

This invention relates to new borehole servicing formulations which flow freely under normal conditions and which are made up using an oil phase. As a characteristic example of servicing formulations of the type in question, the invention is described hereinafter with reference to drilling fluids and drilling muds based thereon. However, the modification according to the invention of auxiliary fluids of the type in question is by no means limited to this particular application and may also be applied in particular to spotting fluids, spacers, auxiliary workover, stimulation and fracturing fluids.

The invention is concerned both with auxiliary fluids of the type mentioned which are based on oils, i.e. which work with a continuous oil phase, and with auxiliaries in which the oil phase is emulsified in an aqueous continuous phase. Drilling fluids and drilling muds based thereon are characteristic examples of the various corresponding possibilities.

On the one hand, water-based drilling fluids containing around 1 to 50% of emulsified oil phase in addition to other typical auxiliaries encountered in drilling fluids are known and are referred to as emulsion fluids. On the other hand, oil-based drilling fluids in which the oil forms the fluid phase or at least a substantial part of the fluid phase are widely used in practice. Particular significance is attributed in this regard to so-called invert drilling muds which - on the basis of w/o emulsions - contain a dispersed aqueous phase in the continuous oil phase. The content of dispersed aqueous phase is typically in the range from about 5 to 50% by weight. The invention relates equally to the two fields in question, namely oil-based drilling fluids and water-based drilling emulsions.

The use of the new borehole servicing fluids is of

particular significance for the development of oil and gas occurrences, particularly in the marine sector, but is by no means limited to this particular field of application. The new systems may also be generally used in land-supported drilling operations, for example in geothermal drilling, water drilling, geoscientific drilling and mine drilling.

Prior Art

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

water-based drilling fluids, oil-based drilling fluids which are generally used as so-called invert emulsion muds and water-based o/w emulsions which contain a heterogeneous finely dispersed oil phase in a continuous aqueous phase.

Drilling fluids on a continuous oil basis are generally made up of a three-phase system, namely: oil, water and fine-particle solids. 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, weighting agents, fluid loss additives, alkali reserves, viscosity regulators and the like. 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.

Drilling fluids based on aqueous o/w emulsion

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

In practice, the oil phases of drilling fluids of the type described in these references and other borehole servicing formulations of comparable composition are now formed almost exclusively by mineral oil fractions. Accordingly, considerable environmental pollution occurs when, for example, the drilling muds enter the environment either directly or via the drilled rock. Mineral oils are not readily biodegradable and, anaerobically, are virtually non-degradable and may therefore be regarded as long-term pollution.

Proposals for easing these problems have recently been put forward. Thus, US-PSS 4,374,737 and 4,481,121 describe oil-based invert drilling fluids in which so-called non-polluting oils are said to be used. Dearomatized mineral oil fractions and ester oils of vegetable and animal origin are mentioned alongside one another as non-polluting oils of equal rank. The ester oils are triglycerides of natural fatty acids which are known to show high environmental compatibility and which are distinctly superior to hydrocarbon fractions on ecological grounds.

Proposals for replacing the mineral oil fractions by ecologically safe, readily degradable oil phases are put

forward in a relatively large number of applicants' earlier applications. According to these various applications, there are three different types of replacement oils which may even be used in admixture with one another. The replacement oils in question are selected oleophilic carboxylic acid esters, at least substantially water-insoluble alcohols flowable under working conditions and corresponding ethers, cf. earlier applications P 38 42 659.5 (D 8523), P 38 42 703.6 (D 8524), P 39 07 391.2 (D 8606), P 39 07 392.0 (D 8607), P 39 03 785.1 (D 8543), P 39 03 784.3 (D 8549), P 39 11 238.1 (D 8511) and P 39 11 299.3 (8539). All the earlier applications mentioned are concerned with oil-based drilling fluids, more particularly of the w/o invert type. Water-based emulsion drilling fluids using oil phases of increased degradability are described in earlier applications P 39 15 876.4 (D 8704), P 39 15 875.6 (D 8705) and P 39 16 550.7 (D 8714).

20 The Problem Addressed by the Invention and its Technical Solution

The problem addressed by the present invention was to enable a class of substances, of which the use in borehole servicing formulations had never been previously described, to be at least partly used as the oil phase of borehole servicing formulations of the type in question. At the same time, the invention set out to follow the objectives of the numerous earlier applications cited above by providing an oil phase which would be distinguished by excellent ecological compatibility and favourable - even improved in relation to known oil phases - performance properties in the particular application envisaged.

35 The teaching of the invention is based on the discovery that selected diesters of carbonic acid are

excellent replacement oils in the context of the problem addressed by the present invention. These carbonic acid diesters may form the particular oil phase as a whole or, alternatively, may even be used in admixture with other oils, more particularly from the class of so-called non-polluting oils. Carboxylic acid ester oils, oleophilic alcohols and/or ethers from applicants' earlier applications cited above are particularly suitable mixture components.

10 In a first embodiment, therefore, the present invention relates to the use of oleophilic diesters of carbonic acid with the same or different oil-soluble and ecologically safe, monohydric and optionally polyhydric alcohols as a constituent of oil- or water-based drilling
15 fluids and other flowable borehole servicing formulations.

A first variant of this embodiment of the invention is characterized in that the oleophilic carbonic acid diesters are used in the oil phase of oil-based drilling
20 fluids, more particularly invert drilling fluids of the w/o type, and are either present as an additive in a relatively low concentration in the continuous oil phase or preferably make up at least the predominant part of the oil phase.

25 In a second preferred embodiment, the oleophilic carbonic acid diesters are used in water-based emulsion drilling fluids of the o/w type. In this case, too, they are present at least in a relatively low concentration in the dispersed oil phase, but - in a particularly preferred embodiment - make up at least the predominant part of
30 that phase.

In another embodiment, the present invention relates to borehole servicing formulations which flow and can be pumped at temperatures of 5 to 20°C, more particularly
35 drilling fluids based on

- either a continuous oil phase, if desired in admixture with a limited quantity of a dispersed aqueous phase (w/o invert type)
- or on a dispersed phase in a continuous aqueous phase (o/w emulsion type),

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this embodiment of the invention being characterized in that the borehole servicing formulations contain oleophilic carbonic acid diesters based on oil-soluble and ecologically safe monohydric alcohols and optionally water- and/or oil-soluble polyhydric alcohols in their oil phase.

10 In addition, in these embodiments of the teaching according to the invention, the borehole servicing formulations may contain the usual dissolved and/or dispersed auxiliaries, such as viscosity controllers, emulsifiers, fluid loss additives, wetting agents, fine-particle weighting agents, salts, alkali reserves and/or biocides. In another preferred embodiment of the teaching according to the invention, inorganic and/or organic auxiliaries and additives which, ecologically and toxicologically, are at least substantially safe are mainly used.

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Particulars and Preferred Embodiments of the Invention

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Oleophilic oil-soluble carbonic acid diesters, their production and their use in various fields are the subject of numerous printed publications. Thus, EP-A1 0 089 709 describes lubricant mixtures based on diesters of higher alcohols, the alcohols used for esterification preferably having molecular weights in the range from about 100 to 270. This document also describes possibilities for the production of corresponding carbonic acid diesters with reference to the relevant literature (Italian patent 898077 and British patent 1,574,188).

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35 The production of carbonic acid diesters of monohydric

alcohols from alkylene carbonates is described, for example, in US-PS 3,642,858. The alkylene carbonates used as starting material are the carbonic acid esters of lower diols containing vicinal hydroxyl groups. DE-AS 12 42 569 describes the use of neutral carbonic acid esters of monohydric alcohols containing 4 to 22 carbon atoms in the alcohol component as foam-suppressing agents. These carbonic acid diesters are produced by methods known from the literature as described, for example, in Houben-Weyl, Methoden der organischen Chemie, O. Thieme Verlag Stuttgart, Vol. 8, page 106 (4th Edition, 1952). On the other hand, however, it is also known that carbonic acid esters can be modified by incorporation of hydrophilic and hydrophobic groups in the molecule in such a way that the compounds obtained may be used as biodegradable, nonionic surface-active components, cf. for example US-PS 4,504, 418.

The use or rather co-use of the esters based on carbonic acid selected in accordance with the invention for forming the oil phase of borehole servicing formulations of the described type has not been previously described and is not known. As applicants have found, however, this class of compounds is particularly suitable for the application envisaged. Carbonic acid diesters show a balanced ratio of stability and vulnerability to hydrolysis for the application envisaged. The compounds are sufficiently stable to be able to be successfully used under the conditions under which drilling fluids are normally used. However, when stored under environmental conditions, particularly in the marine ecosystem, diesters subsequently undergo biological degradation, the compatibility of the ester being determined by the particular alcohols used. Accordingly, it is possible in accordance with the invention to achieve an optimal balance between performance properties and biocompatibility.

In the context of the definition according to the invention, carbonic acid diesters include both the corresponding compounds in the narrower sense which contain a carbonic acid residue to which two alcohol radicals are attached in ester-like form. However, the definition of carbonic acid diesters according to the present invention also encompasses corresponding oligomeric compounds in which a plurality of carbonic acid residues are attached in one and the same molecule, each carbonic acid residue being attached in the form of the diester. Corresponding oligomeric compounds are obtained when polyhydric alcohols are used together with monohydric alcohols and at least two hydroxyl groups of the polyhydric alcohols interact with various carbonic acid molecules. The use of monohydric alcohols is also crucial to this embodiment so that each carbonic acid residue is ultimately attached in the form of a diester. For the application according to the invention, oleophilic oligomeric carbonic acid diesters of the last-described type contain no more than 10 carbon atoms per molecule, the preferred upper limit being on average about 5 carbonic acid residues per molecule. Particularly suitable oligomeric carbonic acid diesters according to the invention contain on average 2 or 3 carbonic acid residues per molecule.

In addition, in the context of the definition according to the invention, carbonic acid diesters also include certain selected symmetrical diesters - for example as reaction products between carbonic acid and a certain selected oil-soluble monohydric alcohol - and also corresponding asymmetrical esters containing different alcohols attached to the carbonic acid residue. Finally, carbonic acid diesters in the context of the invention also include mixtures of symmetrical and/or asymmetrical - monomeric and/or oligomeric - carbonic acid diesters of the type formed, for example, as a

statistical mixture where the reaction is carried out with a mixture of at least two monohydric alcohols, optionally using polyhydric alcohols.

All compounds corresponding to the above definition and mixtures of such compounds are oleophilic carbonic acid diesters with only minimal residual solubility in water. In general, the solubility of these diesters at 0 to 20°C is at most about 1% by weight and, preferably, is distinctly lower, for example at most 0.5 or even at most about 0.1% by weight. The carbonic acid diesters to be used in accordance with the invention are also all distinguished by their flashpoint characteristic. The flashpoint of the oleophilic diesters used in accordance with the invention should be at least 80°C and is preferably at least 100°C. It may be desirable for reasons of operational safety to apply higher limits to the flashpoint of the oil phase so that flashpoints of the order of at least 135°C and, more particularly, at least 150°C can be of particular practical significance.

Another requirement which all the carbonic acid diesters to be used in accordance with the invention have to satisfy is that they must be ecologically safe. This requirement is ultimately fulfilled by the alcohols used for esterification. The following observations are made in this regard:

Ecological compatibility in the context of the invention is understood on the one hand to mean biodegradability in the particular ecosystem, i.e. in the marine ecosystem in offshore drilling operations. However, there is another consideration which deserves particular attention in the choice of suitable monohydric alcohols, namely: in the practical application of the oil phases according to the invention in admixture with aqueous phases, particularly at the elevated temperatures occurring in the borehole, partial ester cleavage can

occur with formation of corresponding fractions of the free alcohols. The free alcohol is then present in admixture with the remaining constituents of the oil phase. It can be important in this regard that the free alcohols are selected so that the drilling team is not exposed to any inhalation-toxic risks at the drilling site. The problem under discussion applies above all to the monohydric alcohols used. Even in their lowest members, polyhydric alcohols have such low volatility values that the safety required in practice is guaranteed from the outset.

Monohydric alcohols suitable for forming the carbonic acid diesters are, in particular, oil-soluble compounds of this type containing at least 5 and preferably at least 6 carbon atoms. An upper limit to the number of carbon atoms in practice is imposed solely by considerations as to the accessibility of corresponding monoalcohols. For practical reasons, this upper limit is about 40 carbon atoms. Monohydric alcohols in the C_{8-36} range and, more particularly, in the C_{8-24} range can be particularly suitable. These alcohol components are preferably free from aromatic molecule constituents and, in particular, contain linear and/or branched hydrocarbon chains of natural and/or synthetic origin. The corresponding alcohols and, more particularly, alcohols with a relatively large number of carbon atoms, for example 16 to 24 carbon atoms, may even be at least partially monoolefinically or even polyolefinically unsaturated. It is known that the incorporation of olefinic double bonds influences the rheology of corresponding diesters by increasing their flowability, even at low temperatures. Use can be made of this in accordance with the invention. However, this does involve a certain susceptibility to oxidation in practice which may necessitate the use of stabilizing antioxidants and, optionally, synergistic

auxiliaries. The reduction of high rheology, even at low temperatures, is promoted in particular by the use of branched hydrocarbon chains. Optimal ecological compatibility and rheological data of the oil phase for the particular application envisaged can be obtained by
5 suitable coordination. The rheology of the carbonic acid diesters may be additionally controlled through the use of alcohol mixtures. It is readily possible in this way to use carbonic acid diesters based solely on linear
10 fatty alcohols of natural origin in the C_{6-18} range and, in particular, at least predominantly in the C_{8-14} range, even when the material based on carbonic acid diesters is expected to meet stringent requirements in regard to favourable rheology, even at low temperatures.

15 Highly mobile carbonic acid diesters with long carbon chains in the range mentioned above can be obtained by the at least partial use of branched monohydric alcohols, for example corresponding synthetic alcohols or from the oligomerization of linear starting materials of
20 natural origin.

The polyhydric alcohols optionally used also cover a broad range of carbon chain lengths in the molecule. Corresponding polyhydric alcohols containing 2 to 40 carbon atoms are particularly suitable. The polyhydric
25 alcohols used in the formation of the carbonic acid diesters may be soluble in water and/or oils. Even in the form of their lowest members, for example in the case of ethylene glycol, they are not highly volatile. They are generally toxicologically safe and, in particular,
30 inhalation-toxicologically safe. Polyhydric alcohols containing up to five hydroxyl groups and preferably two and/or three hydroxyl groups are preferred ester-forming components of the oil phase based on carbonic acid diesters.

35 Polyhydric alcohols may be incorporated in various

forms in the special structure of the oil phase based on carbonic acid diesters used in accordance with the invention. There are in particular three suitable structure types, namely:

5 The polyhydric alcohol may be attached to the carbonic acid as a hydroxyl-terminated ester group. However, the polyhydric alcohol may also be a binding link between the carbonic acid residue and the esterifying monohydric alcohols to form chain-extending ether groups.

10 Finally, the use of polyhydric alcohols can lead to the formation of oligomeric carbonic acid diesters. This is possible in particular when the hydroxyl groups of the polyhydric alcohol are so far removed from one another that the formation of 5- to 6-membered rings with only
15 one carbonic acid residue is not possible.

 It has been found that favourable rheological properties can be established in oligomeric carbonic acid diesters, even where they have comparatively high molecular weights. For example, a complex carbonic acid
20 diester mixture liquid at room temperature is obtained when a diol obtained from dimer fatty acids statistically containing 36 carbon atoms is reacted together with 2 equivalents of isotridecyl alcohol as monohydric component and 2 equivalents of carbonic acid.

25 However, favourable rheological properties, especially at relatively low temperatures, are established not only by using complex alcohol mixtures. The use of defined monohydric alcohols can also lead to oleophilic carbonic acid diesters which effectively satisfy the
30 various requirements according to the invention. The synthetic alcohols 2-ethylhexyl alcohol and isotridecyl alcohol are mentioned as corresponding examples. Di-2-ethylhexyl carbonate for example has a flow point of -56.6°C and a flashpoint of 154°C . Where this carbonic
35 acid diester is used, the risk of inhalation-toxicologi-

cal damage is as low as with comparable symmetrical carbonic acid diesters with alcohols containing larger numbers of carbon atoms, for example diisotridecyl carbonate.

5 The use of carbonic acid diesters as oil phase can afford important advantages, particularly at comparatively high working temperatures, for example in sufficiently deep boreholes where the temperature can reach at least 120 to 150°C. Compounds of this type generally show high
10 temperature stability, for example up to temperatures of 300°C. Their temperature stability can be influenced in known manner through the choice of suitable alcohol components.

 The following feature is specifically mentioned in
15 conjunction with the use of polyhydric alcohols: through the selective incorporation of, in particular, lower dihydric and/or trihydric alcohols, it is possible to influence the HLB value of the oil phase and, hence, its ability to take up and stabilize a dispersed aqueous
20 phase on the one hand or its dispersion as a dispersed oil phase in a continuous aqueous phase. It is possible in this way to control and reduce the use of the hitherto necessary emulsifiers in terms of type and/or quantity so that, if desired, there is no need at all to use emulsi-
25 fiers. The invention thus opens up important possibilities for the use of ecologically distinctly improved drilling fluids.

 The particular characteristics of the carbonic acid diesters used, particularly their rheology, may vary
30 within wide limits. This is illustrated by the following consideration: if the carbonic acid diester is used as a principal component in oil-based systems, favourable rheological properties, even at low temperatures, generally have to be established at the same time. In this
35 case, the flow point and pour point should be below 0°C

and preferably below -5°C , lower values, for example below -10°C or even below -15°C , being of particular advantage. In preferred systems, the Brookfield (RVT) viscosity should be no more than 55 mPas and is preferably no more than 45 mPas.

If, on the other hand, the carbonic acid diester is used as dispersed phase in water-based emulsion systems, far less stringent demands can be imposed on the flowability of the particular carbonic acid diester. Thus, the flow and pour point may be above 0°C . However, it can be useful to establish corresponding values at least of the order of room temperature. The Brookfield (RVT) viscosity at 20°C may be up to about 2 million mPas or even higher and is preferably up to about 1 million mPas.

The fact that, in this particular embodiment, carbonic acid diesters of comparatively poor mobility can be effective aids is illustrated, for example, by the following consideration: the dispersed oil phase in water-based emulsion drilling fluids has various technical functions to perform, including inter alia lubrication. Even relatively small quantities of a corresponding dispersed oil phase, for example about 1 to 8% by weight of dispersed oil phase, can significantly improve corresponding water-based emulsion drilling fluids. According to the invention, corresponding representatives based on carbonic acid diesters - which are of course known inter alia as superior lubricants - may be used in the form indicated here.

The question of the viscosity of the particular carbonic acid diester material used also loses significance when these materials as defined in accordance with the invention are used in admixture with other oil phases. This is particularly the case when the carbonic acid diesters are present in small quantities in the mixture forming the oil phase and develop certain proper-

ties in a certain way, for example establish increased lubricity without critically influencing the rheology of the system as a whole.

5 Possible Mixture Components for the Oil Phase

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

However, particularly important mixture components in the context of the teaching according to the invention are ecologically safe oleophilic alcohols, corresponding ethers and/or ester oils of the type described in detail in applicants' earlier applications cited above. Accordingly, the disclosures of these earlier applications are hereby specifically included as part of the disclosure of the present invention. Only a few important aspects of these earlier teachings are discussed in the following.

The oleophilic mixture components based on alcohols, ethers and/or carboxylic acid esters can make up the predominant part of the oil phase. In this case, carbonic acid diesters as defined in accordance with the invention are used to establish certain properties. In general, the carbonic acid diester will still make up a few % by weight of the oil phase, for example at least about 5% by weight. Oleophilic alcohols can be of interest for numerous applications as a hydrolysis-stable principal component of the oil phase although, in many cases, corresponding alcohols show inadequate lubricity. By contrast, carbonic acid diesters as defined in accordance with the invention are known as effective lubricants from the relative prior art. For example, it can be

useful to employ mixed oil phases containing at least about 10% by weight of the carbonic acid diester and, more particularly, around 15 to 50% by weight of the carbonic acid diester. It can be particularly useful
5 predominantly or even exclusively to use the carbonic acid diesters, above all under working conditions involving fewer hydrolytic influences, i.e. for example in oil-based drilling fluids, including those of the w/o
6 invert type. Quantities of around 50 to 95% by weight of
10 the oil phase are characteristic of mixed oil phases of the type in question.

Particulars of the chemical nature of the mixture components used based on oleophilic alcohols, ethers and/or carboxylic acid esters can be found in applicants'
15 earlier applications, cf. in particular application P 39 11 238.1 (D 8511) for the oleophilic alcohols and earlier application P 39 11 299.3 (D 8539) for the oleophilic ethers.

Suitable carboxylic acid esters as mixture components are described in detail in earlier applications P
20 38 42 659.5 (D 8523), P 38 42 703.6 (D 8524), P 39 07 391.2 (D 8606) and P 39 07 392.0 (D 8607).

It is important that all these additives also have flashpoints of at least 80°C and, preferably, at least
25 100°C. Substantially higher flashpoints, for example above 150°C, can be particularly useful. In addition, if the objective of the invention is to be optimally pursued, these alcohols, ethers and/or ester oils must also have a biologically and ecologically safe constitution
30 and, in particular, must be inhalation-toxicologically safe in the event of partial hydrolysis. The foregoing observations on the carbonic acid diesters and the alcohol components used apply correspondingly in this regard.

35 The carboxylic acids formed through the partial

hydrolysis of carboxylic acid ester oils also require some explanation. Depending on the particular constitution of the carboxylic acids used, there are two basic types with a fluid transition in between, namely carboxylic acids which lead to carboxylic acid salts with an emulsifying effect or to inert salts. The particular chain length of the carboxylic acid molecule released is particularly crucial in this regard. The salt-forming cation present through the alkali reserve of the drilling fluid is another important factor to be taken into consideration. The following rules generally apply in this regard:

Lower carboxylic acids, for example those containing 1 to 5 carbon atoms, lead to the formation of inert salts, for example to the formation of corresponding acetates or propionates. Fatty acids with relatively long carbon chains, more particularly C_{12-24} fatty acids, lead to compounds with an emulsifying effect. Further particulars of carboxylic acid ester oils as the oleophilic phase of drilling fluids of the w/o type or o/w type can be found in applicants' earlier applications cited above.

Where oleophilic carboxylic acid ester oils are used as a mixture component, they preferably fall into at least one of the following subclasses in accordance with the invention:

- a) esters of C_{1-5} monocarboxylic acids and monohydric and/or polyhydric alcohols, residues of monohydric alcohols containing at least 6 and preferably at least 8 carbon atoms and the polyhydric alcohols preferably containing 2 to 6 carbon atoms in the molecule,
- b) esters of monocarboxylic acids of synthetic and/or natural origin containing 6 to 16 carbon atoms, more

particularly esters of corresponding aliphatically saturated monocarboxylic acids, and monohydric and/or polyhydric alcohols of the type mentioned under a),

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

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Starting materials for many of the monocarboxylic acids which fall into these subclasses, more particularly with relatively long carbon chains, are vegetable and/or animal oils, including coconut oil, palm kernel oil and/or babassu oil, more particularly as starting materials for monocarboxylic acids predominantly containing up to 18 carbon atoms and substantially saturated components. Vegetable ester oils, more particularly for monoolefinically and, optionally, polyolefinically unsaturated C_{16-24} carboxylic acids are, for example, palm oil, peanut oil, castor oil, sunflower oil and, more particularly, rapeseed oil. Carboxylic acids of animal origin of this type are, in particular, corresponding mixtures of tallow and/or fish oils, such as herring oil.

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Additives in the Oil-based or Water-based Drilling Fluid

The general rules apply to the composition of the particular servicing fluids for which exemplary data are presented in the following with reference to corresponding drilling muds.

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Invert drilling muds normally contain the finely dispersed aqueous phase together with the continuous oil phase in quantities of about 5 to 45% by weight and preferably in quantities of about 5 to 25% by weight.

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The following rheological data apply to the rheology

of preferred invert drilling fluids as defined in accordance with the invention: plastic viscosity (PV) in the range from about 10 to 60 mPas and preferably in the range from about 15 to 40 mPas, 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 determined at 50°C. The determination of these parameters, the corresponding methods used and the otherwise standard composition of the invert drilling fluids described herein are as described in detail in the prior art cited at the beginning and, for example, in "Manual of Drilling Fluids Technology", published by NL-Baroid, London, GB, cf. in the particular the chapter entitled "Mud Testing - Tools and Techniques" and "Oil Mud Technology" which is freely available to interested experts.

In emulsion drilling fluids, the dispersed oil phase is typically present in quantities of at least about 1 to 2% by weight, often in quantities of at least about 5% by weight and preferably in quantities of at least about 7 to 8% by weight in the case of an o/w emulsion. The oil content should be preferably be no more than about 50% by weight and, in particular, makes up no more than about 40% by weight. (based on the sum total of the unweighted liquid components oil/water).

In addition to water, it is possible to use any of the additives designed for comparable types of drilling fluids, of which the addition is normally intended to provide the fluid with a specific property spectrum. The additives may be water-soluble, oil-soluble and/or dispersible in water or oil.

Conventional additives include emulsifiers, fluid loss additives, soluble and/or insoluble substances which build up pseudoplasticity, alkali reserves, additives for inhibiting the unwanted exchange of water between drilled formations - for example water-swellable clays and/or

salt layers - and the water-based drilling fluid, wetting agents for improving the absorption of the emulsified oil phase by solid surfaces, for example for improving lubricity, and also for improving the oleophilic sealing of exposed rock formations or rock surfaces, biocides, for example for inhibiting the bacterial contamination of o/w emulsions and the like. Full particulars can be found in the relevant prior art as represented, for example, by the specialist literature cited at the beginning, cf. in particular Gray and Darley, loc. cit., chapter 11, "Drilling Fluid Components", of which the following are only a few examples:

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

Agents for building up pseudoplasticity which also act as fluid loss additives: bentonite and hydrophobized bentonite are mentioned in particular. For salt water muds, considerable significance is attributed in practice to other comparable clays, more particularly attapulgite and sepiolite.

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

Diluents for controlling viscosity. The so-called diluents may be organic or inorganic. Examples of organic diluents are tannins and/or quebracho extract.

Further examples are lignite and lignite derivatives, more particularly lignosulfonates. As mentioned above, however, one preferred embodiment of the invention dispenses with the use of toxic components in this very connection, the corresponding salts with toxic heavy metals, such as chromium and/or copper, being mentioned above all in this regard. One example of inorganic diluents are polyphosphate compounds.

Emulsifiers: the emulsifiers used are critically determined by the type of drilling fluid. Emulsifiers suitable for use in practice for forming w/o emulsions are, in particular, selected oleophilic fatty acid salts, for example those based on amidoamine compounds. Examples of such emulsifiers can be found in the above-cited US-PS 4,374,737 and in the literature cited therein.

Other emulsifiers are required for the formation of o/w emulsions, as known per se. However, it has been found that stable dispersion to form an o/w dispersion is very much easier than the corresponding dispersion of pure mineral oils of the type used in the prior art. This represents a first simplification. Another factor to be taken into consideration is that, where ester oils are used, effective o/w emulsifiers are subsequently formed by partial saponification under the effect of suitable alkali reserves where relatively long-chain carboxylic acid esters are used and, hence, contribute towards stabilizing the system.

Additives inhibiting the unwanted exchange of water, for example with clays: suitable additives of this type are the additives known from the prior art on oil- and water-based drilling fluids. The additives in question are in particular halides and/or carbonates of the alkali and/or alkaline earth metals, particular significance being attributed to corresponding potassium salts,

optionally in conjunction with lime.

Further particulars can be found, for example, in the corresponding Articles in "Petroleum Engineer International", September 1987, 32-40 and "World Oil", November 1983, 93-97.

Alkali reserves: suitable alkali reserves are inorganic and/or organic bases adapted to the overall behavior of the drilling fluid, more particularly corresponding basic salts and hydroxides of alkali metals and/or alkaline earth metals and organic bases. The type and quantity of these basic components are selected and adapted to one another in known manner in such a way that the borehole servicing formulations are adjusted to a pH value in the neutral to moderately basic range, more particularly to a pH value in the range from about 7.5 to 11.

So far as organic bases are concerned, a distinction has understandably to be drawn between water-soluble organic bases, for example compounds of the diethanolamine type, and substantially water-insoluble bases of decidedly oleophilic character of the type described as additives in invert drilling muds based on ester oils in applicants' above-cited earlier application P 39 03 785.1 (D 8543). The co-use of oil-soluble bases such as these also falls within the scope of the teaching according to the invention. However, oleophilic bases of this type, which are distinguished in particular by at least one relatively long hydrocarbon radical, for example containing 8 to 36 carbon atoms, are not dissolved in the aqueous phase, but rather in the oil phase. These basic components are important in several respects. On the one hand, they may act directly as an alkali reserve. On the other hand, they provide the dispersed oil droplet with a certain positive charge and hence lead to increased interaction with negative surface charges of the type

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

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2 g lime
 6 g w/o emulsifier (EZ-mul, a product of Baroid
 Drilling Fluids Inc.)
 6 g w/o emulsifier (INVERMUL NT, a product of Baroid
 Drilling Fluid Inc.)
 346 g barite
 9.2 g $\text{CaCl}_2 \cdot 2 \text{H}_2\text{O}$

Example 1

The oil phase is formed by a carbonic acid diester of which the alcohol radicals are derived from a predominantly $\text{C}_{12/14}$ fatty alcohol of natural origin (Lorol Spezial, a product of Henkel KGaA). The corresponding carbonic acid diester has a Brookfield viscosity at 25°C of 12 cp. The characteristic data of the material as determined before and after ageing are set out in the following Table.

	Before ageing	After ageing
Plastic viscosity (PV)	56	71
Yield point (YP)	32	43
Gel strength (lb/100 ft ²)		
10 secs.	14	18
10 mins.	30	32

HTHP 5 ml

Example 2

A carbonic acid diester based on a 1:1 mixture (parts by weight) of isotridecyl alcohol and a C_{12-18} fatty alcohol mixture (Lorol Techn., a product of Henkel KGaA) is used as the continuous oil phase. The carbonic acid diester mixture has a Brookfield viscosity at 25°C of

23.5 cp.

The characteristic data of the material as determined before and after ageing are as follows:

5		Before ageing	After ageing
	Plastic viscosity (PV)	74	84
	Yield point (YP)	29	28
10	Gel strength (lb/100 ft ²)		
	10 secs.	11	11
	10 mins.	22	19

HTHP 3 ml

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Example 3

A symmetrical carbonic acid diester based on 2-ethylhexanol as an oil-soluble alcohol is used as the continuous oil phase. This ester has a Brookfield
20 viscosity at 25°C of 8 cp.

The characteristic data of the material as determined before and after ageing are as follows:

25		Before ageing	After ageing
	Plastic viscosity (PV)	34	30
	Yield point (YP)	8	8
	Gel strength (lb/100 ft ²)		
30	10 secs.	4	4
	10 mins.	8	7

HTHP 3 ml

35 Example 4

A symmetrical carbonic acid diester based on isotri-

decyl alcohol is used as the continuous oil phase in this Example. The carbonic acid ester oil has a Brookfield viscosity at 25°C of 29 cp.

The characteristic data as determined before and after ageing are as follows:

		Before ageing	After ageing
10	Plastic viscosity (PV)	94	100
	Yield point (YP)	32	27
	Gel strength (lb/100 ft ²)		
	10 secs.	11	10
	10 mins.	18	15

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HTHP 3 ml

Comparison Example A

For comparison, a carboxylic acid ester oil in the form of an ester mixture of substantially saturated fatty acids based on palm kernel oil and 2-ethylhexanol is used as the continuous oil phase in the formulation shown at the beginning. The ester mixture is based for by far the most part on C_{12/14} fatty acids and corresponds to the following specification:

C₈ : 3.5 to 4.5% by weight
 C₁₀: 3.5 to 4.5% by weight
 C₁₂: 65 to 70% by weight
 C₁₄: 20 to 24% by weight
 C₁₆: approx. 2% by weight
 C₁₈: 0.3 to 1% by weight

The ester mixture is present as a light yellow liquid with a flashpoint above 165°C and a Brookfield

viscosity at 20°C of 7 to 9 cp.

The characteristic data of the drilling fluid as determined before and after ageing are as follows:

5		Before ageing	After ageing
	Plastic viscosity (PV)	34	34
	Yield point (YP)	10	8
10	Gel strength (lb/100 ft ²)		
	10 secs.	6	5
	10 mins.	10	10

HTHP 4 ml

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Comparison of the characteristic data using this ester oil - of which the use is the subject of earlier application P 38 42 703.6 (D 8524) - with the characteristic data of Example 3 of the present invention shows that they are virtually identical.

If mixtures of the two ester oils in question (carbonic acid diester of Example 3 and carboxylic acid ester of Comparison Example A) are prepared as the oil phase and used in the formulation shown at the beginning, the material shows comparable characteristic data as determined before and after ageing for virtually any mixing ratio.

Examples 5 and 6

In Examples 5 and 6 below, water-based emulsion drilling fluids are prepared as follows using the oleophilic carbonic acid diester as dispersed oil phase:

A 6% by weight homogenized bentonite suspension is initially prepared from commercial bentonite (non-hydrophobicized) using tapwater and adjusting the pH to a

value of 9.2 to 9.3.

Starting out from this pre-swollen aqueous bentonite phase, the individual components of the water-based carbonic acid diester oil emulsion as identified below are incorporated in successive process steps:

350 g 6% by weight bentonite solution
 1.5 g technical carboxymethyl cellulose, low viscosity
 (Relatin U 300 S 9)
 35 g sodium chloride
 70 g carbonic acid diester oil
 1.7 g emulsifier (sulf. castor oil "turkey red oil")
 219 g barite

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

The plastic viscosity (PV), yield point (YP) and gel strength after 10 secs. and 10 mins. are first determined on the emulsion drilling fluid at 50°C before ageing.

The emulsion drilling fluid is then aged in an autoclave (so-called roller oven) for 16 h at 125°C to test the effect of temperature on the stability of the emulsion. Viscosity is then remeasured at 50°C.

Example 5

The isotridecyl carbonic acid diester of Example 4 is used as the dispersed oil phase. The characteristic data of the material as determined before and after ageing are as follows:

	Before ageing	After ageing
Plastic viscosity (PV)	9	14
Yield point (YP)	38	28
Gel strength (lb/100 ft ²)		

10 secs.	28	21
10 mins.	35	47

Example 6

5 The carbonic acid diester mixture of Example 2 is used as the dispersed oil phase. The characteristic data of the material as determined before and after ageing are as follows:

10		Before ageing	After ageing
	Plastic viscosity (PV)	11	13
	Yield point (YP)	39	28
	Gel strength (lb/100 ft ²)		
15	10 secs.	25	20
	10 mins.	34	39

**CLAIMS**

1. The use of oleophilic diesters of carbonic acid with the same or different oil-soluble and ecologically safe monohydric and optionally polyhydric alcohols as a constituent of oil- or water-based drilling fluids and other flowable borehole servicing formulations.
2. The use claimed in claim 1, characterized in that the oleophilic carbonic acid diesters are used in the oil phase of oil-based drilling fluids, more particularly invert drilling fluids of the w/o type, and are either present as an additive in a concentration of at least about 5% by weight of the continuous oil phase or, preferably, make up at least the predominant part of the oil phase.
3. The use claimed in claim 1, characterized in that the oleophilic carbonic acid diesters are used in water-based emulsion drilling fluids of the o/w type, being present in the dispersed oil phase where they make up at least about 5% by weight of this dispersed phase and preferably at least the predominant part thereof.
4. The use claimed in claims 1 to 3, characterized in that the oleophilic carbonic acid diesters have flash-points of at least 80°C and preferably of at least about 135°C.
5. The use claimed in claims 1 to 4, characterized in that carbonic acid diesters flowable at room temperature are used, the use of carbonic acid diesters with pour/flow points below 0°C and preferably below about -5°C being preferred.
6. The use claimed in claims 1 to 5, characterized by the use of symmetrical or mixed carbonic acid diesters and/or mixtures of different carbonic acid diesters which are derived at least partly from ecologically safe monohydric alcohols containing at least 6 carbon atoms and preferably at least 8 carbon atoms and, optionally,



also contain residues of water-soluble and/or oil-soluble polyhydric alcohols preferably containing 2 to 5 hydroxyl groups and more particularly 2 and/or 3 hydroxyl groups in co-condensed form.

5 7. The use claimed in claims 1 to 6, characterized in that the alcohol residues are derived from toxicologically and, more particularly, inhalation-toxicologically safe compounds, residues of monohydric alcohols containing 8 to 40 carbon atoms and residues of the polyhydric
10 alcohols containing 2 to 40 carbon atoms optionally present being preferred.

8. The use claimed in claims 1 to 7, characterized in that, where monohydric and polyhydric alcohols are used together in the carbonic acid esters, the residues of the
15 polyhydric alcohols form

- hydroxyl-terminated ester groups,
- monohydric alcohol residues chain-extended to form ether groups and/or
- oligocarbonic acid esters in which at least two
20 hydroxyl groups are attached in ester form to different carbonic acid residues.

9. The use claimed in claims 1 to 8, characterized by the use of carbonic acid diesters of which the alcohol residues are free from aromatic molecule constituents and
25 are derived in particular from linear and/or branched, optionally unsaturated hydrocarbon chains of natural and/or synthetic origin.

10. The use claimed in claims 1 to 9, characterized by the use of carbonic acid diesters in conjunction with
30 other ecologically safe water-insoluble oils, preferably corresponding oleophilic alcohols, ethers and/or carboxylic acid ester oils of which the ester-forming alcohol components are derived from monohydric and/or polyhydric alcohols which are preferably selected so that
35 there is no risk of toxicological damage, more particu-



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larly inhalation-toxicological damage, in practice in the event of partial ester hydrolysis.

11. The use claimed in claims 1 to 10, characterized in that the carboxylic acid ester oils used are corresponding
5 esters of monohydric alcohols of natural and/or synthetic origin and of pronounced oleophilic character preferably containing at least 6 carbon atoms and, more particularly, at least 8 carbon atoms.

12. The use claimed in claims 1 to 11, characterized in
10 that, where mixtures of the oleophilic carbonic acid diesters with other soluble oil phases are used, the mixture components used are also selected so that the mixed oil phase has a flashpoint of at least about 100°C and, preferably, above about 135°C.

13. The use claimed in claims 1 to 12 characterized by
15 the use of carbonic acid diesters or mixtures thereof with homogeneously miscible, ecologically safe oils which
- in the case of w/o invert drilling fluids, have solidification values (flow and pour point) in the
20 continuous oil phase below 0°C and preferably below -5°C and a Brookfield RVT viscosity at 0 to 5°C of not more than 55 mPas and preferably not more than 55 mPas

- whereas, in the case of o/w emulsion drilling
25 fluids, the oil phase may have a Brookfield RVT viscosity at 20°C of up to about 2 million mPas and preferably up to about 1 million mPas.

14. The use claimed in claims 1 to 13, characterized in
30 that the homogeneous or dispersed oil phase contains carbonic acid diesters in admixture with carboxylic acid esters from at least one of the following subclasses:

a) esters of C₁₋₅ monocarboxylic acids and monohydric
and/or polyhydric alcohols, residues of monohydric
35 alcohols containing at least 6 and preferably at



least 8 carbon atoms and the polyhydric alcohols preferably containing 2 to 6 carbon atoms in the molecule,

- 5 b) esters of monocarboxylic acids of synthetic and/or natural origin containing 6 to 16 carbon atoms, more particularly esters of corresponding aliphatically saturated monocarboxylic acids, and monohydric and/or polyhydric alcohols of the type mentioned under a),
- 10 c) esters of mono- and/or poly-olefinically unsaturated monocarboxylic acids containing at least 16 carbon atoms and, more particularly, 16 to 24 carbon atoms and, in particular, monohydric linear and/or branched alcohols.

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15. The use claimed in claims 1 to 14, characterized by the use in the oil-based or water-based borehole servicing formulation of auxiliaries and additives which, ecologically and toxicologically, are at least substantially safe, for example are free from soluble toxic heavy metal compounds.

20 16. Borehole servicing formulations flowable and pumpable at temperatures of 5 to 20°C, more particularly drilling fluids based

- 25 - either on a continuous oil phase, optionally in admixture with a limited quantity of a dispersed aqueous phase (w/o invert type)
- or on a dispersed oil phase in a continuous aqueous phase (o/w emulsion type),

30 optionally containing typical auxiliaries in dissolved and/or dispersed form, such as viscosity generators, emulsifiers, fluid loss additives, wetting agents, fine-particle weighting agents, salts, alkali reserves and/or biocides, characterized in that they contain in their oil

35 phase oleophilic carbonic acid diesters based on oil-



soluble and ecologically safe monohydric alcohols and, if desired, water- and/or oil-soluble polyhydric alcohols.

17. Borehole servicing formulations as claimed in claim 16, characterized in that mixtures of the oleophilic carbonic acid diesters with ecologically safe oil mixture components are present in the oil phase and in that the oil phase is based solely on the carbonic acid diesters in the form of symmetrical and/or mixed carbonic acid diesters or mixtures of various carbonic acid diesters.

18. Borehole servicing formulations as claimed in claims 16 and 17, characterized in that the carbonic acid diesters are based on inhalation-toxicologically safe monohydric alcohols containing at least 6 and preferably 8 to 40 carbon atoms which are free from aromatic residues and which are linear and/or branched and may even be at least partly unsaturated, polyhydric alcohols containing in particular 2 to 5 hydroxyl groups and 2 to 40 carbon atoms optionally being used in addition to the monohydric alcohols.

19. Borehole servicing formulations as claimed in claims 16 to 18, characterized in that they contain oligomeric carbonic acid diesters preferably containing 2 or 3 fully esterified carbonic acid residues in the molecule.

20. Borehole servicing formulations as claimed in claims 16 to 19, characterized in that they contain carboxylic acid ester oils, oleophilic alcohols and/or ethers as ecologically safe oil mixture components, the carbonic acid diesters and the oil mixture components having flashpoints above 80°C and preferably above 135°C.

21. Borehole servicing formulations as claimed in claims 16 to 20, characterized in that, where carboxylic acid ester oils are used as mixture component, the monohydric alcohols present in the carboxylic acid ester oil are selected so that inhalation toxicologically safe alcohols are formed in the event of partial ester hydrolysis



occurring in practice.

22. Borehole servicing formulations as claimed in claims 16 to 21, characterized in that the typical auxiliaries and additives used are also selected for their ecological compatibility and, for example, are free from soluble toxic heavy metal compounds.

23. Borehole servicing formulations as claimed in claims 16 to 22, characterized in that they have a pH value in the range from substantially neutral to moderately basic and, in particular, are adjusted to a pH value of about 7.5 to 11.