

DECLARATION IN SUPPORT OF A
CONVENTION APPLICATION FOR A PATENT

In support of the Convention Application made for a
patent for an invention entitled:

D 8714

Title of Invention

Use of Selected Oleophilic Ethers in Water-Based Drilling Fluids of the
O/W Emulsion Type and Corresponding Drilling Fluids with Improved
Ecological Acceptability

Full name(s) and
address(es) of
Declarant(s)

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do solemnly and sincerely declare as follows:-

Full name(s) of
Applicant(s)

1. ~~I am/We are the applicant(s) for the patent~~

(or, in the case of an application by a body corporate)

1. I am/~~We are~~ authorised by

HENKEL KOMMANDITGESELLSCHAFT AUF AKTIEN

the applicant(s) for the patent to make this declaration on
its/~~their~~ behalf.

2. The basic application(s) as defined by Section 141 of the
Act was/~~were~~ made

Basic Country(ies)

in the Federal Republic of Germany

Priority Date(s)

on 20th of May 1989

Basic Applicant(s)

by Henkel Kommanditgesellschaft auf Aktien

Full name(s) and
address(es) of
inventor(s)

~~3. I am/We are the actual inventor(s) of the invention referred
to in the basic application(s)~~

(or where a person other than the inventor is the applicant)

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is/are the actual inventor(s) of the invention and the facts upon
which the applicant(s) is/~~are~~ entitled to make the application are
as follows:

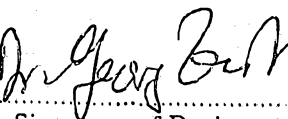
Set out how Applicant(s)
derive title from actual
inventor(s) e.g. The
Applicant(s) is/are the
assignee(s) of the
invention from the
inventor(s)

Henkel Kommanditgesellschaft auf Aktien is entitled by Contract of Employment
between the inventors, Heinz Müller, Claus-Peter Herold, Stephan von
Tapavicza, Gerhard Stoll and Rainer Jeschke as employees and Henkel
Kommanditgesellschaft auf Aktien as employer, as a person who would be
entitled to have the patent assigned to it if a patent were granted upon
an application made by the inventors, and the said applicant is the
assignee of the inventor, Johann Friedrich Fues.

4. The basic application(s) referred to in paragraph 2 of this
Declaration was/~~were~~ the first application(s) made in a Convention
country in respect of the invention(s) the subject of the application.

Declared at Langenfeld, this 30th day of July 19 91

To: The Commissioner of Patents



Signature of Declarant(s)

Dr. Georg Zeit

1/81

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USE OF SELECTED OLEOPHILIC ETHERS IN WATER-BASED DRILLING FLUIDS OF THE O/W EMULSION TYPE AND CORRESPONDING DRILLING FLUIDS WITH IMPROVED ECOLOGICAL ACCEPTABILITY
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- (56) Prior Art Documents
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- (57) Claim

1. A water-based oil in water emulsion drilling fluid suitable for the environmentally friendly development of geological formations comprising an aqueous phase, a dispersed oil phase comprising substantially water-insoluble ethers which are fluid or at least plastically deformable at working temperature, have flash points of at least 80°C and are derived from mono- and/or polyfunctional alcohols of natural and/or synthetic origin or solutions of said ethers with ecologically acceptable water-insoluble oils and if desired, insoluble, finely particulate weighting agents and/or further additives.

2. A drilling fluid according to claim 1 wherein said oil phase comprises at least about 5% by weight, based on the sum of oil and water, of said fluid.

19. A drilling fluid according to any one of claims 1 to 14, wherein said ethers are polyalkylene glycol-(mixed)-ethers.

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(21) Internationales Aktenzeichen: PCT/EP90/00732 (22) Internationales Anmeldedatum: 7. Mai 1990 (07.05.90) (30) Prioritätsdaten: P 39 16 550.7 20. Mai 1989 (20.05.89) DE (71) Anmelder (für alle Bestimmungsstaaten ausser US): HENKEL KOMMANDITGESELLSCHAFT AUF AKTIEN [DE/DE]; TFP-Patentabteilung, Henkelstraße 67, D-4000 Düsseldorf 13 (DE). (72) Erfinder; und (75) Erfinder/Anmelder (nur für US): MÜLLER, Heinz [DE/DE]; Goldregenweg 4, D-4019 Monheim (DE). HEROLD, Claus-Peter [DE/DE]; Ostpreußenstraße 26, D-4020 Mettmann (DE). VON TAPAVIZCA, Stephan [DE/DE]; Thomas-Mann-Straße 12, D-4006 Erkrath 2 (DE). STOLL, Gerhard [DE/DE]; Danziger Straße 69, D-4052 Korschenbroich 1 (DE). JESCHKE, Rainer [DE/DE]; Am Broichgraben 52, D-4000 Düsseldorf 13 (DE). FUES, Johann, Friedrich [DE/DE]; Herzogstraße 15, D-4048 Grevenbroich 5 (DE).	(81) Bestimmungsstaaten: AT (europäisches Patent), AU, BE (europäisches Patent), BR, CA, CH (europäisches Patent), DE (europäisches Patent)*, DK (europäisches Patent), ES (europäisches Patent), FR (europäisches Patent), GB (europäisches Patent), IT (europäisches Patent), JP, LU (europäisches Patent), NL (europäisches Patent), NO, SE (europäisches Patent), SU, US. Veröffentlicht <i>Mit internationalem Recherchenbericht.</i>	
(54) Title: USE OF SELECTED OLEOPHILIC ETHERS IN WATER-BASED DRILLING FLUIDS OF THE O/W EMULSION TYPE AND CORRESPONDING DRILLING FLUIDS WITH IMPROVED ECOLOGICAL ACCEPTABILITY (54) Bezeichnung: VERWENDUNG AUSGEWÄHLTER OLEOPHILER ETHER IN WASSER-BASIERTEN BOHRSPÜLUNGEN VOM O/W-EMULSIONSTYP SOWIE ENTSPRECHENDE BOHRSPÜLFLÜSSIGKEITEN MIT VERBESSERTER ÖKOLOGISCHER VERTRÄGLICHKEIT (57) Abstract The description relates to the use of at least largely water-insoluble ethers of mono and/or polyfunctional natural or synthetic alcohols which are liquid and/or at least plastically deformable at working temperature and have flash-points of at least 80°C, or corresponding solutions of such ethers in ecologically acceptable water-insoluble oils as the dispersed oil phase of water-based O/W emulsion drilling fluids which are suitable for the environmentally acceptable exploitation of geological formations and may, if desired, contain insoluble, finely divided fillers for producing water-based O/W emulsion drilling muds and/or further additives like emulsifiers, fluid-loss additives, wetting agents, alkaline reserves and/or aids for the inhibition of highly water-sensitive drilled rock. (57) Zusammenfassung Beschrieben wird die Verwendung von wenigstens weitgehend wasserunlöslichen, bei Arbeitstemperatur flüssigen und/oder wenigstens plastisch verformbaren und Flammpunkte von wenigstens 80°C aufweisenden Ethern ein- und/oder multifunktionaler Alkohole natürlichen und/oder synthetischen Ursprungs oder entsprechenden Lösungen solcher Ether in ökologisch verträglichen wasserunlöslichen Ölen als disperse Ölphase von Wasser-basierten O/W-Emulsions-Bohrerspülungen, die für eine umweltschonende Erschließung geologischer Formationen geeignet sind und dabei gewünschtenfalls unlösliche, feinteilige Beschwerungsmittel zur Ausbildung von Wasser-basierten O/W-Emulsionsbohrschlämmen und/oder weitere Zusatzstoffe wie Emulgatoren, Fluid-Loss-Additive, Netzmittel, Alkalireserven und/oder Hilfsstoffe zur Inhibierung erbohrten Gesteins erhöhter Wasserempfindlichkeit enthalten.		

Use of selected oleophilic ethers in water-based drilling fluids of the O/W-emulsion type and corresponding drilling fluids with improved ecological acceptability

The invention discloses new drilling fluids based on water-based O/W-emulsions and O/W-emulsion drilling muds based thereon, which are distinguished by high ecological acceptability with at the same time good standing and application properties. An important area of use for the new drilling mud systems is in off-shore wells for the development of petroleum and/or natural gas deposits, the aim of the invention being particularly to make available technically usable drilling fluids with high ecological acceptability. The use of the new drilling mud systems admittedly has particular significance in the marine environment, but is not limited thereto. The new mud systems can also be put to quite general use in land-based drilling, i.e. also serve for the development of petroleum and/or natural gas deposits here. They are, however, new valuable working agents, for example, also in geothermal wells, in water bore-holes, in the drilling of geoscientific bores and in drilling for the mining industry. It is also essentially true here that the associated ecotoxic problems are substantially simplified by the new water-based O/W-drilling fluids selected according to the invention.

The Prior Art

Liquid mud systems used in the sinking of rock bores for bringing up the loosened drill cuttings are known to be flowable systems, thickened to a limited extent, which can be assigned to one of the three following classes:

Purely aqueous drilling fluids; drilling mud systems based on oil, which as a rule are used in the form of so-called invert emulsion muds, and represent preparations of the W/O-emulsion type in which the aqueous phase is distributed as a heterogeneous fine dispersion in the continuous oil phase. The third class of the known drilling fluids is composed of water-based O/W-emulsions, i.e. fluid systems which contain a heterogeneous, finely-dispersed oil phase in a continuous aqueous phase. The invention discloses improved systems of this latter type.



The application properties of the drilling fluids of such O/W-emulsion systems take an intermediate position between those of the purely aqueous systems and those of the oil-based invert fluids. The advantages, but also the disadvantages, of the purely aqueous systems are connected with the advantages and disadvantages of the oil-based invert-emulsions disclosed hitherto. Detailed information on this subject can be found in the relevant specialist literature, refer, for example, to the text book by George R. Gray and H.C.H. Darley, "Composition and Properties of Oil Well Drilling Fluids", 4th. edition, 1980/1981, Gulf Publishing Company, Houston, and the extensive specialist and patent literature cited therein and to the manual "Applied Drilling Engineering", Adam T. Bourgoyne, Jr. et al., First Printing Society of Petroleum Engineers, Richardson, Texas (USA).

One of the main weaknesses of purely water-based drilling mud systems lies in the interaction of water-sensitive, particularly water-swelling, rock and/or salt formations with the aqueous drilling fluid and the secondary effects initiated thereby, in particular bore-hole instability and thickening of the drilling fluid. Many proposals are concerned with the reduction of this problem area and have, for example, resulted in the development of the so-called inhibitive water-based muds, cf. for example, "Applied Drilling Engineering", loc. cit., Chapter 2, Drilling Fluids, 2.4 and Gray and Darley loc. cit., Chapter 2, in particular the sub-section on pages 50 to 62 (Muds for "Heaving Shale", Muds for Deep Holes, Non-Dispersed Polymer Mud, Inhibited Mud: Potassium Compounds).

In more recent practice, in particular drilling fluids based on oil, which consist of the 3-phase system oil, water and finely particulate solids and are preparations of the W/O-emulsion type, have succeeded in overcoming the difficulties described above. Oil-based drilling fluids were originally based on diesel oil fractions containing aromatics. For detoxification and to reduce the ecological problems created thereby, it was then proposed to use hydrocarbon fractions which are largely free of aromatics - now also known as "non-polluting oils" - as the continuous oil phase, see in this regard, for example, the publications by E.A. Boyd et al. "New Base Oil Used in Low Toxicity Oil Mud", Journal of Petroleum Technology, 1985, 137 - 143 and R.B.



Bennet "New Drilling Fluid Technology - Mineral Oil Mud", Journal of Petroleum Technology, 1984, 975 - 981 and the literature cited therein.

Drilling fluids of the water-based O/W-emulsion system type have also hitherto used pure hydrocarbon oils as the dispersed oil phase, cf. here, for example, Gray, Darley loc. cit., p. 51/52 under the section "Oil Emulsion Muds" and the tabular summary on p. 25 (Tables 1-3) with details of water-based emulsion fluids of the salt-water mud, lime mud, gyp mud and CL-CLS mud type.

In this context in particular it is known that water-based O/W-emulsion fluids represent a substantial improvement in many regards to the purely water-based drilling mud systems. Particularly in more recent times, however, the advantages and disadvantages of such water-based emulsion fluids have also been examined critically in comparison with the oil-based invert-systems. This is due to the considerable ecological reservations felt towards the oil-based invert drilling fluids commonly used today.

These ecological reservations can be subdivided into two problem areas:

In addition to the basic constituents, i.e. oil and water, all drilling fluid systems based on water and/or oil require a large number of additives for the establishment of the desired application properties. The following can be mentioned here purely by way of example: emulsifiers or emulsifier systems, weighting agents, fluid-loss additives, wetting agents, alkali reserves, viscosity regulators, in some cases auxiliary agents for the inhibition of drilled rock with high water-sensitivity, biocides and the like. A detailed summary can be found, for example, in Gray and Darley, loc. cit., Chapter 11, "Drilling Fluid Components". The industry has developed additives which currently appear ecologically harmless, but also additives which are ecologically questionable or even ecologically undesirable.

The second problem area is caused by the oil phases used in such drilling fluids. Even the hydrocarbon fractions which are largely free from aromatics, currently known as "non-polluting oils", are not completely harmless when released into the environment. A further



reduction in the environmental problems, which are caused by the fluid oil phases of the type referred to here, appears urgently necessary. This is true in particular for the sinking of off-shore wells, e.g., for the development of petroleum or natural gas deposits, because the marine eco-system reacts particularly sensitively to the introduction of toxic and poorly degradable substances.

There have recently been some proposals for reducing these latter problems. For example, the US Patent Specifications 4,374,737 and 4,481,121 disclose oil-based invert-drilling fluids in which non-polluting oils are to be used. The following can be mentioned together as of equal value as non-polluting oils: mineral oil fractions which are free from aromatics, and vegetable oils, such as groundnut oil, soybean oil, linseed oil, corn oil, rice oil or even oils of animal origin, such as whale oil. These named ester oils of vegetable and animal origin are all, without exception, triglycerides of natural fatty acids, which are known to have high environmental acceptability and are clearly superior from the ecological point of view to hydrocarbon fractions - even when these do not contain aromatic hydrocarbons.

In the above US Patent Specifications, however, not one concrete example describes the use of such natural ester oils in invert drilling fluids. Without exception, mineral oil fractions are used as the continuous oil-phase. In fact, oils of vegetable and/or animal origin of the type mentioned here are not considered for invert drilling fluids for practical reasons. The rheological properties of such oil phases cannot be controlled over the wide temperature range generally required in practice, from 0 to 5°C on the one hand, up to 250°C and more on the other.

The Applicant's earlier proposals

A series of earlier Applications by the Applicant describes the use of easily biodegradable and ecologically harmless ester oils as the continuous oil phase in W/O-invert drilling mud systems. Refer here in particular to the earlier Australian Patent Applications Nos. 46551/89 and 49549/89 (D 8523 and D 8524) and the modifications of the ester oils that can be



used according to the details of the earlier Australian Patent Applications 51823/90 and 51802/90.

The subject of these earlier Applications is the use of ester oils based on
5 selected monocarboxylic acids and monocarboxylic acid mixtures and
monofunctional and optionally polyfunctional alcohols as the continuous oil
phase in W/O-invert systems. The earlier Applications show that, using the
esters and ester mixtures disclosed therein, not only can satisfactory
rheological properties be established in the fresh drilling fluid, but it is also
10 possible by the additional use of selected, known alkali reserves in the drilling
fluid, for work to be carried out without fearing undesired thickening effects
when there is a partial ester hydrolysis.

An important further development of such invert drilling fluids based on ester
15 oils is the subject of the Applicant's earlier Australian Patent Application No.
49579/90.

The teaching of this earlier Application starts with the concept of also using a
further additive in invert drilling fluids based on ester oils which is suitable for
20 keeping the desired rheological data of the drilling fluid in the required range,
even when in practice larger and larger amounts of free carboxylic acids are
formed by partial ester hydrolysis. The Application provides for the additional
use of basic amine compounds which are capable of forming salts with
carboxylic acids and have a marked oleophilic nature and at most limited
25 water-solubility, as additives in the oil phase.

A modified form of such W/O-invert drilling mud systems is disclosed in the
Applicant's earlier Australian Patent Application 5344/90 which discloses the
use of:

- 30
- a) at least largely water-insoluble mono- and/or polyfunctional alcohols of
natural and/or synthetic origin which are fluid and pumpable in the
temperature range of 0 to 5°C
 - or of
 - 35 b) solutions, which are fluid and pumpable in the given temperature range,
of at least largely water-insoluble mono- and/or



- polyfunctional alcohols of natural and/or synthetic origin in ecologically acceptable water-insoluble oils as the continuous oil phase of drilling fluids which exist in W/O-emulsion form and in the alcohol-containing oil phase have a dispersed aqueous phase and also, if desired, further conventional additives. Ester oils are provided, at least in part, as the ecologically acceptable, water-insoluble oils for admixture with the water-insoluble alcohols, such as described in the aforementioned earlier Applications of the Applicant.
- 10 The Applicant's earlier Australian Patent Application No. 53308/90, finally, discloses the use of water-insoluble ethers having flash points above 80°C of monohydric alcohols of natural and/or synthetic origin with at least 4 carbon atoms, preferably at least 6 carbon atoms, in the alcohol radicals as the oil phase or a constituent of the oil phase of such invert drilling fluids as exist in W/O-emulsion form. The additional use of the aforementioned ester oils for admixture with the ethers is also provided here.

The invention problem and its technical solution

- 20 The present invention starts with the problem of providing drilling mud systems of the highest, and in this form previously unknown, ecological acceptability which simultaneously have good application properties and which also in particular enable satisfactory application even in problem areas. In the invention a conscious decision has therefore been made to reject the oil-based type of invert drilling mud systems and to return to the oil-modified water-based type of O/W-emulsion systems. At the same time, however, the auxiliary agents described in the cited earlier Applications of the Applicant, and the ecological advantages herewith, are now also to be used in this class of drilling mud systems.
- 30 In a first embodiment of the present invention there is provided a water-based oil in water emulsion drilling fluid suitable for the environmentally friendly development of geological formations comprising an aqueous phase, a dispersed oil phase comprising substantially water-insoluble ethers which are fluid or at least plastically deformable at working temperature, have flash points of at least 80°C and are derived from mono- and/or polyfunctional alcohols of natural and/or synthetic origin or solutions of said ethers with ecologically acceptable water-insoluble oils and if desired, insoluble, finely particulate weighting agents and/or further additives.

~~partially with ecologically harmless ethers of marked oleophilic character.~~

In a further approach, the invention aims also to reduce the ecological concerns of the second problem area, i.e. that associated with the additives and auxiliary agents in drilling fluids, by selecting from the wide range of additives known in this field, at least to a large extent and preferably in all cases, those auxiliary agents which are distinguished by their ecologically harmless nature.

The subject of the invention is accordingly in a first embodiment the use of at least largely water-insoluble ethers, which are fluid and/or at least plastically deformable at working temperature and have flash points of at least 80°C, of mono- and/or polyfunctional alcohols of natural and/or synthetic origin or corresponding solutions of such ethers in ecologically acceptable water-insoluble oils as the dispersed oil phase of water-based O/W-emulsion drilling fluids, which are suitable for an environmentally friendly development of geological formations, and, if desired, contain insoluble, finely particulate weighting agents for the formation of water-based O/W-emulsion drilling muds and/or further additives, such as emulsifiers, fluid-loss additives, wetting agents, alkali reserves and/or auxiliary substances for the inhibition of drilled rock with high water-sensitivity.

In a further embodiment, the invention relates to water-based O/W-emulsion drilling fluids, which in a homogeneous aqueous phase contain, in stable dispersion, an oil phase in amounts of about 5 to 50 % by weight - the percentage by weight referred to the sum of the unweighted water phase and oil phase - together, if required, with dissolved and/or dispersed auxiliary substances such as emulsifiers, fluid-loss additives, wetting agents, finely particulate weighting agents, salts, alkali reserves and/or biocides and are characterized in that at least a substantial part of the dispersed oil phase is formed by water-dispersible ethers which are fluid or at least plastically deformable at working temperature, and have flash points of at least 80°C, from mono- and/or polyfunctional alcohols of natural and synthetic origin or corresponding solutions of such ethers in ecologically acceptable, water-insoluble oils, in particular oleophilic, mono- and/or polyhydric



alcohols and/or corresponding ester oils.

Both embodiments of the teaching according to the invention include the additional preferred step of also using for the water-based emulsion drilling fluids or emulsion drilling muds, at least to a large extent, those inorganic and/or organic auxiliary and loading substances which are at least predominantly ecologically and toxicologically harmless. Thus, for example, in the most important embodiments of the invention the use of auxiliary agents based on soluble, toxic heavy-metal compounds is avoided.

The preferred embodiments of the invention

The mixture ratios of the ether-oil/water phases cover the usual range for the previously known O/W-emulsion drilling fluids based on mineral oils. The lower limit values for the oil phase are usually at least about 5 % by weight, or preferably between about 5 and 10 % by weight, e.g., therefore 7 or 8 % by weight - each percentage by weight referred to the total weight of the fluid phases oil + water, each in the unweighted state. Minimum amounts of the order given ensure that use can be made of the characteristic peculiarities of an O/W-emulsion fluid. The upper limit value for the oil content is usually about 50 % by weight or even slightly higher, e.g., a maximum of about 65 % by weight. Assuming that the droplet size of the dispersed oil phase is sufficiently even, the range with the most dense packing is therefore already achieved, and thus conversion into the fluid type of the W/O-invert fluids is obvious or appears logical.

The upper limit for the content of dispersed oil phase in the O/W-fluids according to the invention is generally determined by cost/benefit considerations and is, for example, about 45 % by weight, preferably less, e.g., about 40 % by weight.

An ether content of about 10 to 40 % by weight - percentage by weight calculated as before - and in particular amounts of the ether phase of about 15 to 35 % by weight give the possibility of exploiting many - known and not previously described - advantages of such emulsion fluids. Oil contents of, for example, 20 % by weight, or in an extreme



case, 30 % by weight provide the basis for high-quality drilling fluids which at least come very close in the way they function to the oil-based invert fluids, but require very much less ether phase.

The various embodiments of the invention

In a first embodiment the dispersed oil phase of the water-based O/W-drilling fluids is formed exclusively, or to much the largest part, by the essentially water-insoluble and preferably markedly oleophilic ethers. The rheology of the ethers used is adapted here to the technical requirements of the drilling fluids, slight rheological corrections are possible by adding the small quantities of thinners provided in this embodiment. In the case described here, consideration can be given in particular to dispersed oil phases which are formed to more than 70 % by weight, preferably to more than 80 % by weight and, if required, exclusively by the ethers themselves.

The oil-mixture components optionally added in small amounts in this embodiment can be pure hydrocarbon compounds, particularly those free from aromatics, but in particular selected ester oils and/or oleophilic alcohols of the type described in the above earlier Applications of the Applicant. This embodiment will be discussed in more detail below.

A second embodiment of the invention relates to the use of dispersed oil-phases in systems of the type referred to here, which have considerable or even predominant amounts of non-water-miscible oils, which are not identical with the oleophilic ethers, but are present in admixture with them.

In this embodiment, the content of the ethers selected according to the invention in the dispersed oil phase is in the region of at least about 10 % by weight to about 70 % by weight - each referred to the fluid oil phase - in which ether proportions can be preferred in quantities of at least about 35 % by weight, and preferably at least about 50 % by weight, of the oil phase. Ecologically harmless ester oils of the type to be described in detail below are preferred mixture components of this second embodiment also. The additional use of pure hydrocarbon oils is not, however, excluded.



The ethers of marked oleophilic character used according to the invention

The use of ethers as the oil phase, but also their combined use in smaller or larger amounts in the oil phase, requires that these ethers are sufficiently insoluble in water. The water-solubility of suitable ethers at room temperature is preferably less than 1 % by weight and preferably not more than about 0.5 % by weight.

The following general rules apply for the chemical nature of the ethers: Ethers of monofunctional and/or polyfunctional alcohols are suitable. In particular, besides the ethers of monofunctional alcohols, those of difunctional and monofunctional alcohols can be considered. The alcohols themselves should be ecologically acceptable and thus should have no aromatic constituents in the preferred embodiment. The preferred ether-forming compounds are straight-chain and/or branched aliphatic, or also corresponding unsaturated, in particular mono- and/or poly-olefin-unsaturated alcohols. Cycloaliphatic alcohols or ether can be considered.

An important general requirement in the sense of the treatment according to the invention is that these alcohols or ethers as such are not only ecologically acceptable, but also do not cause any other toxicological hazards, particularly when inhaled.

From the wide range of suitable ethers, preferably based at least partly on markedly oleophilic alcohols, in particular those ethers can be considered of alcohols with a straight-chain and/or branched hydrocarbon structure. From the group of corresponding monofunctional alcohols, corresponding compounds with at least 5, preferably at least 6 or 7 carbon atoms are suitable compounds, with corresponding alcohols with at least 8 carbon atoms in the molecule being particularly usable. The upper limit for the number of carbon atoms is determined by technical accessibility and is, for example, in the region of about 36, preferably about 20 to 24. The ether-forming alcohols themselves can be straight-chain and/or branched, they can be aliphatic-saturated or also mono- and/or poly-olefin-unsaturated.



Essentially, ethers from alcohols of natural and/or synthetic origin are suitable. In particular, the synthetic alcohols of the range of about 8 to 24 carbon atoms, which is of particular interest here, which can also contain unsaturated parts, are frequently low-cost components which are available commercially and can be used for the purposes of the invention.

The ethers themselves should have flash points of at least 80°C, preferably of at least 100°C and in particular of at least 120°C. As well as the named ethers based on monofunctional alcohols with preferably at least 8 carbon atoms, ethers of selected polyols can also be considered here. Suitable polyols for the formation of the esters are in particular lower diols, such as ethylene glycol and/or the propylene glycols, but also in some cases branched-chain diols with a higher oleophilic hydrocarbon radical in the molecule. For example, oleophilic diols are suitable with hydroxyl groups in the alpha,omega position and/or longer chain diols, which have their hydroxyl groups on adjacent carbon atoms. Typical examples of compounds of this type are 2,2-dimethyl-1,3-propanediol (neopentyl glycol) or the saponification products of epoxidized olefins.

The mixture components in the dispersed oil-phase

Suitable oil components for the admixture according to the invention are the mineral oils currently used in practice in drilling fluids, and preferably the aliphatic and/or cycloaliphatic hydrocarbon fractions which are essentially free from aromatics. Refer here to the relevant prior-art publications and the commercial products available on the market.

Particularly important mixture components are, however, oleophilic alcohols and/or ester oils which are ecologically acceptable in the sense of the invention, and to which the following general considerations here immediately apply:

The alcohols or ester oils should be fluid at ambient temperature, but also under the conditions of use, with the range of materials thought



to be fluid, however, also including materials which are at least plastically deformable at ambient temperature and which soften to become fluid at the usually elevated working temperatures. For reasons of easier processability in practice, alcohols and ester oils with solidification values (pour point and setting point) below 10°C and usefully below 0°C are preferred. Corresponding compounds with solidification values not above -5°C can be particularly suitable. One should take into account here the fact that the drilling fluids are usually produced on site using, for example, sea water at comparatively low water-temperatures.

For reasons of operational safety, it must be a requirement that the additives have flash points of at least 80°C, however, higher flash points of at least 100°C and substantially higher values are preferred, for example, those above 150 or 160 °C.

A further important requirement for the optimal employment of the subject of the invention is that these alcohols and/or ester oils should have a biologically or ecologically acceptable constitution, i.e. in particular that they are free from undesired toxic constituents. In the preferred embodiment of the invention, alcohols and/or ester oils are accordingly used which are free from aromatic constituents and in particular have saturated and/or olefin-unsaturated, straight-chain and/or branched hydrocarbon chains. The use of components containing cycloaliphatic structural constituents is possible from the ecological point of view, but for reasons of cost will be of little significance in practice.

Carboxylic acid esters of the type in question here are subject to a limited degree, as the highly dispersed oil-phase in a continuous aqueous phase, to hydrolytic ester-cleavage with liberation of the ester-forming constituents, i.e. carboxylic acid and alcohol. Two closely linked issues should be taken into account as regards the application properties of the ester oils in the sense of the invention, namely considerations of the possible toxicity of the liberated components, in particular of the alcohol components, when inhaled and also any change in the composition of the emulsion fluid and associated change which may take place in its application properties.



For comprehension of the teaching according to the invention, these considerations should be examined separately for each of the ester-forming basic constituents - on the one hand the alcohols and on the other the carboxylic acids.

According to the invention, both monohydric alcohols and polyhydric alcohols are suitable as the ester-forming alcohol components, and any mixtures of these types can also be used. A further distinction can be made between alcohols according to their solubility behavior in water. Alcohols can be water-soluble and/or water-insoluble.

In a first group, polyhydric alcohols are to be considered. Particularly preferred here are the industrially easily available lower, polyfunctional alcohols with 2 to 5, preferably 2 to 4 hydroxyl groups and in particular 2 to 6 carbon atoms, which form esters of suitable rheology.

Typical representatives are ethylene glycol, the propanediols and particularly glycerin.

Polyhydric alcohols of the type referred to here are distinguished by high water-solubility and at the same time by such low volatilization values that considerations of the exclusion of toxic hazards when inhaled do not usually apply.

Polyhydric lower alcohols of the type referred to here can be used as totally esterified oil components and/or as partial esters with some free hydroxyl groups and/or can be formed in the practical use of the emulsion fluid according to the invention. Provided that the partial esters formed retain the at least largely water-insoluble character of the oil phase, no substantial change takes place in the oil/water ratio in the emulsion fluid. The situation only becomes different when water-soluble hydrolysis products form - in particular therefore the free lower polyhydric alcohols. The changes which occur in practical operation in such emulsion fluids as a result of this process are, however, insignificant. Firstly, a comparatively high stability of the ester bond is ensured under the working conditions according to the



invention. O/W-emulsion fluids are known usually to operate in the pH-range of approx. neutral to moderately alkaline, for example, in the pH-range of about 7.2 to 11 and in particular about 7.5 to 10.5, and thus for these reasons alone there is no aggressive hydrolytic attack on the ester bond. In addition, and moreover, the following is in particular also true:

In the practical use of the drilling fluid, and the associated driving forward of the bore into ever deeper earth strata, a continual consumption of the drilling fluid and, in particular of the oil-phase used in the drilling fluid takes place. Emulsion fluids are known - and this is an important advantage of their use - for the fact that the emulsified oil phase clings on to solid surfaces and therefore both seals the filter bed to the wall of the bore-shaft and hinders, or even prevents, interaction between the drilled rock and the aqueous phase of the drilling fluid. This continual consumption of drilling fluid, and in particular of the oil-phase, necessitates a continual supply of oil-based mud. In practical operation, a state of equilibrium is therefore rapidly established in the drilling fluid which governs and makes possible continuous operation for long periods of time.

The above considerations, naturally, are only important in the context of the present invention when not inconsiderable amounts of the dispersed oil phase are formed by the ester oils also used. The oleophilic ethers and their admixture with hydrolysis-resistant mixture constituents are not affected by such additional considerations and so that largely, or even completely, dispensing with ester oils can be regarded as an important and preferred embodiment of the use of the invention.

From some viewpoints, further considerations should be taken into account when monohydric alcohols are used as the ester-forming constituent of the ester oils. Here only the lower members of these alcohols are water-soluble or, in an unlimited quantity, water-miscible. However, their volatility can also be regarded as an important consideration in the case of these alcohols. In the practical operation of drilling work, at least moderately increased temperatures are rapidly established in the circulated drilling fluid



and therefore the parts exposed by the pumping to remove the drill cuttings have a temperature, for example, in the region of 50 to 70 °C. Considerations of toxicological effects when inhaled must therefore be taken into account here. Even C₄-alcohols, e.g., isobutyl alcohol, can be so volatile under the operating conditions on the drilling platform that possible hazards to personnel must be taken into account. According to the invention, therefore, when ester oils are employed together with monohydric alcohols, the lower carbon number limit for these monohydric alcohols is preferably selected as 6, and working with esters of monofunctional alcohols with at least 8 carbon atoms can be particularly preferred.

The selection and limitation of the carbon number in the ester-forming alcohol, however, at the same time has the following result as regards the composition of the ester-oil phase when there is a partial hydrolysis during operation: The hydrolyzing parts of such ester oils are converted to the free alcohol which remains as a practically water-insoluble mixture constituent in the dispersed ester-oil phase.

A number of points must also be considered with regard to the carboxylic acids formed by the partial hydrolysis of the related ester oils.

Here it is possible, depending on the specific constitution of the carboxylic acids used, to distinguish two basic types - with a smooth transition between the two: carboxylic acids which give rise to carboxylic acid salts with an emulsifier effect, and those which give rise to inert salts.

The respective chain-length of the liberated carboxylic acid molecule is particularly decisive here. Further, the salt-forming cation usually present in the alkali reserves of the drilling fluid should also be taken into consideration.

In general the following rules apply here: Lower carboxylic acids, for example those with 1 to 5 carbon atoms, give rise to the formation of inert salts, for example, the formation of corresponding acetates or propionates. Fatty acids of higher chain-length and in particular



those with from 12 to 24 carbon atoms result in compounds with an emulsifier effect.

It is therefore possible, by selecting suitable ester oils - and to a certain extent also the salt-forming cations in the emulsion fluid - to control specifically the secondary products in the emulsion fluid, which can have considerable influence on the nature and effect of the emulsion fluid. What has been said above, again applies here: It is not only the dispersed organic phase, but also the aqueous phase, which is subject to continual consumption in practice and thus requires replacement. In stationary operation, therefore, controllable states of equilibrium will rapidly be established, even as regards the reaction by-products based on the ester-forming carboxylic acids as discussed here.

General details for the definition of ester oils suitable as mixture components

In the sense of the invention, the corresponding reaction products of monocarboxylic acids with monofunctional and/or polyfunctional alcohols of the type indicated are preferred as the ester oils. The additional use of polyvalent carboxylic acids is not, however, excluded, but they are of less significance, in particular for reasons of cost.

The carboxylic acids here can be of natural and/or synthetic origin, they are, as already indicated, preferably straight-chain and/or branched and optionally cyclic, but not aromatic in structure. The ester-forming carboxylic acids can be saturated and/or unsaturated, with unsaturated compounds here being understood, in particular, to be olefin-unsaturated compounds, which can be either mono- or poly-olefin-unsaturated. Olefin-unsaturated components can be of particular importance for setting the predetermined rheology values. It is known that olefinic longer-chain compounds are suitable as corresponding saturated components for the formation of esters with lower melting points.

The preferred range for the carbon number of the carboxylic acids extends from 1 to 36 and in particular from 2 to 36. For reasons of



easy availability, an upper limit for the carbon number can be about 22 to 24. The respective chain length of the ester-forming carboxylic acid components is selected - depending on the nature of the alcohols component(s) used - by consideration of the numerous issues already discussed, and refers not only, 5 for example, to the ester and/or its rheology directly, but also to the reaction by-products formed in particular by partial hydrolysis.

Suitable alcohols are, as indicated, both monofunctional alcohols - provided the above limitations are taken into consideration - and polyfunctional alcohols, 10 particularly lower polyfunctional alcohols with 2 to 6 carbon atoms and preferably with a maximum of 4 hydroxyl groups.

The alcohol components here can also be of natural and/or synthetic origin, they are straight-chain or branched and in particular in the case of the 15 monofunctional alcohols are saturated and/or also olefin-unsaturated. Monofunctional alcohols have in particular up to 36 carbon atoms, preferably up to about 24 carbon atoms. Alcohols with 6 to 18, in particular 7 to 15 carbon atoms, of natural and/or synthetic origin can only be of particular significance in the formation of the ester oils.

20 Particularly important ester oils in the sense of the use in the invention are the ecologically-acceptable ester oils as described in particular in the cited earlier Australian Patent Applications Nos. 46551/89, 49549/89, 51823/90 and 51802/90. To complete the invention disclosure, the essential characteristics 25 of these ester oils or ester mixtures are briefly summarized below.

The dispersed ester-oil phase accordingly contains carboxylic acid esters from at least one of the following sub-classes:

- 30 a) Esters from C_{1-5} -monocarboxylic acids and mono- and/or polyfunctional alcohols, in which radicals from monohydric alcohols have at least 6, preferably at least 8 carbon atoms, and the polyhydric alcohols preferably have 2 to 6 carbon atoms in the

35



molecule,

- b) esters from monocarboxylic acids of synthetic and/or natural origin with 6 to 16 carbon atoms, in particular esters of corresponding aliphatic-saturated monocarboxylic acids and mono- and/or polyfunctional alcohols of the type indicated under a),
- c) esters of olefin mono- and/or poly-unsaturated monocarboxylic acids with at least 16, in particular 16 to 24 carbon atoms, and in particular monofunctional straight-chain and/or branched alcohols.

The latter esters of olefin mono- and/or poly-unsaturated monocarboxylic acids with at least 16 carbon atoms (c) are preferably assigned to at least one of the following sub-classes:

- c1) esters which are derived by more than 45 % by weight, preferably by more than 55 % by weight from di- and/or poly-olefin-unsaturated C₁₆₋₂₄-monocarboxylic acids,
- c2) esters which are derived by not more than 35 % by weight from di- and poly-olefin-unsaturated acids, and are preferably at least about 60 % by weight mono-olefin-unsaturated.

The raw materials for obtaining many of the monocarboxylic acids in these sub-classes, in particular those with a higher carbon number, are vegetable and/or animal oils. Coconut oil, palm kernel oil and/or babassu oil, can be mentioned in particular as materials used for obtaining monocarboxylic acids mainly in the range with up to 18 carbon atoms, and with essentially saturated components. Examples of vegetable ester oils, in particular for olefin mono- and optionally poly-unsaturated carboxylic acids with from 16 to 24 carbon atoms, are palm oil, groundnut oil, castor oil and in particular colza oil. Carboxylic acids of animal origin of this type are in particular corresponding mixtures of fish oils, such as herring oil.

The teaching of the invention expressly includes also and in particular the use of monocarboxylic-acid triglycerides and therefore in particular also the use of corresponding glyceride oils of natural origin. Here, however, the following must be considered: Natural oils



and fats usually occur in a form so highly contaminated, for example, with free carboxylic acids or other accompanying substances, that there is as a rule no question of immediately processing them in O/W-emulsion fluids of the type referred to here. If such natural feed materials are added in the commercially available form to water-based drilling fluids, then almost immediately, such a large amount of foam forms in the drilling fluid being used as to constitute a serious hindrance or even to result in the drilling fluid becoming unusable. This may not be the case if cleaned and/or synthetically produced selected triglycerides are used in the dispersed oil phase. The teaching according to the invention can be realized without exception with these. In principle, however, with such esters of high-grade alcohols one must always anticipate a not inconsiderable tendency to foam formation. Partial esters of glycerin - the mono- or di-glycerides - are known to be effective emulsifier components.

As already indicated, it is not only the comparatively thin-bodied ester oils as in the disclosure of the cited earlier Applications of the Applicant in the field of invert drilling fluids based on ester-oils, which are suitable for the purposes of the invention, but within the framework of O/W-emulsion fluids, in particular comparatively viscous ester oils can be of advantage as components of the dispersed phase. They are, for example, valuable auxiliary agents for sealing the finest pores in the filter cake of the bore shaft, or in rendering inert swellable rock. The lubricating ability of such comparatively high-viscosity ester oils even at elevated temperatures in the bore-shaft, in particular also in deviated bore-holes, is in some cases distinctly better than that of the comparatively thin-bodied ester oils. A dispersed ester oil phase of comparatively higher-viscosity ester oils does not cause any detrimental effect on the drill-technology, the rheology of the system as a whole is determined by the continuous aqueous phase. In this sense it may be preferred to use ester oils as the dispersed phase which have a Brookfield viscosity of up to about 500,000 mPa.s, preferably up to about 1 million mPa.s or even higher, for example, up to about 2 million mPa.s (determined at ambient temperature). This constitutes an important extension of the teaching in the named earlier Applications of the Applicant in the field of oil-based invert drilling fluids based on ester-oils.



In one embodiment of the invention, branched-chain components and in particular alpha-branched-chain alcohols and/or carboxylic acids can be of particular significance. Branches of this type are known on the one hand to influence rheology, the esters formed by such chain-branching are usually more mobile. Furthermore, such alpha-branching can, moreover, also promote increased hydrolysis stability under working conditions, which is therefore exploited in the invention.

The oleophilic alcohols suitable as possible mixture components

In particular, oleophilic alcohols as disclosed in the Applicant's earlier ^{Australian} Patent Application ^{No. 5344/90} ~~P 39-11-238.1 (D-8511)~~, as cited above, are considered. The most important embodiment thereof has as its subject oleophilic monofunctional alcohols as described in the context of the present invention description for the formation of the ether oils. Reference should be made to these details.

The aqueous phase

All types of water are suitable for the production of the O/W-emulsion fluids according to the invention. These can therefore be based on fresh water and in particular also on salt water - particularly sea water for use in off-shore wells.

Additives in the emulsion fluid

In principle, all the additives provided for comparable drilling fluid types are considered here, which are usually added in connection with a quite specific desired range of drilling fluid properties. The additives can be water-soluble, oil-soluble and/or water- or oil-dispersible.

Classical additives for water-based O/W-emulsion fluids can be: emulsifiers, fluid-loss additives, structure-viscosity-building soluble and/or insoluble substances, alkali reserves, agents for the inhibition of undesired water-exchange between drilled formations - e.g. water-swellable clays and/or salt strata - and the water-based drilling



fluid, wetting agents for better adhesion of the emulsified oil phase to solid surfaces, e.g. for improving the lubricating effect, but also for the improvement of the oleophilic seal of exposed rock formations, or rock surfaces, biocides, e.g., for inhibiting bacterial attack on such O/W-emulsions, and the like. For details, reference should be made here to the relevant prior art, as described in detail in the specialist literature cited above, refer here in particular to Gray and Darley, loc. cit., Chapter 11, "Drilling Fluid Components". We will therefore only cite extracts below:

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

Agents for building up the structure-viscosity, which at the same time also act as fluid-loss additives: First of all bentonite should be mentioned here which is known to be used in water-based fluids in a non-modified form and is therefore ecologically safe. For salt-water fluids other comparable clays, in particular attapulgite and sepiolite, are of considerable significance in practice.

The additional use of organic polymer compounds of natural and/or synthetic origin can also be of considerable importance in this context. The following should in particular be mentioned here: starch or chemically modified starches, cellulose derivatives, such as carboxymethylcellulose, guar gum, xanthan gum, or also purely synthetic water-soluble and/or water-dispersible polymer compounds, such as in particular the polyacrylamide compounds of high molecular weight with or without anionic or cationic modification.

Thinners for viscosity-regulation: So-called thinners can be of organic or inorganic nature; examples of organic thinners are tannins and/or quebracho extract. Further examples are lignite and lignite derivatives, particularly lignosulfonates. As indicated above, in a preferred embodiment of the invention the use of toxic components is particularly to be excluded, and in particular the corresponding salts with toxic heavy metals, such as chromium and/or copper. Polyphosphate compounds are examples of inorganic thinners.



Emulsifiers: For the teaching according to the invention, two features in particular should be considered. It has emerged that a stable dispersion of ethers, alcohols and in some cases ester oils can be very much more easily possible than the corresponding dispersion of pure mineral oils as used in the state of the art. This in itself is a first simplification. Furthermore, it should be considered that, when longer-chain carboxylic acid esters are used, by the partial saponification of the ester oils under the additional effect of suitable alkali reserves, effective O/W-emulsifiers are also formed which contribute to the stabilization of the system.

Additives which inhibit undesired water-exchange with, for example, clays: The additives known from the state of the art for use in water-based drilling fluids are considered here. In particular, this is concerned with halides and/or carbonates of the alkali and/or alkaline-earth metals, with particular importance given to corresponding potassium salts, optionally in combination with lime. Reference is made for example to the appropriate publications in "Petroleum Engineer International", September 1987, 32 - 40 and "World Oil", November 1983, 93 -97.

Alkali reserves: inorganic and/or organic bases adapted to the general behavior of the fluid can be considered, in particular corresponding basic salts or hydroxides of alkali and/or alkaline-earth metals and organic bases.

In the field of organic bases, a conceptual distinction must be drawn between water-soluble organic bases - for example, compounds of the diethanolamine type - and practically water-insoluble bases of marked oleophilic character as described in the Applicant's earlier Patent Application No. 49579/90 (~~Application P 39 03 785.1 (D 8543)~~), cited above, as additives in invert drilling muds based on ester oil. The use of such oil-soluble bases in the framework of the present invention in particular falls within the new teaching. Oleophilic bases of this type, which are distinguished in particular by at least one longer hydrocarbon radical with, for example, 8 to 36 carbon atoms, are, however, not dissolved in the aqueous phase but in the dispersed oil phase. Here these basic



components are of multiple significance. On the one hand they can act directly as alkali reserves. On the other, they give the dispersed oil droplets a certain positive charge and therefore result in increased interaction with negative surface charges which can be found in particular in the hydrophilic clays which are susceptible to ion-exchange. According to the invention the hydrolytic cleavage and the oleophilic sealing of water-reactive rock strata can thus be influenced.

The quantity of auxiliary substances and additives used in each case moves essentially within the usual boundaries and can therefore be taken from the cited relevant literature.

Examples

Firstly, a 6% by weight homogenized bentonite suspension is prepared using commercially available bentonite (not hydrophobized) and tap water, and a pH value of 9.2 to 9.3 is adjusted by means of a sodium hydroxide solution.

Starting with this pre-swollen aqueous bentonite phase, the individual components of the water-based emulsion as in the following formulation are incorporated in successive stages of the process - each under intensive intermixing:

350 g 6 % by weight bentonite solution
1.5 g industrial carboxymethylcellulose low-viscosity (Relatin U 300 S9)
35 g sodium chloride
70 g ether (as in the definition given below)
1.7 g emulsifier (sulf. castor oil "Turkey-red oil")
219 g barite

Viscosity measurements are carried out on the thus prepared O/W-emulsion fluids as follows:

Firstly, the plastic viscosity (PV), the yield point (YP) and the gel strength after 10 sec. and after 10 min. of the emulsion fluid are



determined at 50°C on the unaged material.

The emulsion fluid is then aged for 16 hours at 125°C in an autoclave in the so-called "roller-oven" to examine the effect of temperature on the stability of the emulsion. Then the viscosity values at 50°C are determined once again. In each of the following examples the nature of the ether used, the values determined for the unaged and aged material and - if necessary - general comments are given.

Example 1

Oil-phase used: n-C₁₀-dialkylether

	unaged material	aged material
plastic viscosity [mPa.s]	10	13
yield point [Pa]	15.3	9.6
gel strength [Pa]		
10 sec.	10.5	6.7
10 min.	11.5	9.1

Example 2

The formulation in Example 1 is repeated, but without using the emulsifier (Turkey-red oil).

The viscosity values measured on the unaged and aged material are as follows:

	unaged material	aged material
plastic viscosity [mPa.s]	8	7
yield point [Pa]	16.2	17.7
gel strength [Pa]		
10 sec.	17.2	18.2
10 min.	16.8	13.4



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Even in the fresh formulation a slight droplet formation can be seen on the surface.



Example 3

Oil phase used: di-isotridecylether

The viscosity values measured on the unaged and the aged drilling fluid are as follows:

	unaged material	aged material
plastic viscosity [mPa.s]	15	15
yield point [Pa]	11.5	14.4
gel strength [Pa]		
10 sec.	11.0	13.4
10 min.	16.8	12.5

Examples 4 and 5 (Comparative Examples)

For comparison with the emulsion fluids based on ethers according to the invention, emulsion fluids are made up according to the formulation given above - once with and once without the emulsifier Turkey-red oil - based on a pure hydrocarbon oil and tested. The commercial product "WP83HF", which is employed widely in drilling fluids in current practice, is used as the hydrocarbon oil.

The table of values for Example 4 refers to the emulsion fluid containing an emulsifier, the table of values for Example 5 describes the product used without the addition of an emulsifier.



Example 4:

	unaged material	aged material
plastic viscosity [mPa.s]	10	10
yield point [Pa]	16.3	9.1
gel strength [Pa]		
10 sec.	10.1	4.8
10 min.	11.9	8.6

Example 5:

	unaged material	aged material
plastic viscosity [mPa.s]	9	8
yield point [Pa]	16.8	17.7
gel strength [Pa]		
10 sec.	16.8	17.2
10 min.	28.7	14.8



The claims defining the invention are as follows:-

1. A water-based oil in water emulsion drilling fluid suitable for the environmentally friendly development of geological formations comprising an aqueous phase, a dispersed oil phase comprising substantially water-insoluble
5 ethers which are fluid or at least plastically deformable at working temperature, have flash points of at least 80°C and are derived from mono- and/or polyfunctional alcohols of natural and/or synthetic origin or solutions of said ethers with ecologically acceptable water-insoluble oils and if desired, insoluble, finely particulate weighting agents and/or further additives.
- 10 2. A drilling fluid according to claim 1 wherein said oil phase comprises at least about 5% by weight, based on the sum of oil and water, of said fluid.
3. A drilling fluid according to claim 2 wherein said oil phase comprises at least about 8% by weight of said ethers.
- 15 4. A drilling fluid according to claim 2 wherein said oil phase comprises not more than about 50% by weight of said fluid.
5. A drilling fluid according to claim 2 wherein said oil phase comprises not more than about 40% by weight of said fluid.
6. A drilling fluid according to claim 2 wherein said oil phase
20 comprises about 5 to 50% of said fluid.
7. A drilling fluid according to claim 2 wherein said oil phase comprises about 10 to 35% of said fluid.
8. A drilling fluid according to any one of claims 1 to 7 wherein said ethers comprise a substantial part of said dispersed oil phase.
- 25 9. A drilling fluid according to claim 8 wherein said ethers comprise more than 10% by weight of said oil phase.
10. A drilling fluid according to claim 8 wherein said ethers comprise more than 50% by weight of said oil phase.
11. A drilling fluid according to any one of claims 1 to 10, wherein
30 said ethers are of oleophilic nature and are derived from mono- and/or difunctional alcohols.
12. A drilling fluid according to any one of claims 1 to 11, wherein said ethers are free from aromatic molecular constituents.
13. A drilling fluid according to claim 12 wherein said ethers are
35 derived from straight and/or branched hydrocarbon chains.
14. A drilling fluid according to claim 13 wherein said hydrocarbon chains are unsaturated.



15. A drilling fluid according to any one of claims 1 to 14 wherein said ethers are derived from monofunctional alcohols having at least 4 carbon atoms.

16. A drilling fluid according to claim 15 wherein said monofunctional
5 alcohols have at least 6 to 8 carbon atoms.

17. A drilling fluid according to claims 15 or 16 wherein said monofunctional alcohols have up to 36 carbon atoms.

18. A drilling fluid according to any one of claims 1 to 14 wherein said ethers are mixed ethers or mixtures thereof with monofunctional alcohols
10 with up to 24 carbon atoms.

19. A drilling fluid according to any one of claims 1 to 14, wherein said ethers are polyalkylene glycol-(mixed)-ethers.

20. A drilling fluid according to claim 19 wherein said ethers are derived from lower alkylene glycols.

15 21. A drilling fluid according to claim 20 wherein said lower alkylene glycols are ethylene oxide and/or propylene oxide.

22. A drilling fluid according to any one of claims 1 to 21, wherein said ecologically acceptable water-insoluble oils are at least part oleophilic alcohols and/or ester oils derived from mono- and/or polyfunctional alcohols.

20 23. A drilling fluid according to claim 22 wherein said alcohols after undergoing partial ester-saponification during practical use are not toxicologically harmful.

24. A drilling fluid according to claim 23 wherein said alcohols are not harmful when inhaled.

25 25. A drilling fluid according to any one of claims 22 to 24 wherein said ester oils are esters of monofunctional alcohols of natural and/or synthetic origin and of marked oleophilic character.

26. A drilling fluid according to claim 25 wherein said monofunctional alcohols have at least 6 carbon atoms.

30 27. A drilling fluid according to claim 25 wherein said monofunctional alcohols have at least 8 carbon atoms.

28. A drilling fluid according to any one of claims 22 to 24 wherein said ester oils are complete and/or partial esters derived from polyfunctional alcohols.

35 29. A drilling fluid according to claim 28 wherein said ester oils are cderived from lower alcohols with up to 40 H groups.

30. A drilling fluid according to claim 29 wherein said ester oils may be partial ethers of water-soluble polyols.



31. A drilling fluid according to claim 30 wherein said water-soluble polyols are ethylene glycol, propylene glycol and/or glycerin.

32. A drilling fluid according to any one of claim 31, wherein said ethers or admixtures with oils have solidification values (pour point and setting
5 point) below 0°C and have flash points of at least 100°C.

33. A drilling fluid according to claim 32 wherein said solidification value is below -5°C.

34. A drilling fluid according to any one of claims 1 to 33 wherein said ethers or mixtures thereof with oils have a Brookfield RVT viscosity of up
10 to about 2 million mPa.s at 20°C.

35. A drilling fluid according to claim 34 wherein said viscosity is up to about 1 million mPa.s.

36. A drilling fluid according to any one of claims 1 to 35 wherein said dispersed oil phase comprises ethers in admixture with carboxylic acid
15 esters from at least one of the following sub-classes:

a) esters from C₁₋₅-monocarboxylic acids and mono- and/or polyfunctional alcohols, in which radicals of monohydric alcohols have at least 6 carbon atoms,

b) esters from C₆₋₁₆-monocarboxylic acids of synthetic and/or
20 natural origin,

c) esters of olefin mono- and/or poly-unsaturated monocarboxylic acids with at least 16 carbon atoms.

37. A drilling fluid according to claim 36 wherein said monohydric alcohols in (a) have at least 8 carbon atoms.

25 38. A drilling fluid according to claim 36 or 37 wherein said polyhydric alcohols in (a) have 2 to 6 carbon atoms.

39. A drilling fluid according to claim 36 wherein said monocarboxylic acids in (b) are aliphatic and saturated.

40. A drilling fluid according to claim 36 or claim 39 wherein said
30 esters of (b) are derived from alcohols of the type of (a).

41. A drilling fluid according to claim 36 wherein said monocarboxylic acids of (c) have 16 to 24 carbon atoms.

42. A drilling fluid according to claim 36 or claim 41 wherein said
35 esters of (c) are derived from monofunctional straight-chain and/or branched alcohols.

43. A drilling fluid according to any one of claims 36, 41 or 42 wherein said esters of (c) are derived by more than 45% by weight from di- and/or poly-olefin-unsaturated C₁₆₋₂₄-monocarboxylic acids.



44. A drilling fluid according to claim 43 wherein said esters are derived by more than 55% by weight of said C₁₆₋₂₄ monocarboxylic acids.

45. A drilling fluid according to claims 36, 40 or 41 wherein said esters of (c) are derived by not more than 35% by weight from di- and/or poly-
5 olefin-unsaturated acids.

46. A drilling fluid according to claim 45 wherein said esters of (c) are derived from at least about 60% by weight mono-olefin unsaturated acids.

47. A drilling fluid according to any one of claims 1 to 46 wherein basic amine compounds of marked oleophilic character and at most limited
10 water-solubility are further added to said oil phase.

48. A drilling fluid according to claim 47 wherein said oleophilic amine compounds are at least largely free from aromatic constituents, and have a water-solubility at room temperature of not more than about 1% by weight.

49. A drilling fluid according to claim 47 or claim 48 wherein said
15 basic amine compounds have at least one long-chain hydrocarbon radical.

50. A drilling fluid according to claim 49 wherein said long-chain hydrocarbon radical has 8 to 36 carbon atoms.

51. A drilling fluid according to any one of claims 47 to 50 wherein said oil phase comprises up to 10% by weight of said oleophilic amine
20 compounds.

52. A drilling fluid according to claim 51 wherein said oil phase comprises about 0.1 to 2% by weight of said oleophilic amine compounds.

53. A drilling fluid according to any one of claims 1 to 52 wherein said aqueous phase comprises fresh water or water containing dissolved or
25 suspended salts.

54. A drilling fluid according to claim 53 wherein said suspended salts are halides and/or carbonates of the alkali and/or alkaline earth-metals.

55. A drilling fluid according to any one of claims 1 to 52 wherein said aqueous phase is modified sea water.

30 56. A drilling fluid according to any one of claims 1 to 55 wherein said further additives are emulsifiers, fluid loss additives, wetting agents, alkali reserves, salts, disinfectants, loading agents and auxiliary substances for the inhibition of drilled rock of high water-sensitivity or mixtures of two or more thereof.

35 57. A drilling fluid according to claim 1 or claim 56 wherein said additives are substantially ecologically and toxicologically harmless.

58. A drilling fluid according to claim 57 wherein said additives are free from soluble toxic heavy-metal compounds.



59. A drilling fluid according to claim 57 or claim 58 wherein said loading substance inhibits the water-absorption of swellable rock strata or clays.

60. A drilling fluid according to any one of claims 1 to 59 wherein
5 said fluid limits the rock hydration of mineral strata which are prone thereto.

61. A drilling fluid according to any one of claims 1 to 60 wherein said fluid has a neutral to moderately alkaline pH.

62. A drilling fluid according to claim 61 wherein said pH is from about 7.5 to 11.

10 63. A water-based oil in water emulsion drilling fluid suitable for the environmentally friendly development of geological formations, substantially as hereinbefore described with reference to any one of Examples 1 to 3.

64. A process for preparing a water-based oil in water emulsion drilling fluid suitable for the environmentally friendly development of geological
15 formations, substantially as hereinbefore described with reference to any one of Examples 1 to 3.

DATED this EIGHTH day of JULY 1992
Henkel Kommanditgesellschaft auf Aktien
Patent Attorneys for the Applicant
SPRUSON & FERGUSON

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Abstract

Use of selected oleophilic ethers in water-based drilling fluids of the O/W-emulsion type, and also corresponding drilling fluids with improved ecological acceptability

The use is disclosed of at least largely water-insoluble ethers which are fluid and/or at least plastically deformable at working temperature and have flash points of at least 80°C, of mono- and/or polyfunctional alcohols of natural and/or synthetic origin or corresponding solutions of such ethers in ecologically acceptable water-insoluble oils as the dispersed oil phase of water-based O/W-emulsion drilling fluids which are suitable for the environmentally friendly development of geological formations and which contain, if desired, insoluble, finely particulate weighting agents for the formation of water-based O/W-emulsion drilling muds and/or further additives, such as emulsifiers, fluid-loss additives, wetting agents, alkali reserves and/or auxiliary substances for the inhibition of drilled rock of high water-sensitivity.



INTERNATIONAL SEARCH REPORT

International Application No PCT/EP90/00732

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ⁶ According to International Patent Classification (IPC) or to both National Classification and IPC Int.Cl.5 C09K 7/02																				
II. FIELDS SEARCHED Minimum Documentation Searched ⁷ <table border="1" style="width: 100%; border-collapse: collapse; margin-top: 5px;"> <tr> <th style="width: 25%;">Classification System</th> <th style="width: 75%;">Classification Symbols</th> </tr> <tr> <td style="padding: 5px;">Int.Cl.5</td> <td style="padding: 5px;">C09K 7, C10M 173/02, C10M 101/04, C10M 105/32</td> </tr> </table> Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸			Classification System	Classification Symbols	Int.Cl.5	C09K 7, C10M 173/02, C10M 101/04, C10M 105/32														
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Int.Cl.5	C09K 7, C10M 173/02, C10M 101/04, C10M 105/32																			
III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹ <table border="1" style="width: 100%; border-collapse: collapse; margin-top: 5px;"> <thead> <tr> <th style="width: 10%;">Category [*]</th> <th style="width: 60%;">Citation of Document, ¹¹ with Indication, where appropriate, of the relevant passages ¹²</th> <th style="width: 30%;">Relevant to Claim No. ¹³</th> </tr> </thead> <tbody> <tr> <td style="text-align: center; vertical-align: top;">Y</td> <td style="vertical-align: top;">EP, A, 0271943 (SHELL) 22 June 1988 see page 3, lines 3-52; page 4, lines 28-51 ---</td> <td style="vertical-align: top;">1,16-18,20,21</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">Y</td> <td style="vertical-align: top;">US, A, 4631136 (R. W. JONES) 23 December 1986; see column 3, lines 32-68; column 4, lines 1-54; column 5, lines 41-68 ---</td> <td style="vertical-align: top;">1,16-18,20,21</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">Y</td> <td style="vertical-align: top;">US, A, 3630898 (F.C. TEETER) 28 December 1971 see column 2, lines 19-35; column 3, lines 1-35,44-50 ---</td> <td style="vertical-align: top;">1,4-11,16-18</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">Y</td> <td style="vertical-align: top;">FR, A, 1297556 (CHEMISCHE WERKE HULS AKTIENGESELLSCHAFT) 1962 see page 1, right hand column, lines 15-16; page 2, left hand column, lines 23-37, right hand column, lines 20-38 ---</td> <td style="vertical-align: top;">1,4-11,15-18</td> </tr> <tr> <td colspan="3" style="text-align: center; padding-top: 20px;">.../...</td> </tr> </tbody> </table>			Category [*]	Citation of Document, ¹¹ with Indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³	Y	EP, A, 0271943 (SHELL) 22 June 1988 see page 3, lines 3-52; page 4, lines 28-51 ---	1,16-18,20,21	Y	US, A, 4631136 (R. W. JONES) 23 December 1986; see column 3, lines 32-68; column 4, lines 1-54; column 5, lines 41-68 ---	1,16-18,20,21	Y	US, A, 3630898 (F.C. TEETER) 28 December 1971 see column 2, lines 19-35; column 3, lines 1-35,44-50 ---	1,4-11,16-18	Y	FR, A, 1297556 (CHEMISCHE WERKE HULS AKTIENGESELLSCHAFT) 1962 see page 1, right hand column, lines 15-16; page 2, left hand column, lines 23-37, right hand column, lines 20-38 ---	1,4-11,15-18	.../...		
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[*] Special categories of cited documents: ¹⁰ "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "&" document member of the same patent family																				
IV. CERTIFICATION <table border="1" style="width: 100%; border-collapse: collapse; margin-top: 5px;"> <tr> <td style="width: 50%; padding: 5px;"> Date of the Actual Completion of the International Search 3 July 1990 (03.07.90) </td> <td style="width: 50%; padding: 5px;"> Date of Mailing of this International Search Report 31 July 1990 (31.07.90) </td> </tr> <tr> <td style="width: 50%; padding: 5px;"> International Searching Authority European Patent Office </td> <td style="width: 50%; padding: 5px;"> Signature of Authorized Officer </td> </tr> </table>			Date of the Actual Completion of the International Search 3 July 1990 (03.07.90)	Date of Mailing of this International Search Report 31 July 1990 (31.07.90)	International Searching Authority European Patent Office	Signature of Authorized Officer														
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International Searching Authority European Patent Office	Signature of Authorized Officer																			

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No
Y	DE, B, 1218096 (CHEMISCHE WERKE HULS AKTIENGESELLSCHAFT) 2 June 1966 see column 1, lines 1-52; column 2, lines 1-4, column 3, lines 12-26 -----	1,4,5,8,16

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.**

EP 9000732

SA 36497

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 20/07/90. The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A- 0271943	22-06-88	AU-B- 596251	26-04-90
		AU-A- 8260487	23-06-88
		OA-A- 8786	31-03-89
		US-A- 4828724	09-05-89
US-A- 4631136	23-12-86	None	
US-A- 3630898	28-12-71	None	
FR-A- 1297556		DE-B- 1158696	
DE-B- 1218096		FR-A- 1335195	
		GB-A- 1006940	

INTERNATIONALER RECHERCHENBERICHT

Internationales Aktenzeichen PCT/EP 90/00732

I. KLASSIFIKATION DES ANMELDUNGSGEGENSTANDS (bei mehreren Klassifikationssymbolen sind alle anzugeben) ⁶		
Nach der Internationalen Patentklassifikation (IPC) oder nach der nationalen Klassifikation und der IPC		
Int.Ci. ⁵ C 09 K 7/02		
II. RECHERCHIERTE SACHGEBIETE		
Recherchierter Mindestprüfstoff ⁷		
Klassifikationssystem	Klassifikationssymbole	
Int.Cl. ⁵	C 09 K 7, C 10 M 173/02, C 10 M 101/04, C 10 M 105/32	
Recherchierte nicht zum Mindestprüfstoff gehörende Veröffentlichungen, soweit diese unter die recherchierten Sachgebiete fallen ⁸		
III. EINSCHLÄGIGE VERÖFFENTLICHUNGEN⁹		
Art*	Kennzeichnung der Veröffentlichung ¹¹ , soweit erforderlich unter Angabe der maßgeblichen Teile ¹²	Betr. Anspruch Nr. ¹³
Y	EP, A, 0271943 (SHELL) 22. Juni 1988 siehe Seite 3, Zeilen 3-52; Seite 4, Zeilen 28-51 --	1,16-18, 20,21
Y	US, A, 4631136 (R.W. JONES) 23. Dezember 1986 siehe Spalte 3, Zeilen 32-68; Spalte 4, Zeilen 1-54; Spalte 5, Zeilen 41-68 --	1,16-18, 20,21
Y	US, A, 3630898 (F.C. TEETER) 28. Dezember 1971 siehe Spalte 2, Zeilen 19-35; Spalte 3, Zeilen 1-35,44-50 --	1,4-11, 16-18
./.		
* Besondere Kategorien von angegebenen Veröffentlichungen¹⁰: "A" Veröffentlichung, die den allgemeinen Stand der Technik definiert, aber nicht als besonders bedeutsam anzusehen ist "E" älteres Dokument, das jedoch erst am oder nach dem internationalen Anmeldedatum veröffentlicht worden ist "L" Veröffentlichung, die geeignet ist, einen Prioritätsanspruch zweifelhaft erscheinen zu lassen, oder durch die das Veröffentlichungsdatum einer anderen im Recherchenbericht genannten Veröffentlichung belegt werden soll oder die aus einem anderen besonderen Grund angegeben ist (wie ausgeführt) "O" Veröffentlichung, die sich auf eine mündliche Offenbarung, eine Benutzung, eine Ausstellung oder andere Maßnahmen bezieht "P" Veröffentlichung, die vor dem internationalen Anmeldedatum, aber nach dem beanspruchten Prioritätsdatum veröffentlicht worden ist "T" Spätere Veröffentlichung, die nach dem internationalen Anmeldedatum oder dem Prioritätsdatum veröffentlicht worden ist und mit der Anmeldung nicht kollidiert, sondern nur zum Verständnis des der Erfindung zugrundeliegenden Prinzips oder der ihr zugrundeliegenden Theorie angegeben ist "X" Veröffentlichung von besonderer Bedeutung; die beanspruchte Erfindung kann nicht als neu oder auf erfinderischer Tätigkeit beruhend betrachtet werden "Y" Veröffentlichung von besonderer Bedeutung; die beanspruchte Erfindung kann nicht als auf erfinderischer Tätigkeit beruhend betrachtet werden, wenn die Veröffentlichung mit einer oder mehreren anderen Veröffentlichungen dieser Kategorie in Verbindung gebracht wird und diese Verbindung für einen Fachmann naheliegend ist "&" Veröffentlichung, die Mitglied derselben Patentfamilie ist		
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Datum des Abschlusses der internationalen Recherche	Absenddatum des internationalen Recherchenberichts	
3. Juli 1990	3. 7. 90	
Internationale Recherchenbehörde	Unterschrift des bevollmächtigten Bediensteten	
Europäisches Patentamt	H. DANIELS	

III.EINSCHLÄGIGE VERÖFFENTLICHUNGEN (Fortsetzung von Blatt 2)		
Art *	Kennzeichnung der Veröffentlichung, soweit erforderlich unter Angabe der maßgeblichen Teile	Betr. Anspruch Nr.
Y	FR, A, 1297556 (CHEMISCHE WERKE HÜLS AKTIENGESELLSCHAFT) 1962 siehe Seite 1, rechte Spalte, Zeilen 15-16; Seite 2, linke Spalte, Zeilen 23-37, rechte Spalte, Zeilen 20-38 --	1,4-11, 15-18
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**ANHANG ZUM INTERNATIONALEN RECHERCHENBERICHT
ÜBER DIE INTERNATIONALE PATENTANMELDUNG NR.**

EP 9000732
SA 36497

In diesem Anhang sind die Mitglieder der Patentfamilien der im obengenannten internationalen Recherchenbericht angeführten Patentdokumente angegeben.
Die Angaben über die Familienmitglieder entsprechen dem Stand der Datei des Europäischen Patentamts am 20/07/90
Diese Angaben dienen nur zur Unterrichtung und erfolgen ohne Gewähr.

Im Recherchenbericht angeführtes Patentdokument	Datum der Veröffentlichung	Mitglied(er) der Patentfamilie	Datum der Veröffentlichung
EP-A- 0271943	22-06-88	AU-B- 596251	26-04-90
		AU-A- 8260487	23-06-88
		OA-A- 8786	31-03-89
		US-A- 4828724	09-05-89
US-A- 4631136	23-12-86	Keine	
US-A- 3630898	28-12-71	Keine	
FR-A- 1297556		DE-B- 1158696	
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		GB-A- 1006940	