

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 o/w drilling fluids selected in accordance with the invention simplify ecotoxic problems to a considerable extent.

20

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 muds 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 of 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 de-aromaticized 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, even drilling fluids of the water-based o/w emulsion type have used pure hydrocarbon oils as the disperse oil phase, see for example Gray, Darley, loc. cit., pages 51/52, Chapter entitled "Oil Emulsion Muds" and the tabular summary 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 muds 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 muds 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 muds 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, disinfectants 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 phases used in such drilling fluids. Even the substantially de-aromaticized 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. De-aromaticized 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 de-aromaticized.

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 muds. 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 muds 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.

15 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 P 38 42 659.5 and P 38 42 703.6 (D 8523 and D 8524) and the modifications of useful ester oils according to earlier patent applications P 39 07 391.2 and P 39 07 392.0 (D 8606 and D 8607).

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 mud 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.

35 A modified form of such w/o invert drilling muds is

described in Applicants' earlier application P 39 11 238.1 (D 8511). This application describes the use of

- 5 a) at least substantially water-insoluble monohydric and/or polyhydric alcohols of natural and/or synthetic origin which are flowable and pumpable at temperatures of 0 to 5°C

or of

- 10 b) solutions of at least substantially water-insoluble monohydric and/or polyhydric alcohols of natural and/or synthetic origin - flowable and pumpable at temperatures in the above-mentioned range - in ecologically safe water-insoluble oils

15 as the continuous oil phase of drilling fluids which are present in the form of w/o emulsions and contain a disperse aqueous phase and optionally other typical additives in the alcohol-containing phase. Ester oils of the type described in applicants' earlier applications
20 mentioned above are at least partly used as the ecologically safe water-insoluble oils for mixing with the water-insoluble alcohols.

An important further development of these invert drilling muds based on ester oils is the subject of
25 earlier application P 39 03 785.1 (D 8543).

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
30 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, distinctly oleophilic amine compounds capable of forming salts with carboxylic acids and showing at most
35 limited solubility in water as additive in the oil phase.

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 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 emulsion systems. At the same time, however, it would 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, therefore, the invention seeks to utilize the advantages of o/w emulsion muds over pure water-based drilling fluids, but at the same time to replace the mineral oil phase at least substantially and preferably completely or partly by ecologically safe alcohols of distinctly oleophilic character.

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 additives.

In a first embodiment, therefore, the present invention relates to the use of at least substantially water-insoluble monohydric and/or polyhydric alcohols of natural and/or synthetic origin, which are liquid or at least plastic at the working temperature and have flash points of at least 80°C, or corresponding solutions of monohydric and/or polyhydric alcohols in ecologically safe water-insoluble oils as the disperse 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
5 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.

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

The additional preferred feature that ecologically and toxicologically at least substantially safe inorganic and/or organic auxiliaries and additives are at least predominantly used for water-based emulsion drilling
30 fluids or emulsion drilling muds applies to both embodiments of the teaching according to the invention. For 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

The mixing ratios of the alcohol/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 around 5% by weight or preferably between 5 and 10% by weight, i.e. for 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 oil content is typically 50% by weight or even slightly higher, for example at most 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 the w/o invert mud type appears logical or appropriate.

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

A quantity of alcohol of 10 to 40% by weight (on the same basis as before) and, in particular, quantities of the alcohol phase of 15 to 35% by weight enable numerous hitherto unknown and hitherto unreported advantages of such emulsion drilling fluids to be utilized. 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 alcohol or ester oil phase.

The Various Embodiments of the Invention

In a first embodiment, the dispersed oil phase of the water-based o/w drilling muds is formed exclusively or by far predominantly by the substantially water-insoluble and, preferably, distinctly oleophilic alcohols. The rheology of the alcohols used is adapted to the technical requirements of the drilling muds; small rheological corrections can be made by using the small quantities of diluents envisaged in this embodiment. Dispersed oil phases of which more than 70% by weight, preferably more than 80% by weight and, if desired, even the complete oil phase is formed by the alcohols as such are particularly suitable for the case under discussion.

The oil mixing components optionally used in small quantities in this embodiment may be pure and, in particular, de-aromatized hydrocarbon compounds, but especially selected ester oils of the type mentioned in applicants' earlier applications cited above. This embodiment is described in detail in the following.

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

In this embodiment, the content of alcohols selected in accordance with the invention in the dispersed oil phase is in the range from at least 10% by weight to 70% by weight, based on the liquid oil phase, alcohol contents of at least about 35% by weight and preferably of at least about 50% by weight, based on the oil phase being preferable. Preferred mixing components for this second embodiment are, again, ecologically safe ester oils of the type described in detail hereinafter. However, pure hydrocarbon oils may also be used.

Finally, in a third variant, the invention relates to the use of substantially water-insoluble alcohols of, in particular, distinctly oleophilic character as an additive in the oil phase which is present in small quantities, typically in the range from about 0.1 to at most 10% by weight, based on the oil phase - in order to impart selected important additional properties to the dispersed oil phase. In one preferred embodiment, the predominant part of the oil phase is again formed by ester oils of the type described hereinafter.

The Alcohol Components of Distinctly Oleophilic Character used in Accordance with the Invention

The use of the alcohols as oil phase and also their use as a small or large part of the oil phase presupposes their adequate insolubility in water. The solubility of suitable alcohols in water at room temperature is preferably below 5% by weight, more particularly below 1% by weight and preferably no more than about 0.5% by weight.

The following general principles apply to the chemical characteristics: both monohydric and/or polyhydric alcohols may be used providing the oleophilic character of the alcoholic component remains intact. In addition to monohydric alcohols, dihydric alcohols and/or partial ethers of polyhydric alcohols containing at least one free hydroxyl group are particularly suitable. The alcohols themselves should be ecologically safe so that, in the preferred embodiment, they do not contain any aromatic constituents. Linear and/or branched aliphatic or even corresponding unsaturated, more especially mono- and/or polyolefinically unsaturated alcohols, are the preferred compounds. Cycloaliphatic alcohols may be considered.

An important general requirement in the context of the teaching according to the invention is that the

alcohols as such should not only be ecologically safe, they should also involve no other toxicological risks, more particularly inhalation-toxicological risks. However, alcohols of distinctly oleophilic character, as
5 required for the purposes of the invention are generally distinguished by such low volatility that this requirement is satisfied in any event.

So far as the mixing of the alcohols used in accordance with the invention with ester oils is concerned, the
10 following principle applies: the free alcohols used in accordance with the invention may be the same as or different from the alcohol components used in the ester oil.

Whereas, in the ester oils, the alcohol component is
15 determined, for example, by considerations relating to the rheology of the ester oil and/or to the accessibility of the ester-forming alcohols, the use of the free alcohols in accordance with the invention is aimed at the desired improvements in the emulsion drilling mud.

20 From the basically broad range of distinctly oleophilic alcohols, alcohols with a linear and/or branched hydrocarbon structure are particularly suitable, especially in the embodiment where the alcohols themselves form the at least predominant part of the disperse oil phase.
25 Among monohydric alcohols of this type, corresponding 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
30 the number of carbon atoms is imposed by the accessibility factor and, for example, is of the order of 36 and preferably between 20 and 24. The alcohols themselves may be linear and/or branched, aliphatically saturated or even mono- and/or polyolefinically unsaturated.

35 The rheology of the alcohols is largely determined

in known manner by their structure. Saturated and linear alcohols tend to thicken or solidify earlier than olefinically unsaturated and/or branched alcohols. For example, saturated linear fatty alcohols in the $C_{16/18}$ range are known to have solidification points around 50°C whereas olefinically unsaturated oleyl alcohol solidifies below 4°C.

Basically, alcohols of natural and/or synthetic origin are suitable. In particular, synthetic alcohols in the C_{8-24} range of particular interest in the present context, which may even contain unsaturated components, are often inexpensive commercially available components and may be used for the purposes of the invention.

The alcohols themselves should have flash points 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 monohydric alcohols preferably containing at least 8 carbon atoms, selected polyols or partial ethers thereof may also be used. Suitable polyols are, in particular, optionally branched diols with an adequate content of the oleophilic hydrocarbon in the molecule. Suitable diols are, for example, oleophilic diols with hydroxyl groups in the alpha,omega-position and/or diols in which the hydroxyl groups are situated at adjacent carbon atoms. Characteristic examples of compounds of this type are 2,2-dimethylpropane-1,3-diol (neopentyl glycol) or the saponification products of epoxidized olefins. However, partial ethers of such diols with monohydric alcohols are also particularly suitable.

Increasing freedom in the choice of suitable alcohol components exists in particular in those embodiments where the dispersed oil phase is predominantly formed by water-insoluble mixture components, i.e. in particular by the ester oils described hereinafter. At least substantially water-insoluble polyalkylene glycol ethers or

corresponding mixed ethers of lower alkylene glycols inter alia have proved to be useful additives. For example, corresponding mixed ethers of ethylene oxide and/or propylene oxide are useful additives for the purposes of the invention even when they reach molecular weights of, for example, 5,000 and show adequate insolubility in water in the system as a whole. Compounds of the last-mentioned type are particularly important in the embodiment where the water-insoluble alcohols are used as an additive in a quantity of at most about 10% by weight.

One important embodiment of the invention is characterized by the use of water-insoluble alcohols which, in turn, are free from basic amino groups and, preferably, also contain no other reactive groups, for example carboxyl groups.

The Mixture Components in the Dispersed Oil Phase

Oil components suitable for mixing in accordance with the invention are the mineral oils typically used at present in drilling muds, preferably substantially de-aromaticized aliphatic and/or cycloaliphatic hydrocarbon fractions. Reference is made to the relevant prior art literature and to the products available on the market.

However, particularly important mixture components in the context of the teaching according to the invention are environmentally safe ester oils which satisfy the following general requirements:

The ester oils should be fluid at 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 easier processability under practical conditions, it is preferred to use ester oils having solidification values (flow point

and pour point) below 10°C and preferably below 0°C. Corresponding ester oils with solidification values no higher than -5°C can be particularly suitable. A factor to be taken into consideration in this regard is that the
5 drilling fluids are normally made up on site using seawater, for example, at comparatively low water temperatures.

In the interests of operational safety, the ester oils should have flash points of at least 80°C, higher
10 flash points 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 the ester oils have a biologically or ecologically compatible
15 constitution, i.e. in particular are free from unwanted toxic constituents. Accordingly, the preferred embodiment of the invention uses ester oils which are free from aromatic constituents and, in particular, contain saturated and/or olefinically unsaturated, linear and/or
20 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
25 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
30 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
35 the emulsion drilling fluid and, hence, possible vari-

ations 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
5 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
10 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
15 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.

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

20 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 measures to rule out inhalation-toxic risks.

Lower polyhydric alcohols of the type in question
25 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 drilling fluid according to the invention. Providing any partial esters formed retain the substantially water-
30 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 state of water-soluble hydrolysis products, i.e. in particular the free lower polyhydric alcohols, is reached.
35 However, the changes occurring in practice in such emul-

sion drilling fluids from this source are insignificant. Above all, comparatively high stability of the ester bond is established under the working conditions according to the invention. It is known that o/w emulsion drilling
5 fluids normally work at pH values in the neutral to moderately alkaline range, for example at pH values of 7.2 to 11 and, more particularly, at pH values of 7.5 to 10.5, so that for this reason alone there is no aggressive hydrolytic attack on the ester bond. In addition,
10 however, the following observations above all also apply:

In the practical application of the drilling fluid 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
15 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 shaft wall and also impedes or even completely suppresses any interaction between the drilled
20 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
25 rapidly established in the drilling fluid, enabling continuous operation to be carried out over prolonged periods.

The foregoing considerations are of course only relevant to the present invention when considerable
30 quantities of the dispersed oil phase are formed by ester oils. The oleophilic alcohols and mixtures thereof with hydrolysis-resistant components are not affected by such additional considerations so that an important and preferred embodiment of the teaching according to the
35 invention also lies in the substantial or even complete

absence of ester oils.

Considerations delving further into 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 unlimited 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 is a danger to personnel. According to the invention, therefore, the number 6 is selected as the lower carbon limit where ester oils using monohydric alcohols are used. It is particularly preferred to use esters of monohydric, substantially water-insoluble oleophilic alcohols of natural and/or synthetic origin 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: 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.

It is possible in accordance with the teaching of the invention, to use identical alcohols both in free form and in the ester oil used, although this is not necessary. Accordingly, the invention also encompasses

embodiments in which different alcohols compared with the free alcohol content originally used and present are formed by ester hydrolysis.

5 The carboxylic acids formed by partial hydrolysis of the ester oil drilling fluid also require a number of considerations.

10 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 salts.

15 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 taken into consideration.

20 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 propionates, while fatty acids of longer chain length, particularly those in the C_{12-24} range, lead to emulsifying compounds.

25 Accordingly, by suitably selecting the ester oils and, to a certain extent, the salt-forming cations in the emulsion mud, it is possible selectively to control the secondary products in the emulsion mud which can have a major influence on the quality and effect of the emulsion mud. However, the foregoing observations also apply in
30 this regard: not only the disperse 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
35 reaction products based on the ester-forming carboxylic

acids under discussion herein.

General Definition of Suitable Ester Oils

Preferred ester oils according to the invention are
5 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.

10 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
15 understood in particular to be olefinically unsaturated
compounds which may be mono- or even polyolefinically un-
saturated. Olefinically unsaturated components may be of
particular significance for establishing predetermined
rheological data. It is known that olefinic relatively
20 long-chain compounds are more suitable for the formation
of esters of lower melting point than corresponding
saturated components.

The preferred range for the carbon number of the
carboxylic acids extends from 1 to 36 and, more particu-
25 larly, from 2 to 36. In the interests of ready avail-
ability, the upper limit to the carbon value may be about
22 to 24. The choice of the particular chain length in
the ester-forming carboxylic acid component is made - in
consistency with the nature of the alcohol component(s)
30 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
partial hydrolysis.

35 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 and preferably at most 4 hydroxyl groups.

5 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 alcohols contain in particular up to 36 carbon atoms and
10 preferably up to 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 oils.

15 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, P 38 42 659.5, P 38 42 703.6, P 39 07 391.2 and P 39 07 392.0 (D 8523, D 8524, D 8606 and D 8607). To complete the disclosure
20 of the invention, key characteristics of such ester oils or ester mixtures are briefly summarized in the following.

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

- 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
30 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
35 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),

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

10

The last-mentioned esters of mono- and/or polyolefinically unsaturated monocarboxylic acids containing at least 16 carbon atoms (c) may advantageously be assigned to 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

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

30

35

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.

5 The teaching of the invention also specifically encompasses the use of monocarboxylic acid triglycerides and hence, more particularly, the use of corresponding glyceride oils of natural origin. However, the following factors have to be taken into consideration in this
10 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 muds of the type in question. If such natural starting materials are added
15 to water-based drilling fluids in their commercial form, intensive foaming of the drilling mud occurs almost instantaneously in operation to such an extent that the drilling mud is seriously affected to the point where it can no longer be used. The situation may appear dif-
20 ferent when purified and/or synthetic selected triglycerides are used in the dispersed oil phase. In this case, too, the teaching according to the invention may readily be put into practice. Basically, such esters of relatively high alcohols can always be expected to show a
25 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-viscosity ester oils corresponding to the disclosure of
30 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 advantage as the dispersed phase of o/w emulsion
35 drilling fluids. For example, they are valuable auxilia-

ries 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 or comparatively high 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 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 or even higher, for example up to about 1,000,000 or even 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.

In one embodiment of the invention, particular significance is attributed to branched-chain components and, more particular, 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.

The Aqueous Phase

Water of any type may be used for the production of o/w emulsion muds according to the invention. Accordingly, the water may be based on fresh water and, in particular, on seawater, especially seawater from offshore fields.

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.

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 - 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 exposed rock formations or rock surfaces, disinfectants, 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 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:

Finely dispersed additives for increasing the density of the fluid: barium sulfate (barite) is widely used, although calcium carbonate (calcite) or the mixed carbonate of calcium and magnesium (dolomite) are also used.

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 other comparable clays, more particularly attapulgite and sepiolite, for saltwater muds.

5

Considerable significance can also be attributed in this regard to the use of organic polymer compounds of natural and/or synthetic origin, including in particular starch or chemically modified starches, cellulose derivatives, 10 such as carboxymethyl cellulose, guar gum, xanthan gum, or even purely synthetic water-soluble and/or water-dispersible polymer compounds, more particularly of the high molecular weight polyacrylamide compound type with or without anionic or cationic modification.

15

Diluents for controlling viscosity: the so-called diluents may be organic or inorganic. Examples of organic diluents are tannins and/or quebracho extract. Further examples are lignite and lignite derivatives, more 20 particularly lignosulfonates. As mentioned above, however, the preferred embodiment of the invention does not use any toxic components of this type which include above all the corresponding salts with toxic heavy metals, such as chromium and/or copper. Examples of 25 inorganic diluents are polyphosphate compounds.

Emulsifiers: two special factors in particular have to be taken into account in this regard so far as the teaching according to the invention is concerned. It has been 30 found that 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 represents a first simplification. Another factor to be taken into account is that, where relatively long-chain carboxylic 35 acid esters are used, effective o/w emulsifiers are

reformed through partial saponification of the ester oils under the effect of suitable alkali reserves, thus contributing towards stabilization of the system.

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

15

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

In the field of organic bases, a distinction has to be drawn between water-soluble organic bases, for example compounds of the diethanolamine type, and substantially
25 water-insoluble bases of oleophilic character, more particularly basic oleophilic amine compounds of limited solubility in water of the type described in applicants' above-cited earlier application P 39 03 785.1 (D 8543) as an additive in invert drilling muds based on ester oils.
30 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 are distinguished in particular by at least one relatively long hydrocarbon chain containing for example 8 to 36
35 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 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. 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.

15

Examples

A 6% by weight homogenized bentonite suspension is first prepared from commercial bentonite (non-hydrophobized) using tap water, 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 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
	1.5 g technical carboxymethyl cellulose, low viscosity (Relatin U 300 S9)
30	35 g sodium chloride
	70 g oleophilic alcohol (corresponding to the following definition)
	1.7 g emulsifier (sulf. castor oil "turkey red oil")
219	g barite.

Viscosity measurements are carried out as follows on the o/w emulsion muds 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 mud are measured at 50°C before ageing.

The emulsion mud 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 oleophilic alcohol used, the values measured before and after ageing and, where necessary, general observations are set out in the following Examples.

Example 1

Oil phase used: isotridecyl alcohol

	Unaged material	Aged material
Plastic viscosity [mPa·s]	14	14
Yield point [Pa]	20.1	14.4
Gel strength [Pa]		
10 secs.	15.8	11.5
10 mins.	15.3	18.7

Example 2

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

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

		Unaged material	Aged material
	Plastic viscosity [mPa·s]	9	10
5	Yield point [Pa]	17.7	18.7
	Gel strength [Pa]		
	10 secs.	16.8	16.8
	10 mins.	15.8	17.7
10	Even in the fresh state, a few droplets are formed on the surface.		

Example 3

Oil phase used: C₁₀ synthetic alcohol (Etoxos C10)

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

		Unaged material	Aged material
20	Plastic viscosity [mPa·s]	16	15
	Yield point [Pa]	12.9	19.6
	Gel strength [Pa]		
	10 secs.	11.5	13.9
25	10 mins.	18.2	35.4

Example 4

30 Example 3 is repeated using a C₁₂₋₁₈ alcohol of natural origin (commercial product "Lorol techn.").

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

	Unaged material	Aged material
Plastic viscosity [mPa·s]	9	21
5 Yield point [Pa]	14.4	16.8
Gel strength [Pa]		
10 secs.	8.6	14.8
10 mins.	8.6	17.7

**CLAIMS**

1. The use of at least substantially water-insoluble monohydric and/or polyhydric alcohols of natural and/or synthetic origin, which are liquid or at least plastic at the working temperature and have flash points of at least 80°C, or corresponding solutions of monohydric and/or polyhydric alcohols in ecologically safe water-insoluble oils as the disperse 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 disperse alcohol 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 alcohol 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 alcohols make up an at least substantial part of the oil phase, forming more than 10% by weight and preferably more than 50% by weight thereof.
4. The use claimed in claims 1 to 3, characterized in that oleophilic monohydric and/or dihydric alcohols and/or corresponding partial ethers of polyhydric, more particularly dihydric, alcohols are used.
5. The use claimed in claims 1 to 4, characterized in that alcohols which are free from aromatic molecular



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

5 6. The use claimed in claims 1 to 5, characterized in that monohydric alcohols containing at least 6 carbon atoms and preferably at least 8 carbon atoms, which are linear and/or branched and, if desired, may be at least partly olefinically unsaturated and, in particular, contain up to 36 carbon atoms are used.

10 7. The use claimed in claims 1 to 5, characterized in that oleophilic, optionally branched diols with hydroxyl groups in the alpha,omega-position and/or at adjacent carbon atoms or partial ethers thereof, for example with monohydric alcohols, are used.

15 8. The use claimed in claim 7, characterized in that at least substantially 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 at least one free hydroxyl group, are used in the continuous oil phase.

20 9. The use claimed in claims 1 to 8, characterized in that ester oils of which the ester-forming alcohol components are derived from monohydric and/or polyhydric alcohols and which are preferably selected in such a way that there are no toxicological risks, above all no inhalation-toxicological risks, through partial ester saponification under in-use conditions, are at least partly used as the ecologically safe water-insoluble oils for mixing with the water-insoluble alcohols.

25 10. The use claimed in claims 1 to 9, characterized in that esters of monohydric alcohols of natural and/or synthetic origin and distinctly oleophilic character preferably containing at least 6 and, more preferably, at least 8 carbon atoms, which are the same as or different from the oleophilic alcohols of the dispersed oil phase,

30

35



are used as the ester oils.

11. The use claimed in claims 1 to 10, characterized in that, where ester oils based on polyhydric alcohols are used, full and/or partial esters of, in particular, lower
5 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.

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

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

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

25

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
30 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
35 particularly esters of corresponding aliphatically



saturated monocarboxylic acids and monohydric and/or polyhydric alcohols of the type mentioned in a),

- 5 c) esters of mono- and/or polyolefinically unsaturated 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 disperse 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 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 1% by weight are co-used.
- 35 18. The use claimed in claims 1 to 17, characterized in that basic amine compounds containing at least one long-



chain, preferably C_{8-36} hydrocarbon radical are used as an additive.

19. The use claimed in claims 1 to 18, characterized in that a disperse oil phase containing up to 10% by weight and preferably 0.1 to 2% by weight of oleophilic amine compounds, based on oil phase, is used.

20. The use claimed in claims 1 to 19, characterized in that 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 sea water, is used as the homogeneous aqueous phase.

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

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

23. Water-based o/w emulsion drilling fluids which, in a homogeneous aqueous phase, contain a stably dispersed oil phase in quantities of 5 to 50% by weight (based on the sum of the unweighted water and oil phase), if desired together with dissolved and/or dispersed auxiliaries, such as emulsifiers, fluid loss additives, wetting agents, fine-particle weighting agents, salts, alkali reserves and/or disinfectants, and which are characterized in that an at least substantial part of the disperse oil phase is formed by water-dispersible, monohydric and/or polyhydric alcohols of natural and/or synthetic origin, which are liquid or at least plastic at



the working temperature and have flash points of at least 80°C, or corresponding solutions of monohydric and/or polyhydric alcohols in ecologically safe water-insoluble oils.

- 5 24. Emulsion drilling fluids as claimed in claim 23, characterized in that the disperse 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
- 10 preferred.
25. Emulsion drilling fluids as claimed in claims 23 and 24, characterized in that the oleophilic alcohols and the ester oils optionally present are free from ecologically unsafe, more particularly aromatic constituents.
- 15 26. Emulsion drilling fluids as claimed in claims 23 to 25, characterized in that, together with the oleophilic alcohols, ester oils at least predominantly formed by monocarboxylic acids and mono- and/or polyhydric alcohols which may preferably be assigned at least partly to one
- 20 of the following classes:
- a) esters of C₁₋₅ monocarboxylic acids and monohydric and/or polyhydric alcohols, residues of monohydric alcohols containing at least 6 and preferably at
- 25 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
- 30 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),
- 35 c) esters of mono- and/or polyolefinically unsaturated



monocarboxylic acids containing at least 16 and, more particularly, 16 to 24 carbon atoms and, in particular, monohydric linear and/or branched alcohols,

5

are present as the ecologically safe oils.

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 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 60% by weight are monoolefinically unsaturated.

20

28. Emulsion drilling fluids as claimed in claims 23 to 27, characterized in that ester oils based on monohydric, substantially water-insoluble alcohols of pronounced oleophilic character, which are the same as or different from the constituent of the oil phase present in the form of free alcohols, are present as a mixture component in the oil phase.

25

29. Emulsion drilling fluids as claimed in claims 23 to 28, characterized in that the constituents of monohydric alcohols present in the ester oil are selected so that, in practical application, no inhalation-toxicologically harmful alcohols are formed in the event of partial ester hydrolysis occurring in use.

30

30. Emulsion drilling fluids as claimed in claims 23 to

35



29, characterized in that basic amine compounds of pronounced oleophilic character and at most limited solubility in water, which are free from aromatic constituents and which preferably contain at least one preferably C₈₋₃₆ hydrocarbon radical, are co-used in the disperse alcohol oil phase.

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 their ecological compatibility and, in particular, are free from toxic heavy metal compounds.

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.

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 mildly basic range, more particularly to a pH value in the range from 7.5 to 11.