

This invention relates to new drilling fluids based on ester oils and to invert drilling muds based thereon which combine high ecological compatibility with good stability and performance properties. One important application for the new drilling fluids is in offshore drilling for the development of oil and/or gas sources, 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 ester-based drilling fluids selected in accordance with the invention basically simplify ecotoxic problems to a considerable extent.

It is known that liquid drilling fluids for sinking bores in rock and bringing up the rock cuttings are slightly thickened, water-based or oil-based fluid systems. Oil-based systems are being increasingly used in practice, particularly in offshore drilling or in the penetration of water-sensitive layers.

Oil-based drilling fluids are generally used in the form of so-called invert emulsion muds which consist of a three-phase system, namely: oil, water and finely divided solids. The emulsions in question are of the w/o emulsion type, i.e. the aqueous phase is present in the continuous oil phase in heterogeneous fine dispersion. There are a whole range of additives, including in particular emulsifiers and emulsifier systems, weighting agents, fluid loss additives, alkali reserves, viscosity regulators and the like, for stabilizing the system as a whole and for establishing the desired performance properties. Full particulars can be found, for example, in the Article by P. A

Boyd et al entitled "New Base Oil Used in Low-Toxicity Oil Muds" in Journal of Petroleum Technology, 1985, 137 to 142 and in the Article by R.B. Bennet entitled "New Drilling Fluid Technology - Mineral Oil Mud" in Journal of Petroleum Technology, 1984, 975 to 981 and the literature cited therein.

Oil-based drilling muds were originally made from diesel oil fractions containing aromatic constituents. For the purposes of detoxification and reducing the ecological problems thus created, it was then proposed to use hydrocarbon fractions substantially free from aromatic compounds - now also known as "nonpolluting oils" - as the continuous oil phase, cf. the literature cited above. Although certain advances were achieved in this way through elimination of the aromatic compounds, a further reduction in the environmental problems caused by drilling fluids of the type in question here seems to be urgently required. This applies in particular to the sinking of offshore wells for the development of oil and gas sources because the marine ecosystem is particularly sensitive to the introduction of toxic and non-readily degradable substances.

The relevant technology has for some time recognized the significance of ester-based oil phases for solving these problems. Thus, US-PSS 4,374,737 and 4,481,121 describe oil-based drilling muds in which nonpolluting oils are said to be used. Non-aromatic mineral oil fractions and vegetable oils of the peanut oil, soybean oil, linseed oil, corn oil and rice oil type, and even oils of animal origin, such as whale oil, are mentioned alongside one another as 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-aromaticized.

Interestingly, however, not one of the Examples in the US patents cited above mentions the use of such natural ester oils in invert drilling muds of the type in question here. Mineral oil fractions are used throughout as the continuous oil phase.

The investigations on which the present invention is based have shown that the use of readily degradable oils of vegetable and/or animal origin, which was considered in the prior art, is not feasible for practical reasons. The rheological properties of such oil phases cannot be controlled for the wide temperature range required in practice of 0 to 5°C on the one hand up to 250°C and higher on the other hand.

Ester oils of the type in question here do not in fact show the same in-use behavior as the pure hydrocarbon-based mineral oil fractions used hitherto. In practice, ester oils irrespective of their constitution undergo partial hydrolysis precisely in the w/o invert drilling muds, resulting in the formation of free carboxylic acids. These free carboxylic acids in turn react with the alkaline constituents always present in the drilling mud systems of the type in question here, for example with the alkali reserve used for corrosion prevention, to form the corresponding salts. However, salts of highly hydrophilic bases and the acids having carbon chain lengths of about C12 to C24 predominantly encountered in oils of natural origin are known to be compounds having comparatively high HLB values which, in particular, lead to the formation and stabilization of o/w emulsions. Use is made of this on a very wide scale in the field of detergents and cleaning preparations. However, the formation of even limited quantities of such o/w emulsifier systems must interfere with the w/o emulsions required for solving the problem addressed by the invention and, hence, must lead to problems.

Earlier German applications P 38 42 659.5 "The use of selected ester oils in drilling muds (I)" and P 38 42 703.6 "The use of selected ester oils in drilling muds (II)" relate to the use of ester oils based on selected monocarboxylic acids or monocarboxylic acid mixtures and monofunctional alcohols containing at least 2 and preferably at least 4 carbon atoms. The earlier applications show that it is possible with the disclosed esters or ester mixtures of monofunctional reactants not only to establish satisfactory rheological properties in the fresh drilling mud, but also to work with selected known alkali reserves in the drilling mud and thus to prevent unwanted corrosion. The alkali reserve is formed by the addition of lime (calcium hydroxide) and/or by the presence of zinc oxide or comparable zinc compounds. However, an additional limitation is appropriate in this regard. If unwanted thickening of the oil-based invert drilling mud is to be prevented in practice, the quantity of alkalizing additive and, in particular, the quantity of lime have to be limited. According to the disclosure of the earlier applications mentioned, the maximum addition envisaged is put at about 2 lb/bbl oil mud.

In these earlier applications, the alcohol component used in the ester oil is consciously limited to at least 2 and preferably to at least 4 carbon atoms. The reason for this is the fact well known among experts in the field in question that, in the presence of water, the methylesters of carboxylic acids are hydrolyzed particularly easily with formation of the free carboxylic acids. With higher alcohol components, this tendency towards hydrolysis is weakened. The use of monocarboxylic acid methylesters in invert drilling muds of the w/o emulsion type appeared pointless. Their pronounced tendency towards hydrolysis and the resulting premature formation of relatively large quantities of the free carboxylic acids or the salts with o/w

emulsifier properties formed therefrom had been expected to result in lasting damage to the system as a whole.

The teaching of the present invention is based on the surprising observation that the opposite is the case.

5 Methylesters of monocarboxylic acids are particularly valuable ester oil components in w/o invert drilling muds, even when considerable quantities of conventional basic materials are present as alkali reserve in the drilling mud. Thus, in invert drilling muds based on ester oils as

10 the continuous oil phase, larger quantities of lime may be used as additive than described in the earlier applications cited above without the mud undergoing unwanted premature thickening. The methylesters of the C range in question which is described in detail hereinafter may form the ester

15 oil phase as a whole, although it has additionally been found that even the use of limited quantities of methylesters in the continuous oil phase leads to substantial improvements in the rheology of the drilling mud, in its ageing behavior and in its sensitivity to the use of alkali reserves for protection against unwanted corrosion.

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In a first embodiment, therefore, the present invention relates to the use of the methylesters of C_{6-24} monocarboxylic acids in quantities of 10 to 100% by weight, based on the oil phase, as the oil phase or as part of the

25 oil phase of invert drilling muds which are suitable for the environment-friendly development of, for example, oil and gas occurrences and which, in a continuous oil phase, contain a disperse aqueous phase together with emulsifiers, weighting agents, fluid loss additives and, if desired,

30 other standard additives.

In another embodiment, the invention relates to w/o invert drilling muds which are suitable for the offshore development of oil and gas sources and which, in a continuous oil phase, contain a disperse aqueous phase together

35 with emulsifiers, weighting agents, fluid loss additives

and, if desired, other standard additives, this embodiment of the invention being characterized in that the oil phase contains methylesters of C_{6-24} monocarboxylic acids in quantities of 10 to 100% by weight, based on the oil phase,,
5 if desired in admixture with other oil components from the class of so-called nonpolluting oils.

It is preferred to use monocarboxylic acid methylesters or mixtures of such methylesters which are flowable and pumpable at room temperature and, in particular, even
10 at temperatures in the range from 0 to 5°C. The methylester-containing oil phase of the invert drilling muds best has a Brookfield (RVT) viscosity at 0 to 5°C of no more than 50 mPa.s, preferably no more than 40 mPa.s and, more preferably, at most about 30 mPa.s. These figures for preferred invert drilling muds according to the invention
15 apply both to mixtures containing methylesters or methylester mixtures as sole constituent of the continuous oil phase and also to materials in which the methylesters make up only one mixture constituent of the oil phase.

20 The monocarboxylic acid methylesters or oil mixtures containing such components used in the drilling mud preferably have solidification values (pour point and setting point) below 0°C, preferably below -5°C and more preferably below -10°C. At the same time, the flash point of the
25 methylester-containing oil phase is preferably at or above about 70°C and preferably at at least about 90°C. Flash points above 100°C and, in particular, above 150°C can be particularly suitable.

Where the methylesters used in accordance with the
30 invention only form one mixture constituent in the continuous oil phase of the invert drilling muds, virtually any oil components already known and/or already described in the field in question may be used as further oil components. The methylesters used in accordance with the
35 invention are generally homogeneously miscible with such

components in any mixing ratios.

Possible mixture constituents are, in particular, mineral oils and mineral oil fractions which are included among the so-called nonpolluting drilling oils and which are described in the literature cited at the beginning. The mineral oils and mineral oil fractions in question are generally saturated aliphatic and/or cycloaliphatic hydrocarbons of comparatively low toxicity. However, particularly important mixture components for admixture with methylesters of the type in question here are carboxylic acid ester oils of other alcohols, particular significance being attributed to the corresponding esters of monofunctional alcohols.

15 The preferred methyl esters

Preferred methylesters are derived from C_{8-24} monocarboxylic acids. The methylesters of higher carboxylic acids in this range, namely those of monocarboxylic acids containing 16 and more carbon atoms, are best at least partly olefinically unsaturated. The lower C chain length range may include olefinically unsaturated carboxylic acid residues. Normally, however, the methylester is at least predominantly derived from saturated monocarboxylic acids.

One important embodiment of the invention is characterized by the use of methylesters of carboxylic acids which may be exclusively or at least predominantly assigned to the C_{16-24} range. The carboxylic acids may be derived from unbranched or branched hydrocarbon chains, particular significance being attributed to the linear chains. Monocarboxylic acids of this type and of the C_{16-24} range in question and methylesters thereof are unsuitable as predominantly saturated hydrocarbon compounds on account of their comparatively high solidification values. Even then, however, esters of the type in question here are flowable and pumpable at temperatures of down to 0 to 5°C providing

an adequate level of olefinically unsaturated ester constituents is guaranteed. Accordingly, the preferred embodiment of the invention is characterized by the use of methylesters of the type described here of which more than
5 70% by weight and preferably more than 80% by weight are derived from olefinically unsaturated C_{16-24} carboxylic acids. Important natural starting materials are provided by carboxylic acid mixtures containing at least 90% by weight olefinically unsaturated carboxylic acids within the
10 C range in question here. The unsaturated carboxylic acids may be mono- and/or polyolefinically unsaturated. Where carboxylic acids or carboxylic acid mixtures of natural origin are used, a certain significance is assumed in particular by the double ethylenic bond and, to a lesser
15 extent, also by a triple ethylenic double bond per carboxylic acid molecule in addition to a single ethylenic double bond in the molecule. Among the unsaturated methylesters described herein, there are two sub-classes of particular importance.

20 The first of these sub-classes is based on unsaturated C_{16-24} monocarboxylic acids of which no more than about 35% by weight are diolefinically and, optionally, polyolefinically unsaturated. In their case, therefore, the content of polyunsaturated carboxylic acid residues in the ester oil
25 is comparatively limited. Within this sub-class, however, it is preferred that at least about 60% by weight of the carboxylic acid residues are monoolefinically unsaturated.

In contrast to the first sub-class described above, the second sub-class of ester oils of practical significance is derived from C_{16-24} monocarboxylic acid mixtures of
30 which more than 45% by weight and preferably more than 55% by weight are derived from diolefinically and/or polyolefinically unsaturated acids within the C range mentioned.

The most important monoethylenically unsaturated carboxylic acids within the range in question here are hexa-
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decenoic acid (C_{16}), oleic acid (C_{18}), the related ricinoleic acid (C_{18}) and erucic acid (C_{22}). The most important di-unsaturated carboxylic acid within the range in question here is linoleic acid (C_{18}) while the most important
5 triethylenically unsaturated carboxylic acid is linolenic acid (C_{18}).

According to the invention, selected individuals of this ester type may be used as the methylester component. One example of such an ester is the methylester of oleic
10 acid. However, so far as the rheology of the system is concerned and/or for reasons of availability, it is generally best to use acid mixtures. This is essential for the definition of the two above-mentioned sub-classes of preferred methylester oils.

15 The first of these two sub-classes is distinguished by the fact that its content of di- and polyolefinically unsaturated acids is limited and does not exceed about 35% by weight. Vegetable oils of natural origin, of which the hydrolysis or transesterification with methanol gives
20 mixtures of carboxylic acids or methylesters of the type required herein, are, for example, palm oil, peanut oil, castor oil and, in particular, rapeseed oil. Suitable rapeseed oils are both traditional types of high erucic acid content and also the more modern types of reduced
25 erucic acid content and increased oleic acid content.

Methylesters corresponding to this definition can be particularly important simply because problems of vulnerability to oxidation which may possibly arise in practice are alleviated in their case.

30 However, carboxylic acid mixtures of the second sub-class mentioned above have also proved extremely valuable in the form of the methylester. They are readily available from natural fats of vegetable and/or animal origin. Classic examples of oils which have a high content of C_{16-18}
35 or C_{16-22} carboxylic acids and which, at the same time,

contain at least about 45% by weight of at least diethylenically unsaturated carboxylic acids are cottonseed oil, soybean oil, sunflower oil and linseed oil. The tall oil acids isolated during the recovery of cellulose also fall within this range. A typical example of an animal starting material for the production of corresponding carboxylic acid mixtures is fish oil, particularly herring oil.

However, another equally important embodiment of the invention is characterized by the use of methylesters of at least predominantly saturated monocarboxylic acids. Particular significance is attributed in this regard to carboxylic acids having relatively short C chain lengths, i.e. in particular to monocarboxylic acids containing 6 to 16 carbon atoms, preferably 8 to 16 carbon atoms and more preferably about 9 to 15 carbon atoms. Carboxylic acids having C chain lengths within this range can be obtained both from renewable oils and fats of natural origin and by the various known processes for the industrial synthesis of such carboxylic acids.

Possible methods for the industrial synthesis of such fatty acids are described in detail, for example, in Ullmann, Enzyklopädie der technischen Chemie, Vol. 11, Chapter "Fettsäuren (Fatty Acids)", in particular the Table on page 543 (4th Edition).

Within this range of methylesters having comparatively short C chain lengths, particular importance is attributed to the carboxylic acids and carboxylic acid mixtures obtainable from natural sources, particularly vegetable oils and fats. One important embodiment is characterized by the use of methylesters of substantially saturated aliphatic monocarboxylic acids containing from 12 to 16 and more especially 12 to 14 carbon atoms. The use of esters of other aliphatic monocarboxylic acids, particularly those having shorter C chains, can be useful.

In this particular case also, the methylesters are

derived from monocarboxylic acids having linear or branched hydrocarbon chains. Particular significance is attributed to the methylesters of corresponding linear acids. Carboxylic acids or carboxylic acid mixtures of vegetable origin predominantly containing saturated monocarboxylic acids of the range in question here may be obtained, for example, from renewable triglycerides, such as coconut oil, palm kernel oil and/or babassu oil. Fatty acid mixtures of this origin generally contain a limited quantity of lower fatty acids (C_{6-10}) of generally at most about 15%. Their content of C_{12-14} acids predominates by far, generally making up at least 50% and typically 60% or more of the carboxylic acid mixture. The small balance remaining is made up of higher fatty acids, particular significance being attributed in this range to unsaturated components.

By suitably choosing and mixing the carboxylic acid residues in the methylester mixture used, it is possible on the one hand to control and predetermine the rheological properties of the methylesters themselves in such a way that the high flowability and pumpability required are obtained, even at low temperatures of 0 to 5°C, without on the other hand an unwanted reduction in the flash points of the oil phase having to be accepted. In addition, however, it has been found that it is even possible by using the methylesters to control the rheological properties of those ester oils of higher alcohols which, as such, show unsatisfactory flowability and pumpability, particularly at temperatures in the low range mentioned. Methylesters of the type used in accordance with the invention can clearly serve as effective diluents for the continuous oil phase of the invert drilling muds. As already mentioned, however, not only are the rheological data of the drilling mud improved, their stability to unwanted premature thickening during ageing in use is also suppressed and their sensitivity to the addition of typical components as a cor-

rosion-inhibiting alkali reserve is reduced.

Mixture components in the oil phase

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

According to the invention, however, particularly im-
portant mixture components are environment-friendly ester
oils of the type described in particular in the earlier
German applications cited above. To complete the disclo-
15 sure 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,
20 C₄₋₁₂ alcohols and aliphatic saturated C₁₂₋₁₆ monocarboxylic
acids or mixtures thereof with at most substantially equal
quantities of other monocarboxylic acids are used as the
oil phase. Preferred ester oils are those of which at
least about 60% by weight, based on the particular car-
25 boxylic acid mixture, are esters of aliphatic C₁₂₋₁₄ monocar-
boxylic acids and optionally, for the rest, small quan-
tities of relatively short-chain aliphatic and/or relative-
ly long-chain, in that case more especially mono- and/or
polyolefinically unsaturated monocarboxylic acids. Prefer-
30 red esters are those which have a Brookfield (RVT) vis-
cosity 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 solidifica-
tion values (pour point and setting point) below -10°C and
35 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 at least predominantly linear and, preferably, of vegetable 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 4 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.

The other class of particularly suitable ester oils is derived from mono- and/or polyolefinically unsaturated C_{16-24} monocarboxylic acids or mixtures thereof with small quantities of other, in particular saturated monocarboxylic acids and monofunctional C_{2-12} alcohols. These ester oils are also flowable and pumpable at temperatures in the range from 0 to 5°C. Particularly suitable esters of this type are those of which more than 70% by weight, preferably more than 80% by weight and, in particular, more than 90% by weight are derived from olefinically unsaturated C_{16-24} carboxylic acids.

In their case, too, the solidification values (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 about 60% by weight of the acid residues being mono-olefinically unsaturated. In the second sub-class, more than 45% by weight and preferably more than 55% by weight of the C_{16-24} monocar-

boxylic acids in the ester mixture are derived from di- and/or polyolefinically unsaturated acids. Saturated C₁₆₋₁₈ carboxylic acids in the ester mixture best make up no more than about 20% by weight and, in particular, no more than about 10% by weight. However, saturated carboxylic acids preferably have relatively low C chain lengths of the acid residues. In this case, too, the carboxylic acid residues present are at least predominantly linear and are of preferably vegetable and/or animal origin. Vegetable starting materials are, for example, palm oil, peanut oil, castor oil and, in particular, rapeseed oil. Carboxylic acids of animal origin are, in particular, corresponding mixtures of fish oils, such as herring oil.

In another important embodiment of the invention, however, the esters of corresponding monocarboxylic acids with polyfunctional alcohols, particularly lower polyfunctional alcohols containing 2 and/or 3 hydroxyl groups, are also suitable as ester-based mixture components. The most important representatives of this class are the reaction products of the monocarboxylic acids mentioned with glycerol, more especially the triglycerides. Among natural oils and fats, materials such as these are abundantly available at an acceptable price, the following natural products being mentioned by way of example: coconut oil, palm kernel oil, palm oil, soybean oil, peanut oil, rapeseed oil, olive oil, linseed oil, sunflower oil and/or castor oil.

As already mentioned, the idea of using esters of this type in drilling muds has already been discussed in the literature. However, on account of the totally inadequate rheological properties of these glycerol esters, invert drilling muds based on these starting materials which would be suitable for use in practice have not hitherto been known. The invention opens up the possibility of making glycerol esters of this type for the first time a substantial constituent of drilling muds of high ecological

compatibility. The fatty acid methylesters of the type described in accordance with the invention are also highly effective diluents and stabilizers for such glycerol esters and not only for materials of natural origin, but also for synthetic glycerol esters.

In combination with the ester oils of polyfunctional alcohols, particularly glycerides of the described type, it can be useful to use those ester oils based on the methylesters which are distinguished by high structural mobility and flowability, even at low temperatures. Methylester cuts of comparatively low monocarboxylic acids, particularly saturated monocarboxylic acids, for example methylesters of C_{8-12} and, in particular, C_{8-10} carboxylic acids, are particularly suitable. However, ester oil mixtures in the context of the invention are not solely confined to representatives such as these. The methylesters of higher carboxylic acids are also valuable mixture components for liquefying the triglycerides; in their case, the proportion of ester oil based on methylester may have to be somewhat higher than in the case of the lower methylesters mentioned above to obtain satisfactory rheological data, even at low temperatures.

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

The mixing ratios in the oil phase

It has surprisingly been found that even comparatively

small quantities of methylester oil of the type used in accordance with the invention lead on the one hand to a substantial improvement in the rheological properties of the drilling mud and, on the other hand, to an improvement in ageing resistance and a reduction in sensitivity to the addition of alkali to the drilling mud. For example, ready-to-use drilling muds may be obtained using predominant quantities of ester oils based on natural and/or synthetic triglycerides providing the ester oil mixtures used contain from about 15 to 50% by weight and, in particular, from about 15 to 30% by weight methylester. The resistance to ageing of the ester oils based on monofunctional alcohols containing at least 2 carbon atoms and their resistance to the addition of alkali reserves are substantially improved by the use of comparatively limited quantities of methylester.

As already mentioned, however, the invention is not limited to the use of the methylester oils in such small quantities. The methylesters may make up the predominant part of the continuous oil phase or even the entire oil phase. In numerical terms, therefore, the methylester may form in particular about 10 to 100% by weight of the continuous oil phase providing the basic rheological requirements for the invert mud are satisfied.

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 dispersed aqueous phase, emulsifiers, weighting agents, fluid loss additives, thickeners and alkali reserves are particularly important in this regard.

In one particularly important embodiment of the inven-

tion, use is also made here of the further development of such invert drilling muds based on ester oils which is the subject of earlier German application P 39 03 785.1 "Oleophilic basic amine compounds as an additive for invert drilling muds".

The teaching of this earlier application is based on the concept of introducing into invert drilling muds based on ester oils an additional additive which is capable of keeping the desired rheological data of the drilling mud in the required range, even when increasingly larger quantities of free carboxylic acids are formed in use by partial ester hydrolysis. Not only are these carboxylic acids to be trapped in a harmless form, it is also intended to be possible to convert these free carboxylic acids if desired into 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 alkoxyated to a limited degree and/or substituted by, in particular, hydroxyl groups. Other examples are corresponding aminoamides and/or heterocycles containing nitrogen as a constituent of the ring. Suitable amine compounds of the type in question are, for example, basic amine compounds containing at least one long-chain, preferably C_{8-36} and more preferably C_{10-24} hydrocarbon radical which may even be mono- or polyolefinically unsaturated. The oleophilic basic amine compounds may be added to the drilling mud in quantities of up to about 10 lb/bbl, preferably in quantities of up to about 5 lb/bbl and more preferably in quantities of from about 0.1 to 2 lb/bbl.

It has been found that the use of such oleophilic basic amine compounds can effectively prevent thickening of the drilling mud presumably attributable to a disturbance of the w/o invert system and to the formation of free carboxylic acids by ester hydrolysis. Although the use of methylester-based ester oils on their own or in combination in accordance with the teaching of the invention provides substantial assistance against unwanted thickening of the invert drilling muds, the combination with the teaching of the earlier application cited above is nevertheless an important embodiment of the invention disclosed herein.

The following observations also apply:

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

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

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

Emulsifiers suitable for use in practice are systems which are capable of forming the required w/o emulsions. Selected oleophilic fatty acid salts, for example those based on amidoamine compounds, are particularly suitable, examples being described in the already cited US-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 from about 2.5 to 5% by weight and more especially in quantities of from about 3 to 4% by weight, based in each case on the ester oil phase.

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

In drilling muds of the type in question here, the

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

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

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 aminoamides 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.

In addition to the advantages already mentioned, the drilling fluids based in accordance with the invention on the co-use of ester oils of the described type are also distinguished by distinctly improved lubricity. This is particularly important when the path of the drill pipe and hence the well deviate from the vertical during drilling, for example at considerable depths. In such cases, the rotating drill pipe readily comes into contact with the well wall and embeds itself therein. Ester oils of the type used as oil phase in accordance with the invention have a distinctly better lubricating effect than the

mineral oils hitherto used, which is an important advantage of the teaching according to the invention.

Examples

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

230 ml ester oil
10 26 ml water
6 g organophilic bentonite (Geltone II, a product of NL Baroid)
6 g organophilic lignite (Duratone, a product of NL Baroid)
15 2 g lime
6 g w/o emulsifier (EZ-mul NT, a product of NL Baroid)
346 g baryta
9.2 g $\text{CaCl}_2 \cdot 2 \text{H}_2\text{O}$

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

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

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

The material is aged by treatment in an autoclave (so-called roller oven) for 48 hours (Examples 1 to 3) and for 24 hours (Examples 4, 5 and Comparison Example) at 125°C.

35 **Example 1**

A rapeseed oil fatty acid methylester having the following characteristic data is used as the ester oil: acid value (max.) 1; saponification value 187 to 197; iodine value 100 to 115; chain distribution of the carboxylic acid residues: C₁₆ 5 to 10, C₁₈ 1 to 3, C₁₈ 54 to 62, C₁₈ 17 to 23 and C₁₈ 7 to 12, C₂₀ 1 to 4, remainder traces of various C₁₂₋₂₂ acids.

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

10

	Unaged material	Aged material
Plastic viscosity (PV)	21	25
15 Yield point (YP)	6	6
Gel strength (lb/100 ft ²)		
10 secs.	6	7
10 mins.	9	9

Example 2

Soybean oil fatty acid methylester having the following characteristic data is used as the ester oil phase: acid value (max.) 1, saponification value 189 to 195; iodine value 115 to 135; chain distribution of the carboxylic acid residues: C_{16} 8 to 13, C_{18} 3 to 6, C_{18} 23 to 30, C_{18} 40 to 50 and C_{18} 4 to 12, remainder traces of C_{10-22} monocarboxylic acids.

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

		Unaged material	Aged material
15	Plastic viscosity (PV)	19	23
	Yield point (YP)	11	6
	Gel strength (lb/100 ft ²)		
	10 secs.	7	6
	10 mins.	7	7

20

Example 3

Technical oleic acid methylester having the following characteristic data is used as the ester oil phase: acid value (max.) 1, saponification value 192 to 197; iodine value 84 to 92; chain distribution of the carboxylic acid residues: C_{14} 2 to 5, C_{16} 4 to 6, C_{16} 4 to 6, C_{17} 1 to 3, C_{18} 1 to 3, C_{18} 63 to 73, C_{18} 7 to 12, remainder traces of various carboxylic acids up to C_{22} .

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

30

	Unaged material	Aged material
Plastic viscosity (PV)	21	23
5 Yield point (YP)	6	6
Gel strength (lb/100 ft ²)		
10 secs.	5	7
10 mins.	7	9

10 In Examples 4 and 5 below, mixtures of a head-fractionated fatty acid methylester (chain length of the saturated carboxylic acid residues C₆₋₁₂) with an undistilled isobutyl rapeseed oil ester are used as the continuous oil phase. The isobutyl rapeseed oil ester is based on a mixture of predominantly unsaturated linear carboxylic acids substantially corresponding to the following distribution: 60% oleic acid, 20% linoleic acid, 9 to 10% linolenic acid, olefinically unsaturated C₂₀₋₂₂ monocarboxylic acids approx. 4%, remainder saturated, predominantly C₁₆₋₁₈ monocarboxylic acids.

20 The rapeseed oil ester used has the following characteristic data: density (20°C) 0.872 g/cm³; pour point below -15°C; flash point (DIN 51584) above 180°C; acid value (DGF-CV2) 1.2; viscosity at 0°C 32 mPa.s, viscosity at 5°C 24 mPa.s; no aromatics.

25 The characteristic data of the head-fractionated fatty acid methyl ester are as follows: saponification value 320 to 325, iodine value max. 1, pour point -28°C, chain length distribution C₆ 3 to 8, C₈ 50 to 60, C₁₀ 30 to 40, C₁₂ 1 to 5.

30 Blends of 20% by weight of the head-fractionated fatty acid methylester with 80% by weight of the isobutyl rapeseed oil ester are used in Examples 4 and 5. In Example 4, only 1 g lime is used as alkali reserve in the starting formulation shown above. For comparison, Example 5 uses 2 g lime as alkali reserve.

35 The characteristic data of the material are as fol-

		Unaged material	Aged material
5	Plastic viscosity (PV)	27	28
	Yield point (YP)	10	18
	Gel strength (lb/100 ft ²)		
	10 secs.	6	7
	10 mins.	8	8

**CLAIMS**

1. The use of the methylesters of C_{6-24} monocarboxylic acids in quantities of 10 to 100% by weight, based on the oil phase, as the oil phase or as part of the oil phase of
5 invert drilling muds which are suitable for the environment-friendly development of oil and gas sources and which, in a continuous oil phase, contain a disperse aqueous phase together with emulsifiers, weighting agents, fluid loss additives and, if desired, other typical additives.
- 10 2. The use claimed in claim 1, characterized in that monocarboxylic acid methylesters which are liquid and pumpable at room temperature and, in particular, even at temperatures of 0 to 5°C, or mixtures thereof, are used.
- 15 3. The use claimed in claims 1 and 2, characterized in that methylesters or mixtures of methylesters and non-polluting oils which have a Brookfield (RVT) viscosity at 0 to 5°C of no more than 50 mPa.s, preferably no more than 40 mPa.s and, at most, approximately 30 mPa.s are used as the oil phase.
- 20 4. The use claimed in claims 1 to 3, characterized in that the methylesters or methylester mixtures used in the drilling mud have solidification values (pour point and setting point) below 0°C, preferably below -5°C and, more preferably, below -10°C and flash points of at least about
25 70°C and preferably above 90°C.
- 30 5. The use claimed in claims 1 to 4, characterized in that, in the case of methylester-containing oil mixtures, low-toxicity hydrocarbon drilling oils and/or carboxylic acid ester oils of other alcohols are used as further oil components in the oil phase, esters of monofunctional and/or lower monofunctional alcohols being particularly preferred and glycerol esters of natural or synthetic origin being particularly suitable as esters of polyfunctional alcohols.
- 35 6. The use claimed in claims 1 to 5, characterized in



that methylesters of C_{8-24} monocarboxylic acids are used; in the range of carboxylic acids containing 16 and more carbon atoms, at least partly olefinically unsaturated methylesters are preferred whereas the shorter C chain length range may include olefinically unsaturated carboxylic acid residues, although in this case the methylesters are typically derived from saturated monocarboxylic acids.

5 7. The use claimed in claims 1 to 6, characterized in that no more than 35% by weight of the unsaturated C_{16-24} monocarboxylic acid residues present in the methylester are derived from di- and polyolefinically unsaturated acids, at least about 60% by weight preferably being monoolefinically unsaturated, and/or in that more than 45% by weight and preferably more than 55% by weight of the C_{16-24} monocarboxylic acid residues present in the ester mixture are derived from di- and/or polyolefinically unsaturated acids.

10 8. The use claimed in claims 1 to 7, characterized in that saturated C_{16-18} carboxylic acids present in the methylester mixture make up no more than about 20% by weight and, in particular, no more than about 10% by weight, but are preferably in the shorter C chain length range.

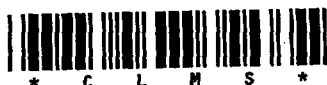
15 9. The use claimed in claims 1 to 8, characterized in that ester oils of monofunctional C_{2-12} and preferably C_{4-10} alcohols and olefinically mono- and polyunsaturated monocarboxylic acids containing 16 to 24 C atoms, which preferably have solidification values (pour point and setting point) below -10°C and preferably below -15°C and flash points above 100°C and preferably above 150°C , are present as ester-based mixture components in the continuous oil phase.

20 10. The use claimed in claim 9, characterized in that olefinically unsaturated carboxylic acid esters of which more than 70% by weight, preferably more than 80% by weight and more preferably more than 90% by weight are derived from olefinically unsaturated C_{16-24} carboxylic acids and

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which 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 are used together with the methylesters as mixture component.

- 5 11. The use claimed in claims 9 and 10, characterized in that, of the esters of unsaturated monocarboxylic acids used as mixture components, no more than 35% by weight are derived from di- and polyolefinically unsaturated acids, of which at least about 60% by weight are monoolefinically un-
- 10 saturated, and/or more than 45% by weight and preferably more than 55% by weight are derived from di- and/or polyolefinically unsaturated acids.
12. The use claimed in claims 1 to 8, characterized in that the methylesters are used together with esters of
- 15 monofunctional C₂₋₁₂ and, in particular, C₄₋₁₂ monofunctional alcohols and aliphatic, saturated monocarboxylic acids containing up to 16 carbon atoms and, preferably, predominantly from 12 to 14 carbon atoms.
13. The use claimed in claims 1 to 12, characterized in
- 20 that the methylesters of carboxylic acids of natural and, in particular, vegetable origin and/or methylesters of synthetic carboxylic acids are used.
14. The use claimed in claims 1 to 13, characterized in that the methylesters are used in the invert drilling mud
- 25 together with alkali reserves, lime being a particularly preferred alkali reserve.
15. The use claimed in claims 1 to 14, characterized in that the methylesters are used in the invert drilling muds
- 30 together with amine compounds of pronounced oleophilic character and at most limited solubility in water which are capable of forming salts with free carboxylic acids.
16. The use claimed in claims 1 to 15, characterized in that the methylesters are used as diluents and for improving the rheological properties of the oil phase, particu-
- 35 larly at temperatures of 0 to 5°C, and/or for reducing the



sensitivity of the oil mud to alkalis during ageing.

17. The use claimed in claims 1 to 16, characterized in that the esters are used in drilling muds which, in the invert drilling mud, contain the finely disperse aqueous phase together with the ester-based continuous oil phase in quantities of from about 5 to 45% by weight and preferably in quantities of from about 5 to 25% by weight.

18. Invert drilling muds which are suitable for the environment-friendly development of oil and gas sources and which, in a continuous oil phase, contain a disperse aqueous phase together with emulsifiers, weighting agents, fluid loss additives and, if desired, other standard additives, characterized in that the oil phase contains methylesters of C_{6-24} monocarboxylic acids in quantities of 10 to 100% by weight, based on the oil phase, if desired in admixture with other oil components from the class of non-polluting oils.

19. An invert drilling mud as claimed in claim 18, characterized in that the oil phase contains selected methylesters or methylester mixtures in quantities of at least about 10% by weight, based on oil phase.

20. An invert drilling mud as claimed in claims 18 and 19, characterized in that, together with the methylesters, esters of other, preferably monofunctional and/or lower monofunctional alcohols with monocarboxylic acids make up at least the main part of the oil phase, triglycerides of natural and/or synthetic origin being particularly suitable polyfunctional esters.

21. An invert drilling mud as claimed in claims 18 to 20, characterized in that the drilling mud contains an alkali reserve, preferably of lime and/or other comparable metal oxides, such as zinc oxide, and/or basic amine compounds of pronounced oleophilic character and at most limited solubility in water which are capable of forming salts with carboxylic acids.



22. An invert drilling mud as claimed in claims 18 to 21, characterized in that it has a plastic viscosity (PV) in the range from about 10 to 60 mPa.s and a yield point (YP) in the range from about 5 to 40 lb/100 ft², determined in each case at 50°C.

23. An invert drilling mud as claimed in claims 18 to 22, characterized in that its disperse water component makes up about 5 to 45% by weight and preferably about 10 to 25% by weight and, in particular, contains dissolved salts of the CaCl₂ and/or KCl type.

24. An invert drilling mud as claimed in claims 18 to 23, characterized in that the oil phase of the invert mud has a Brookfield (RVT) viscosity at 0 to 5°C below 50 mPa.s and preferably no more than 40 mPa.s