long-chain, preferably C₈₋₃₆ hydrocarbon radical are co-used in the dispersed ether oil phase.

5 31. Emulsion drilling fluids as claimed in claims 23 to 30, characterized in that the typical auxiliaries and additives of water-based emulsion drilling fluids are also selected for ecological safeness and, in particular, are free from toxic heavy metal compounds.

10 32. Emulsion drilling fluids as claimed in claims 23 to 31, characterized in that they contain additives for inhibiting the water-absorption of swellable rock strata or clays.

15 33. Emulsion drilling fluids as claimed in claims 23 to 32, characterized in that they are adjusted to a pH value in the neutral to moderately basic range and, more particularly, to a pH value in the range from of 7.5 to 11.



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