

This invention relates to new drilling fluids and to invert drilling muds based thereon which combine high ecological compatibility with good stability and performance properties. One important application for the new drilling fluids is in offshore drilling for the development of oil and/or gas occurrences, the particular object of the invention in this regard being to provide technically useful drilling fluids of high ecological compatibility. The use of the new drilling fluids is of particular importance in, but is not limited to, the offshore sector. The new drilling fluids may also be used quite generally for land-supported drilling, including for example geothermal drilling, water drilling, geoscientific drilling and mine drilling. In this case, too, the drilling fluids selected in accordance with the invention basically simplify ecotoxic problems to a considerable extent.

Prior Art

Oil-based drilling fluids are generally used in the form of so-called invert emulsion muds which consist of a three-phase system, namely: oil, water and fine-particle solids. The emulsions in question are of the w/o emulsion type, i.e. the aqueous phase is present in the continuous oil phase in heterogeneous fine dispersion. There are a whole range of additives, including in particular emulsifiers and emulsifier systems, weighting agents, fluid loss additives, alkali reserves, viscosity regulators and the like, for stabilizing the system as a whole and for establishing the desired performance properties. Full particulars can be found, for example, in the Article by P. A. Boyd et al. entitled "New Base Oil Used in Low-Toxicity Oil Muds" in Journal of Petroleum Technology, 1985, 137 to 142 and in the Article by R.B. Bennet entitled "New Drilling Fluid Technology - Mineral Oil Mud" in Journal of Petroleum Technology, 1984, 975 to 981 and the literature cited

therein.

The relevant technology has for some time recognized the significance of ester-based oil phases for solving these problems. Thus, US-PSS 4,374,737 and 4,481,121 describe oil-based drilling fluids in which nonpolluting oils are said to be used. De-aromatized mineral oil fractions and vegetable oils of the peanut oil, soybean oil, linseed oil, corn oil and rice oil type, and even oils of animal origin, such as whale oil, are mentioned alongside one another as nonpolluting oils of equivalent rank. The ester oils of vegetable and animal origin mentioned here are all triglycerides of natural fatty acids which are known to be environmentally safe and which, ecologically, are distinctly superior to hydrocarbon fractions, even where they have been de-aromatized.

Interestingly, however, not one of the Examples in the US patents cited above mentions the use of such natural ester oils in invert drilling muds of the type in question here. Mineral oil fractions are used throughout as the continuous oil phase. The use of oils of vegetable and/or animal origin is not feasible for practical reasons. The rheological properties of such oil phases cannot be controlled for the wide temperature range required in practice of 0 to 5°C on the one hand and up to 250°C and higher on the other hand.

Applicants' Earlier Proposals

Ester oils of the type in question here do not in fact show the same in-use behaviour as the pure hydrocarbon-based mineral oil fractions used hitherto. In practice, ester oils undergo partial hydrolysis precisely in the w/o invert drilling muds, resulting in the formation of free carboxylic acids. Earlier applications DE-A-38 42 659 and DE-A-38 42 703 describe the problems which this causes and put forward proposals for solving those problems. Further

modifications of useful ester oils are described in earlier patent applications DE-A-39 07 391 and DE-A-39 07 392.

5 These earlier applications relate to the use of ester oils based on selected monocarboxylic acids or monocarboxylic acid mixtures and monohydric and optionally higher alcohols. The earlier applications show that it is possible with the disclosed esters or ester mixtures not only to establish satisfactory rheological properties in the fresh drilling mud, but also to work with selected known
10 alkali reserves in the drilling mud and thus to prevent unwanted corrosion. The alkali reserve is formed by the addition of lime (calcium hydroxide) and/or by the presence of zinc oxide or comparable zinc compounds, particularly in cases where ester oils based on at least C₆ carboxylic acids
15 are used. However, an additional limitation is appropriate in this regard. If unwanted thickening of the oil-based invert drilling mud is to be prevented in practice, the quantity of alkalizing additive and, in particular, the quantity of lime have to be limited. According to the
20 disclosure of the earlier applications mentioned, the maximum addition envisaged is put at about 2 lb/bbl oil mud.

An important further development of such invert drilling fluids based on ester oils is the subject of
25 applicants' earlier patent application DE-A-39 03 785.

The teaching of this earlier application is based on the concept of introducing into invert drilling muds based on ester oils an additional additive which is capable of keeping the desired rheological data of the drilling mud
30 in the required range; even when increasingly larger quantities of free carboxylic acids are formed in use by partial ester hydrolysis. Not only are these carboxylic acids to be trapped in a harmless form, it is also intended to be possible to convert these free carboxylic acids if desired
35 into valuable components having stabilizing or emulsifying

properties for the system as a whole. According to the teaching of this earlier application, basic amine compounds of pronounced oleophilic character and at most limited solubility in water, which are capable of forming salts with carboxylic acids, are to be used as an additive in the oil phase. The oleophilic amine compounds may be simultaneously used at least partly as alkali reserve of the invert drilling mud, although they may also be used in combination with conventional alkali reserves, particularly lime. It is particularly preferred to use oleophilic amine compounds which are at least predominantly free from aromatic constituents. Optionally olefinically unsaturated aliphatic, cycloaliphatic and/or heterocyclic, oleophilic basic amine compounds containing one or even more N groups capable of forming salts with carboxylic acids are particularly suitable. In one preferred embodiment, these amine compounds have a solubility in water at room temperature of at most about 5% by weight and best below 1% by weight.

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

It has been found that the use of such oleophilic

basic amine compounds can effectively prevent thickening of the drilling mud presumably attributable to a disturbance of the w/o invert system and to the formation of free carboxylic acids by ester hydrolysis.

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The problem addressed by the invention and its solution

10 The problem addressed by the present invention was further to develop systems of the type in question and, in particular, drilling fluids of high ecological compatibility. In a first embodiment, the invention sought to provide oils or oil mixtures for the production of drilling fluids based on w/o emulsions which would be industrially useful and easy to obtain and which at the same time would be distinguished by high ecological value. In another
15 embodiment, the invention sought to provide additives for above-described systems of the type in question which would endow drilling fluids based on w/o emulsions with valuable additional properties without at the same time adversely affecting their ecological compatibility.

20 The technical solution to the problems addressed by the invention is based on the discovery that selected alcohols adapted to the particular application can lead to new and improved drilling fluids of the described type. These alcohols are water-insoluble or substantially water-insoluble components, i.e. in particular corresponding
25 compounds of decidedly oleophilic character which, however, are distinguished from pure hydrocarbon compounds by the presence of the functional hydroxyl groups. Important technological improvements can be achieved in this way and, at the same time, high ecological compatibility is guaranteed. It is known that non-toxic hydrocarbon compounds containing alcohol functions are readily degraded in the natural cycle.

30 In a first embodiment, therefore, the present invention relates to the use of monohydric and/or polyhydric
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alcohols of natural or synthetic origin, which are flowable and pumpable at temperatures of 0 to 5°C and which have a solubility in water at room temperature of less than 5% by weight, in the continuous oil phase of drilling fluids which are present as w/o emulsions, contain a disperse aqueous phase and, optionally, other typical additives in the alcohol-containing oil phase and are suitable for the ecologically safe development of, for example oil, and gas occurrences,

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a) the continuous oil phase being formed solely by the alcohols mentioned

or

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b) the alcohols mentioned - dissolved in ecologically safe water-insoluble oils - making up a substantial part of the continuous oil phase, i.e. forming more than 10% by weight of the continuous oil phase or being added thereto in quantities of 0.1 to 10% by weight.

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In another embodiment, the present invention relates to invert drilling fluids of the described type which, in a continuous oil phase, contain a disperse aqueous phase together with typical other auxiliaries, preferably emulsifiers, weighting agents, fluid loss additives and alkali reserves and which are characterized in that they contain in the continuous oil phase monohydric and/or polyhydric alcohols of natural or synthetic origin which are flowable and pumpable at temperatures of 0 to 5°C and which have a solubility in water at room temperature below 5% by weight,

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a) the continuous oil phase being formed solely by the alcohols mentioned

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or

b) the alcohols mentioned - dissolved in ecologically safe water-insoluble oils - making up a substantial part of the continuous oil phase, i.e. forming more than 10% by weight of the continuous oil phase or being added thereto in quantities of 0.1 to 10% by weight,

and the particular oil phase being flowable and pumpable at temperatures of 0 to 5°C and having flash points above 80°C.

The various embodiments of the invention

In a first embodiment, the continuous oil phase of the invert drilling fluids is exclusively or at least predominantly formed by the substantially water-insoluble and, preferably, strongly oleophilic alcohols. The rheology of the alcohols used must of course be adapted to the technical requirements which the drilling fluids are expected to meet. Slight rheological corrections can be made through the use of the small quantities of diluents envisaged in this first embodiment. Oil phases of which more than 70% by weight, preferably more than 80% by weight and, if desired, 100% by weight is formed solely by the alcohols as such are particularly suitable for use in the present case.

The rheological requirements which such oils are expected to satisfy for use in drilling fluids are generally known among experts, as will be discussed once more in the following. From the broad range of strongly oleophilic alcohols with, in particular, a linear and/or branched hydrocarbon structure, monohydric alcohols containing at least 6 or 7 carbon atoms and preferably at least 8 carbon atoms (the possible upper limit to the number of carbon atoms is influenced to a large extent by the structure of the hydrocarbon radical) are particularly suitable. Monohydric alcohols such as these, which if desired may be

partly olefinically unsaturated, preferably contain up to 36 carbon atoms. It is known that the rheology of branched-chain and/or unsaturated alcohols of the type in question satisfy the requirements of flowability and pumpability, even at low temperatures, more readily than the linear saturated hydrocarbon skeleton. It is known that linear $C_{16/18}$ fatty alcohols have solidification points around 50°C whereas the olefinically unsaturated oleyl alcohol solidifies below 4°C . Depending on the extent and degree of branching, branched alcohols containing the same number of carbon atoms may readily represent useful flowable and pumpable oil phases in the context of the present invention. Among the saturated monohydric alcohols, however, short carbon chains, i.e. in the C_{8-14} range, are particularly suitable. In this case, too, rheological advantages can be attributed to the branched-chain alcohols.

The oil mixture components optionally used in small quantities in this embodiment may be pure, more particularly de-aromatized, hydrocarbon compounds, but above all are selected ester oils of the type described in applicants' earlier applications cited above.

The natural rheology of the alcohol components used in accordance with the invention is increasingly less important, the larger the percentage content of these mixture components in the mixture with one or more oil components. Accordingly, a second embodiment of the invention relates to the use in systems of the type in question of oil phases which still contain considerable or even predominant quantities of water-immiscible oils which are used in admixture with the strongly oleophilic alcohols to be used in accordance with the invention. In this embodiment, the content of alcohols selected in accordance with the invention is generally above 10% by weight to 70% by weight, based on the liquid oil phase, alcohol contents of at least 35% by weight and preferably at least 50% by weight of the

oil phase being preferred. The rheology of such systems is determined to a very large extent by the characteristics of the compounds used as mixture components. However, it will be shown that the use of alcohols in accordance with the present invention can be of considerable practical significance for these embodiments also.

Suitable mixture components for this second embodiment of the invention are again both pure and, in particular, de-aromaticized hydrocarbon oils and, above all, ester oils of the type described in applicants' earlier applications. Mixtures such as these also fall within the scope of the present invention; both mixtures of ester oils with pure hydrocarbon compounds and mixtures of various ester oils may represent mixture components for use in conjunction with the oleophilic alcohols. In preferred embodiment of the invention, the pure hydrocarbon oils containing no functional groups may be used in the oil phase in quantities of at most 50% by weight, preferably in quantities of at most 35% by weight and more preferably in quantities of at most 25% by weight, based on the oil phase. In the most important embodiments of this particular variant, mixtures of the alcohols defined in accordance with the invention and ester oils with no addition of pure hydrocarbon compounds are used as the oil phase.

Finally, in a third variant, the invention relates to the use of the substantially water-insoluble alcohols of, above all, decidedly oleophilic character as an additive in the oil phase of drilling fluids based on w/o emulsions of the type described above. The alcohols used in accordance with the invention are typically present in quantities of 0.1% by weight to at most 10% by weight and preferably in quantities of 1 to 5% by weight of the oil phase. The range of suitable water-soluble alcohols can of course be significantly broadened in this embodiment. The rheology of the system as a whole is no longer determined by the

rheological values of the alcohol. However, important improvements in the behaviour of drilling fluids of the type described above are achieved in this particular embodiment where the alcohols defined in accordance with the invention are used as an additive.

This applies in particular to invert systems in which the principal component of the continuous oil phase is formed exclusively or predominantly by ester oils of the type described in applicants' earlier applications cited above. Accordingly, in the embodiment in question, at least 25% by weight, preferably at least 50% by weight and more preferably at least 75 to 80% by weight of the oil phase as ester oil are present as principal components of the oil phase. Pure hydrocarbon oils known in the prior art may make up the balance, although they are best not used at all.

According to the invention, therefore, ester oils make up at least one third and preferably the predominant part of these ecologically safe oils where they are used in the continuous oil phase.

By adding the water-insoluble alcohols defined in accordance with the invention to invert systems, important improvements can be obtained in the practical application of the drilling fluids. The following four aspects in particular are affected: reducing fluid loss values, simplifying and improving the emulsification of the disperse aqueous phase, an optionally distinctly improved lubricating effect of the drilling fluid and, optionally, a distinct improvement in the rheological properties of invert drilling fluids based on ester oils.

The alcohol components used in accordance with the invention

The use of the alcohols as oil phase and also their use as a minor or major part of the oil phase presupposes

the adequate solubility of these alcohol components in water. The solubility in water at room temperature of suitable alcohols is below 1% by weight and, in particular, no more than 0.5% by weight.

5 The following general principles apply to their chemical characteristics: monohydric and/or polyhydric alcohols are suitable providing the oleophilic character of the alcohol component remains intact. Apart from the monohydric alcohols, difunctional compounds and/or partial
10 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
15 corresponding unsaturated, more particularly mono- and/or polyolefinically unsaturated alcohols, are the preferred compounds. Cycloaliphatic alcohols may be considered.

 An important general requirement in the context of the invention is that not only should these alcohols as such be
20 ecologically safe, they should also entail no other toxicological risks, more particularly inhalation-toxicological risks. However, strongly oleophilic alcohols as required in accordance with the invention are generally distinguished by such low volatility that this requirement is
25 satisfied in any event.

 The following principles apply to the mixing of the alcohols used in accordance with the invention with ester oils: 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. According to the invention,
30 ester oils which are flowable and pumpable at temperatures of 0 to 5°C and which are derived in particular from monocarboxylic acids and also from monohydric and/or dihydric alcohols are preferably used as ecologically safe
35 oils and hence as the mixture component. In their case,

the ester-forming alcohol component is selected in particular in such a way that no toxicological risks and, above all, no inhalation-toxicological risks are involved in practical application under conditions where partial ester hydrolysis can occur.

Whereas, in the ester oils, the alcohol component is determined for example by factors associated with the rheology of the ester oil and/or the accessibility of the ester-forming alcohols, the use of the free alcohols in accordance with the invention is directed towards achieving the desired improvements in the invert drilling fluid.

If the alcohols are used as a substantial or predominant part of the oil phase or even solely as the oil phase, the alcohols should be flowable and pumpable at low temperatures, more particularly in the range from 0 to 5°C, or should lend themselves to conversion into a flowable phase with the limited quantities of ecologically safe mixture components. The solidification points of such oil phases (flow and pour point) should be below 0°C, preferably below -5°C and in particular below -10°C. The alcohols themselves should have flash points of at least 80°C, preferably at least 100°C and more preferably at least 120°C. In addition to the above-mentioned monohydric alcohols containing at least 8 carbon atoms and the upper limit to the number of carbon atoms imposed by the structure and rheology requirements, selected polyols or partial ethers thereof may also be used. Suitable polyols are, in particular, optionally branched-chain diols with an adequate presence of the oleophilic hydrocarbon radical in the molecule. Suitable diols are, for example, oleophilic diols containing hydroxyl groups in the alpha,omega-position and/or diols of which the hydroxyl groups are present at adjacent carbon atoms. Characteristic examples of compounds of this type are the saponification products of epoxidized olefins. However, partial ethers of such diols

with monohydric alcohols are also particularly suitable.

Increasing freedom is available in the choice of suitable alcohol components, particularly in embodiments where the rheology of the system as a whole is largely determined by the water-insoluble mixture components, i.e. above all by the ester oils. Useful additives in this case are inter alia substantially water-insoluble polyalkylene glycol ethers and corresponding mixed ethers of lower alkylene glycols. For example, corresponding mixed ethers of ethylene oxide and propylene oxide are useful additives according to 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 characterized by the addition of the water-insoluble alcohols as an additive in a quantity of at most 10% by weight.

In one important embodiment of the invention, the water-insoluble alcohols used are free from basic amino groups and, preferably, contain no other reactive groups, for example carboxyl groups.

Mixture components in the oil phase

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

According to the invention, however, particularly important mixture components are environment-friendly ester oils of the type described in particular in the earlier German applications cited above, DE-A-38 42 659, 38 42 703, 39 07 391 and 39 07 392. To complete the disclosure of the invention, essential characteristics of those esters and ester mixtures are briefly summarized in the following.

In a first embodiment, esters - flowable and pumpable at 0 to 5°C - of monohydric C₂₋₁₂ and, more particularly, C₆₋₁₂ alcohols and aliphatic saturated C₁₂₋₁₆ monocarboxylic acids or mixtures thereof with at most substantially equal quantities of other monocarboxylic acids are used as the oil phase. Preferred ester oils are those of which at least 60% by weight, based on the particular carboxylic acid mixture, are esters of aliphatic C₁₂₋₁₄ monocarboxylic acids and optionally, for the rest, small quantities of relatively short-chain aliphatic and/or relatively long-chain, in that case more especially mono- and/or polyolefinically unsaturated monocarboxylic acids. Preferred esters are those which have a Brookfield (RVT) viscosity at 0 to 5°C of no more than 50 mPa.s, preferably of no more than 40 mPa.s and, more preferably, of at most 30 mPa.s. The esters used in the drilling mud have solidification values (pour point and setting point) below -10°C and preferably below -15°C and, in particular, flash points above 100°C and preferably above 150°C. The carboxylic acids present in the ester or ester mixture are linear and/or branched and of vegetable and/or synthetic origin.

They may be derived from corresponding triglycerides, such as coconut oil, palm kernel oil and/or babassu oil. The alcohol radicals of the esters used are derived in particular from linear and/or branched saturated alcohols preferably containing 6 to 10 C atoms. These alcohol components may also be of vegetable and/or animal origin, having been obtained by reductive hydrogenation of corresponding carboxylic acid esters.

Another class of particularly suitable ester oils is derived from mono- and/or polyolefinically unsaturated C_{16-24} monocarboxylic acids or mixtures thereof with small quantities of other, in particular saturated monocarboxylic acids and monohydric preferably C_{6-12} alcohols. These ester oils are also flowable and pumpable at temperatures in the range from 0 to 5°C. Particularly suitable esters of this type are those of which more than 70% by weight, preferably more than 80% by weight and, in particular, more than 90% by weight are derived from olefinically unsaturated C_{16-24} carboxylic acids.

In their case, too, the solidification values (pour point and setting point) are below -10°C and preferably below -15°C while the flash points are above 100°C and preferably above 160°C. The esters used in the drilling mud have a Brookfield (RVT) viscosity at 0 to 5°C of no more than 55 mPa.s and preferably of no more than 45 mPa.s.

Ester oils of the type in question here may be divided into two sub-classes. In the first sub-class, no more than 35% by weight of the unsaturated C_{16-24} monocarboxylic acid residues in the ester are derived from di- and polyolefinically unsaturated acids, preferably at least 60% by weight of the acid residues being monoolefinically unsaturated. In the second sub-class, more than 45% by weight and preferably more than 55% by weight of the C_{16-24} monocarboxylic acids in the ester mixture are derived from di- and/or polyolefinically unsaturated acids. Saturated C_{16-18}

carboxylic acids in the ester mixture best make up no more than 20% by weight and, in particular, no more than 10% by weight. However, saturated carboxylic acids preferably have relatively low C chain lengths of the acid residues.

5 The carboxylic acid residues present may be of vegetable and/or animal origin. Vegetable starting materials are, for example, palm oil, peanut oil, castor oil and, in particular, rapeseed oil. Carboxylic acids of animal origin are, in particular, corresponding mixtures of fish
10 oils, such as herring oil.

Another interesting class of ester oils which may be used as a mixture component in accordance with the present invention are esters of C_{1-5} monocarboxylic acids and monohydric and/or polyhydric alcohols which are flowable at
15 room temperature and have flash points above 80°C and which, preferably are even flowable and pumpable at temperatures of 0 to 5°C. Corresponding esters of these lower carboxylic acids with monohydric alcohols containing at least 8 carbon atoms and/or esters of these acids with
20 dihydric or tetrahydric alcohols preferably containing 2 to 6 carbon atoms are particularly suitable. For practical reasons, acetic acid is a particularly suitable ester-forming acid component of this class. Rheology data and data on the volatility or rather the solidification values
25 of preferred esters of this sub-class correspond to the above-mentioned values.

Suitable mixture components from this sub-class are, in particular, esters of monohydric alcohols of natural and/or synthetic origin of which the chain length may be in
30 the range from C_8 to C_{15} where predominantly aliphatically saturated alcohols are present or may even be longer, for example up to about C_{24} , where mono- and polyolefinically unsaturated alcohols are present. Particulars can be found in applicants' earlier patent application DE-A-39 07 391.

35 Finally, however, suitable mixture components are the

esters of C₆₋₁₁ monocarboxylic acids of synthetic and/or natural origin and monohydric and/or polyhydric alcohols which are described in co-pending application DE-A-39 07 392 and which, preferably, are also flowable and pumpable at temperatures of 0 to 5°C. To complete the disclosure of the invention, reference is made in this connection to the cited co-pending application of which the disclosure along with the disclosure of the previously cited application are hereby included as part of the disclosure of the present invention.

The invention also encompasses multicomponent mixtures which, together with the alcohols defined in accordance with the invention, may contain one or more of the of the mixture components listed in detail in the foregoing. Basically, it is possible in this regard to use any mixtures providing they satisfy the basic rheological requirements for invert drilling muds of the type in question here. Examples of such multicomponent mixtures are materials based on various types of ester oils or mixtures additionally containing mineral oil.

In another preferred embodiment of the invention, the continuous oil phase used in the invert drilling mud has a Brookfield RVT viscosity at 0 to 5°C of no more than 55 mPa.s, preferably below 50 mPa.s and, more particularly, not more than 45 mPa.s and preferably not more than 40 mPa.s.

Other mixture components of the invert drilling mud

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

ticularly important in this regard.

If ester oils - particularly ester oils based on carboxylic acids containing at least 6 carbon atoms - are used as mixture components, it may be advisable not to use significant amounts of strongly hydrophilic inorganic and/or organic bases in the oil mud. Lime may be effectively used as the alkali reserve. In that case, however, it is best to limit the maximum quantity of lime used to 2 lb/bbl. A preferred embodiment is characterized by the use of lime in a quantity just below that limit, i.e. for example in a quantity of 1 to 1.8 lb/bbl (lime/drilling mud). Other known alkali reserves may be used instead of or in addition to lime, including in particular less basic metal oxides of the zinc oxide type. However, even in cases where acid acceptors such as these are used, it is important to ensure that they are not added in excessive quantities in order to prevent unwanted premature ageing of the drilling mud accompanied by an increase in viscosity and hence a deterioration in the rheological properties. The feature of the teaching according to the invention discussed here prevents the formation of unwanted quantities of highly effective o/w emulsifiers or at least limits it to such an extent that the favourable rheological properties are maintained for sufficiently long periods in practice, even in the event of thermal ageing.

The following observations also apply:

Invert drilling muds of the type in question here typically contain the finely disperse aqueous phase, together with the continuous oil phase, in quantities of 5 to 45% by weight and preferably in quantities of 5 to 25% by weight. The range from 10 to 25% by weight of disperse aqueous phase can be particularly important.

The following rheological data apply to the rheology of preferred invert drilling muds according to the invention: plastic viscosity (PV) in the range from 10 to 60

mPa.s and preferably in the range from 15 to 40 mPa.s, yield point (YP) in the range from 5 to 40 lb/100 ft² and preferably in the range from 10 to 25 lb/100 ft², as measured at 50°C. Full information on the determination of these parameters, on the measurement techniques used and on the otherwise standard composition of the invert drilling muds described herein can be found in the prior art cited above and, for example, in "Manual of Drilling Fluids Technology" published by NL-Baroid, London, GB, cf. in particular the Chapter entitled "Mud Testing - Tools and Techniques" and "Oil Mud Technology", which is freely available to interested experts. In the interests of fullness of disclosure, the following summary observations may be made:

Emulsifiers suitable for use in practice are systems which are capable of forming the required w/o emulsions. Selected oleophilic fatty acid salts, for example those based on amidoamine compounds, are particularly suitable, examples being described in the already cited US-A-4,374, 737 and the literature cited therein. One particularly suitable type of emulsifier is the product marketed by NL Baroid under the name of "EZ-mul".

Emulsifiers of the type in question here are marketed in the form of concentrates and may be used, for example, in quantities of 2.5 to 5% by weight and more especially in quantities of 3 to 4% by weight, based in each case on the oil phase.

In practice, hydrophobicized lignite in particular is used as a fluid-loss additive and, hence, in particular for forming an impervious coating in the form of a substantially water-impermeable film over the walls of the well. Suitable quantities are, for example, in the range from 15 to 20 lb/bbl or in the range from 5 to 7% by weight, based on the oil phase.

In drilling muds of the type in question here, the

thickener normally used to create viscosity is a cationically modified, fine-particle bentonite which may be used in particular in quantities of 8 to 10 lb/bbl or in the range from 2 to 4% by weight, based on the oil phase. The weighting agent normally used in practice to establish the necessary pressure equalization is barite which is added in quantities adapted to the particular conditions to be expected in the well. For example, it is possible by addition of barite to increase the specific gravity of the drilling mud to values of up to 2.5 and preferably in the range from 1.3 to 1.6.

In invert drilling muds of the type in question here, the disperse aqueous phase is charged with soluble salts, generally calcium chloride and/or potassium chloride, the aqueous phase preferably being saturated with the soluble salt at room temperature.

The emulsifiers or emulsifier systems mentioned above may also be used to improve the oil wettability of the inorganic weighting materials. In addition to the amino-amides already mentioned, alkyl benzenesulfonates and imidazoline compounds are mentioned as further examples. Additional information on the relevant prior art can be found in the following literature references: GB-A-2,158,437, EP-A-229 912 and DE-A-32 47 123.

The following factors are used as a basis for the conversion of the measured values typically encountered in the field in question which do not correspond to the metric system and which are used in this standard form in the specification and in the following Examples:

1 lb = 0.454 kg; 1 bbl = 159 l;
1 lb/bbl = 2.85 kg/m³, particularly in connection with the quantity of alkali reserve added;
1 lb/100 ft² = 0.4788 Pa, particularly in connection with determination of the yield point (YP) and gel strength.

Examples

Examples 1 to 4

- 5 Invert drilling fluids based on selected alcohols and on alcohol mixtures with an oil-to-water ratio of 80:20 are used in Examples 1 to 4 below, being prepared in accordance with the following basic formulation:

10	200 ml	alcohol
	50.9 ml	water
	1.5 g	organophilic bentonite (Geltone II, a product of NL Baroid)
	1.9 g	diethanolamine
15	7.8 g	organophilic lignite (Duratone, a product of NL Baroid)
	7.8 g	w/o emulsifier (EZ-mul NT, a product of NL Baroid)
	326.2 g	barite
20	17.5 g	KCl

- 25 The invert drilling muds are first measured for viscosity at 50°C before ageing to determine their plastic viscosity (PV), their yield point (YP) and their gel strength after 10 seconds and 10 minutes.

- 30 The invert drilling muds are then aged by autoclaving for 16 hours at 125°C in a so-called roller oven to determine the effect of temperature on the stability of the emulsions. The viscosity values are then remeasured at 50°C.

 The oil phases used in these Examples, i.e. the particular alcohols and alcohol mixtures - are as follows:

- 35 Example 1: Synthetic C₁₀ oxoalcohol (commercial product "Etoxo C 10")

Example 2: 100 ml of the synthetic alcohol of Example 1 in admixture with 100 ml of a C_{8-10} alcohol mixture of natural origin ("Lorol 810", a product of Henkel KGaA)

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Example 3: 100 ml of the alcohol of Example 1 in admixture with 100 ml of a C_{12-18} alcohol mixture of natural origin ("Lorol technisch", a product of Henkel KGaA)

10 Example 4: $C_{12/13}$ synthetic alcohol mixture (commercial product "Lial 123")

The following values are determined before and after ageing:

15

Example 1

	Before ageing	After ageing
20 Plastic viscosity (PV)	45	55
Yield point (YP)	29	39
Gel strength (lb/100 ft ²)		
10 secs.	15	15
10 mins.	14	15

Example 2

		Before ageing	After ageing
5	Plastic viscosity (PV)	36	47
	Yield point (YP)	33	21
	Gel strength (lb/100 ft ²)		
	10 secs.	10	5
10	10 mins.	13	6

Example 3

		Before ageing	After ageing
15	Plastic viscosity (PV)	80	62
	Yield point (YP)	51	27
	Gel strength (lb/100 ft ²)		
	10 secs.	28	6
20	10 mins.	29	9

Example 4

		Before ageing	After ageing
25	Plastic viscosity (PV)	85	108
	Yield point (YP)	45	53
	Gel strength (lb/100 ft ²)		
30	10 secs.	35	40
	10 mins.	38	40

Examples 5 to 8

35 Comparison tests are carried out with an oil mud having the following composition:

200 ml oil phase

50.9 ml water

1.9 g lime

5 7.8 g organophilic lignite (Duratone, a product of NL Baroid)

326.2 g barite

17.9 g $\text{CaCl}_2 \cdot 2 \text{H}_2\text{O}$

10 No w/o emulsifier is used in this formulation. The following alcohols and alcohol/ester oil mixtures are used in Examples 5 to 8:

Example 5: $\text{C}_{8/10}$ alcohol cut of natural origin ("Lorol 810",
15 a product of Henkel KGaA)

Example 6: A mixture of 102 ml of the alcohol of Example 5 and 98 ml of isobutyl oleate

20 Example 7: Synthetic C_{13} oxoalcohol (isotridecyl alcohol)

Example 8: Oxo oil

25 The viscosity values determined before and after ageing are as follows:

Example 5

		Before ageing	After ageing
5	Plastic viscosity (PV)	53	40
	Yield point (YP)	23	10
	Gel strength (lb/100 ft ²)		
	10 secs.	9	3
	10 mins.	15	3
10			

Example 6

		Before ageing	After ageing
15	Plastic viscosity (PV)	36	28
	Yield point (YP)	17	21
	Gel strength (lb/100 ft ²)		
	10 secs.	7	11
20	10 mins.	10	13

Example 7

		Before ageing	After ageing
25	Plastic viscosity (PV)	85	108
	Yield point (YP)	45	53
	Gel strength (lb/100 ft ²)		
30	10 secs.	35	40
	10 mins.	38	40

Example 8

		Before ageing	After ageing
5	Plastic viscosity (PV)	45	55
	Yield point (YP)	29	39
	Gel strength (lb/100 ft ²)		
	10 secs.	14	15
	10 mins.	15	15

10

Examples 9 to 12

A formulation of the following basic composition is used:

15	200 ml oil phase
	50.9 ml water
	1.2 g organophilic bentonite ("Geltone II", a product of NL Baroid)
	1.9 g lime
20	7.8 g organophilic lignite ("Duratone", a product of NL Baroid)
	7.8 g w/o emulsifier ("EZ mul NT", a product of NL Baroid)
	326.2 g barite
25	17.9 g CaCl ₂ · 2 H ₂ O

Mixtures of an ester oil based on rapeseed oil and the C_{8/10} alcohol mixture mentioned at the beginning ("Lorol 810") with increasing amounts of the C_{8/10} alcohol cut in the mixture are used as the oil phase in Examples 9 to 12.

The ester oil used is an undistilled isobutyl rapeseed oil ester based on a mixture of predominantly unsaturated linear carboxylic acids substantially corresponding to the following distribution: 60% oleic acid, 2% linoleic acid, 9 to 10% linolenic acid, olefinically unsaturated C_{20/22}

monocarboxylic acids approx. 4%, remainder saturated monocarboxylic acids mainly in the $C_{16/18}$ range. The rapeseed oil ester has the following characteristic data:

- 5 Density (20°C) 0.872 g/cm³; flow point below -15°C; flash point (DIN 51584) above 180°C; acid value (DGF-C-V 2) 1.2; viscosity at 0°C 32 mPas, viscosity at 5°C 24 mPas; de-aromaticized.

- 10 The mixing ratios of rapeseed oil ester to Lorol 810 are selected as follows and shifted towards an increasing Lorol 810 content:

Example 9: 170 ml ester oil/30 ml alcohol cut

Example 10: 150 ml ester oil/50 ml alcohol cut

- 15 Example 11: 120 ml ester oil/80 ml alcohol cut

Example 12: 100 ml ester oil/100 ml alcohol cut

The viscosity values of the drilling fluids determined before and after ageing are as follows:

20

Example 9

	Before ageing	After ageing
25 Plastic viscosity (PV)	60	43
Yield point (YP)	62	39
Gel strength (lb/100 ft ²)		
10 secs.	33	19
10 mins.	34	21

Example 10

		Before ageing	After ageing
5	Plastic viscosity (PV)	45	39
	Yield point (YP)	51	39
	Gel strength (lb/100 ft ²)		
	10 secs.	25	17
	10 mins.	28	19
10			

Example 11

		Before ageing	After ageing
15	Plastic viscosity (PV)	45	33
	Yield point (YP)	40	24
	Gel strength (lb/100 ft ²)		
	10 secs.	19	13
20	10 mins.	22	14

Example 12

		Before ageing	After ageing
25	Plastic viscosity (PV)	36	28
	Yield point (YP)	17	21
	Gel strength (lb/100 ft ²)		
30	10 secs.	7	11
	10 mins.	10	13

Comparison Example and Examples 13 to 15

35 Drilling fluids with the following formulation are
used in the following Comparison Example and in Examples 13

to 15:

200 ml ester oil
50.9 ml water
5 1.2 g organophilic bentonite ("Geltone II", a product
of NL Baroid)
1.9 g diethanolamine
7.8 g organophilic lignite ("Duratone", a product of
NL Baroid)
10 7.8 g w/o emulsifier ("EZ mul NT", a product of NL
Baroid)
326.2 g barite
12.5 g KCl

15 The Comparison Example uses this formulation with the
undistilled isobutyl rapeseed oil ester of Examples 9 to 12
as the ester oil. In Examples 13 to 15, a selected strong-
ly oleophilic water-insoluble alcohol corresponding to the
teaching of the invention is added to the drilling fluid.
20 The following observations apply to Examples 13 to 15:

Example 13: Addition of 2 g of docosanol, i.e. a linear C₂₂
alkanol

25 Example 14: Addition of 5 g of an EO/PO adduct with a C₁₂₋₁₈
alcohol cut of natural origin ("Lorol technisch", a product
of Henkel KGaA) with the following composition: C₁₂₋₁₈
alcohol cut/3 EO/6 PO ("Dehyton LT 36", a product of Henkel
KGaA)

30 Example 15: Adduct of 5 g of an EO/PO polyalkylene glycol
with an average molecular weight of around 2,000 (commer-
cial product "Dehydran 240")

35 The particular oil muds of Examples 13 to 15 and the
Comparison Example are measured for their viscosity values

and in addition for their fluid loss values by the HTHP method. Information on determination of the HTHP fluid loss value can be found in the above-cited handbook of NL Baroid, London "Manual of Drilling Fluids Technology", subchapter "Oil Mud Technology", chapter PROPERTIES AND TESTING PROCEDURES "HTHP Filtrate".

Comparison of the figures shows that an improvement in rheology and, in every case, a distinct reduction in the HTHP filtrate, i.e. a distinct improvement in the fluid loss value, are obtained by addition of small quantities of selected alcohols.

The following values were measured:

Comparison Example

	Before ageing	After ageing
Plastic viscosity (PV)	61	47
Yield point (YP)	37	41
Gel strength (lb/100 ft ²)		
10 secs.	24	17
10 mins.	26	19

HTHP: 20 ml

Example 13

		Before ageing	After ageing
5	Plastic viscosity (PV)	54	39
	Yield point (YP)	48	31
	Gel strength (lb/100 ft ²)		
	10 secs.	27	14
	10 mins.	29	15
10	HTHP: 6 ml		

Example 14

		Before ageing	After ageing
15			
	Plastic viscosity (PV)	45	42
	Yield point (YP)	36	36
	Gel strength (lb/100 ft ²)		
20	10 secs.	20	18
	10 mins.	23	19
	HTHP: 7 ml		

25 Example 15

		Before ageing	After ageing
	Plastic viscosity (PV)	70	36
30	Yield point (YP)	52	27
	Gel strength (lb/100 ft ²)		
	10 secs.	35	13
	10 mins.	34	14
35	HTHP: 9 ml		

CLAIMS

1. The use of monohydric and/or polyhydric alcohols of natural or synthetic origin, which are flowable and pumpable at temperatures of 0 to 5°C and which have a solubility in water at room temperature of less than 5% by weight, in the continuous oil phase of drilling fluids which are present as w/o emulsions, contain a disperse aqueous phase and, optionally, other typical additives in the alcohol-containing oil phase and are suitable for the ecologically safe development of, for example oil, and gas occurrences,
- a) the continuous oil phase being formed solely by the alcohols mentioned
- or
- b) the alcohols mentioned - dissolved in ecologically safe water-insoluble oils - making up a substantial part of the continuous oil phase, i.e. forming more than 10% by weight of the continuous oil phase or being added thereto as an additive in quantities of 0.1 to 10% by weight.
2. The use claimed in claim 1, characterized in that ester oils flowable and pumpable at temperatures of 0 to 5°C are used as the ecologically safe water-insoluble oils for mixing with the alcohols.
3. The use claimed in claims 1 and 2, characterized in that the ester oils used as the flowable and pumpable mixing component are ester oils of which the ester-forming alcohol components are derived from monohydric and/or dihydric alcohols and are preferably selected so that no toxicological dangers and, in particular, no inhalation-toxicological dangers occur through partial ester hydrolysis, even in practical application.
4. The use claimed in claims 1 to 3, characterized in that the alcohols make up more than 35% by weight, prefer-



* C L M S *

ably more than 70% by weight and, more preferably, more than 80% by weight of the continuous oil phase or are added to the continuous oil phase as an additive in quantities of 1 to 5% by weight.

5 5. The use claimed in claims 1 and 4, characterized in that oleophilic monohydric and/or dihydric alcohols and/or corresponding partial ethers of polyhydric, more particularly dihydric, alcohols are used.

10 6. The use claimed in claims 1 to 5, characterized in that the alcohols used are free from aromatic molecular constituents and are preferably derived from linear and/or branched hydrocarbon chains which may even be olefinically unsaturated.

15 7. The use claimed in claims 1 to 6, characterized in that the alcohols used are monohydric alcohols containing at least 6 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.

20 8. The use claimed in claims 1 to 6, characterized in that oleophilic, optionally branched-chain diols containing hydroxyl groups in the alpha,omega-position and/or at adjacent carbon atoms or partial ethers thereof with preferably monohydric alcohols are used.

25 9. The use claimed in claim 8, characterized in that substantially water-insoluble polyalkylene glycol (mixed) ethers of, in particular, lower alkylene glycols, preferably corresponding mixed ethers of ethylene oxide and propylene oxide containing at least one free hydroxyl group, are added as additive to the continuous oil phase.

30 10. The use claimed in claims 1 to 9, characterized in that the continuous oil phase used in the drilling fluid has solidification points (flow point and pour point) below -5°C, preferably below -10°C, and flash points above 80°C
35 and preferably above 100°C.



* C L H S *

11. The use claimed in claims 1 to 10, characterized in that the continuous oil phase of the drilling fluid has a Brookfield (RVT) viscosity at 0 to 5°C of no more than 25 mPa.s and preferably no more than 45 mPa.s.

5 12. The use claimed in claims 1 to 11, characterized in that the alcohols are used in drilling fluids which, as a w/o invert emulsion, contain the finely disperse aqueous phase in quantities of 5 to 45% by weight and preferably in quantities of 5 to 25% by weight.

10 13. The use claimed in claims 1 to 12, characterized in that the alcohols used are free from basic amino groups and preferably contain no other reactive groups, particularly carboxyl groups.

15 14. The use claimed in claims 1 to 13, characterized in that one or more of the following components are used as the water-insoluble ester oils:

- esters of C₁₋₅ monocarboxylic acids and monohydric and/or polyhydric alcohols,
- 20 - esters of monocarboxylic acids of synthetic and/or natural origin containing 6 to 11 carbon atoms and monohydric and/or polyhydric alcohols,
- esters of aliphatically saturated monocarboxylic acids containing 12 to 16 carbon atoms and monohydric
- 25 alcohols containing 6 to 12 carbon atoms,
- esters of mono- and/or polyolefinically unsaturated polycarboxylic acids containing 16 to 24 carbon atoms and monohydric alcohols containing 6 to 12 carbon atoms.

30 15. The use claimed in claims 1 to 14, characterized in that the alcohols are used in the oil phase to improve the fluid loss properties, to improve the emulsifiability and optionally to improve the rheology and/or lubricity of the

35 drilling fluid.



16. The use claimed in claims 1 to 15, characterized in that the alcohol-containing drilling fluids are used together with typical alkali reserves, particularly lime.
17. The use claimed in claims 1 to 16, characterized in that, where ester oils based on carboxylic acids containing at least 6 carbon atoms are used, any addition of lime is limited to at most 2 lb/bbl drilling fluid.
18. Invert drilling fluids which are suitable for the ecologically safe development of oil and gas occurrences and which, in a continuous oil phase, contain a disperse aqueous phase together with typical other auxiliaries, preferably emulsifiers, weighting agents, fluid loss additives and alkali reserves, characterized in that they contain in the continuous oil phase monohydric and/or polyhydric alcohols of natural or synthetic origin which are flowable and pumpable at temperatures of 0 to 5°C and which have a solubility in water at room temperature below 5% by weight,
- a) the continuous oil phase being formed solely by the alcohols mentioned
- or
- b) the alcohols mentioned - dissolved in ecologically safe water-insoluble oils - making up a substantial part of the continuous oil phase, i.e. forming more than 10% by weight of the continuous oil phase or being added thereto as an additive in quantities of 0.1 to 10% by weight,
- and the particular oil phase being flowable and pumpable at temperatures of 0 to 5°C and having flash points above 80°C.
19. An invert drilling fluid as claimed in claim 18, characterized in that it contains ester oils, more particularly ester oils of monocarboxylic acids and monohydric



and/or dihydric alcohols, as the ecologically safe oils.

20. An invert drilling fluid as claimed in claims 18 and 19, characterized in that it has a plastic viscosity (PV) of 10 to 60 mPa.s and a yield point (YP) of 5 to 40 lb/100 ft², as determined in either case at 50°C.

21. An invert drilling fluid as claimed in claims 18 to 20, characterized in that, where ecologically safe oils are used in the continuous oil phase, ester oils make up at least one third and preferably the predominant part of the ecologically safe oils.

22. An invert drilling fluid as claimed in claims 18 to 21, characterized in that its disperse water content is 5 to 45% by weight and preferably 10 to 25% by weight and, in particular, contains dissolved salt, preferably CaCl₂ and/or KCl.

23. An invert drilling fluid as claimed in claims 18 to 22, characterized in that the oil phase of the invert mud has a Brookfield (RVT) viscosity at 0 to 5°C of less than 50 mPa.s and preferably not more than 40 mPa.s.

