PCT WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 :
C10M 173/02 // (C10M 173/02, 133:50, 129:32, 129:40, 129:48, 135:10, 125:10, 129:08), C10N 10:02, 30:12, 40:08

A1

(11) International Publication Number: **WO 99/35219**

(43) International Publication Date: 15 July 1999 (15.07.99)

(21) International Application Number: PCT/GB98/03805

(22) International Filing Date: 31 December 1998 (31.12.98)

(30) Priority Data:
9727513.5 31 December 1997 (31.12.97) GB

(71) Applicant *(for all designated States except US)*: W CANNING PLC [GB/GB]; 133 Great Hampton Street, Birmingham B18 6AS (GB).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: WAKE, Simon, John [GB/GB]; 78 Pereira Road, Birmingham B17 9JN (GB). MCMANUS, Simon, Paul [GB/GB]; Carter Place Cottage, Hall Park, Haslingden, Rossendale, Lancs BB4 5BQ (GB). MCKECHNIE, Thomas, John [GB/GB]; 12 Hudson Grove, Lowton, Warrington WA3 2LJ (GB). LIDDY, David [GB/GB]; W Canning plc, 133 Great Hampton Street, Birmingham B18 6AS (GB).

(74) Agent: HALL, Robert, Leonard; Dibb Lupton Alsop, Fountain Precinct, Balm Green, Sheffield S1 1RZ (GB).

(81) Designated States: US, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published
With international search report.

(54) Title: HYDRAULIC FLUIDS CONTAINING N–ALKYL MORPHOLINE OR A SALT THEREOF

(57) Abstract

A water based hydraulic fluid comprising an N–alkyl morpholine or a salt thereof.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	**ES**	Spain	**LS**	Lesotho	**SI**	Slovenia
AM	Armenia	**FI**	Finland	**LT**	Lithuania	**SK**	Slovakia
AT	Austria	**FR**	France	**LU**	Luxembourg	**SN**	Senegal
AU	Australia	**GA**	Gabon	**LV**	Latvia	**SZ**	Swaziland
AZ	Azerbaijan	**GB**	United Kingdom	**MC**	Monaco	**TD**	Chad
BA	Bosnia and Herzegovina	**GE**	Georgia	**MD**	Republic of Moldova	**TG**	Togo
BB	Barbados	**GH**	Ghana	**MG**	Madagascar	**TJ**	Tajikistan
BE	Belgium	**GN**	Guinea	**MK**	The former Yugoslav Republic of Macedonia	**TM**	Turkmenistan
BF	Burkina Faso	**GR**	Greece			**TR**	Turkey
BG	Bulgaria	**HU**	Hungary	**ML**	Mali	**TT**	Trinidad and Tobago
BJ	Benin	**IE**	Ireland	**MN**	Mongolia	**UA**	Ukraine
BR	Brazil	**IL**	Israel	**MR**	Mauritania	**UG**	Uganda
BY	Belarus	**IS**	Iceland	**MW**	Malawi	**US**	United States of America
CA	Canada	**IT**	Italy	**MX**	Mexico	**UZ**	Uzbekistan
CF	Central African Republic	**JP**	Japan	**NE**	Niger	**VN**	Viet Nam
CG	Congo	**KE**	Kenya	**NL**	Netherlands	**YU**	Yugoslavia
CH	Switzerland	**KG**	Kyrgyzstan	**NO**	Norway	**ZW**	Zimbabwe
CI	Côte d'Ivoire	**KP**	Democratic People's Republic of Korea	**NZ**	New Zealand		
CM	Cameroon			**PL**	Poland		
CN	China	**KR**	Republic of Korea	**PT**	Portugal		
CU	Cuba	**KZ**	Kazakstan	**RO**	Romania		
CZ	Czech Republic	**LC**	Saint Lucia	**RU**	Russian Federation		
DE	Germany	**LI**	Liechtenstein	**SD**	Sudan		
DK	Denmark	**LK**	Sri Lanka	**SE**	Sweden		
EE	Estonia	**LR**	Liberia	**SG**	Singapore		

HYDRAULIC FLUIDS CONTAINING N-ALKYL MORPHOLINE OR A SALT THEREOF

This invention relates to hydraulic fluids, and more particularly to water-based hydraulic fluids having improved temperature stability.

BACKGROUND TO THE INVENTION

Hydraulic fluids are widely used to transmit power and operate control valves, for example, in factory applications and in sub-sea systems. In the latter systems hydraulic fluids are used, for example, for the remote operation of valves associated with oil production where the well head is beneath the surface of the sea.

Water-based hydraulic fluids, in addition to water, commonly comprise a carboxylic acid and sufficient alkali to give a pH in the range of 7 to 12.

Where low temperature stability is desired, it is known to add a glycol such as ethane 1,2 diol to depress the freezing point of the fluid.

To this basic system are often added other additives, for example, to improve lubricity and/or to reduce corrosion of metals exposed to the fluid. Examples of water-based hydraulic compositions are disclosed in US patents nos. 4434066, 4390440, 4390439, and in European patent

application no. 0367080, the entire disclosures of which are incorporated herein by reference for all purposes.

The water-based hydraulic fluids known to the art exhibit limited thermal stability. This is a particular problem for hydraulic fluids which may be exposed to high temperatures for long periods of time, for example, in fluids used for operating control valves associated with sub-sea oil production, where there is a requirement for stability at 180 degrees C for several years.

As an example, fluids containing ethane 1,2 diol as a freezing point depressant are subject to oxidation at high temperatures, the glycol producing acids, for example, glycollic acid. Unless the fluid is buffered against a fall in pH, the acids produced can render the fluid corrosive to metals with which it may come into contact. It is therefore known to add amines to the hydraulic fluid in order to provide the necessary buffering effect.

Typically, therefore, a water-based hydraulic fluid can comprise a carboxylic acid neutralised with an amine, the amine being present in excess to provide a slightly alkaline pH and to buffer the fluid against a fall in pH.

It is also desirable to include a vapour phase corrosion inhibitor (VPI) that provides protection against the

corrosion of ferrous metal parts exposed to the vapour of the fluid, but not actually immersed in the fluid. Certain amines have also been proposed for this role.

Morpholine has been proposed as an amine for use in hydraulic fluids, but such fluids do not have sufficient thermal stability for many purposes and have an undesirably high rate of corrosion of, for example, aluminium.

European patent application no. 0367080 discloses a water-glycol hydraulic fluid comprising a higher aliphatic acid in a ratio of 2 to 15% by weight, alkali hydroxide in an amount less than an equivalent amount of the higher aliphatic acid, and an organic alkaline compound containing nitrogen atoms in an amount sufficient to adjust the pH of the whole fluid to 10 to 12.

Belgian Patent No. 771150 discloses a hydraulic fluid consisting of water, a glycol, a polyoxyalkyleneglycol, a phosphoric ester of a monohydroxyl polyether, and a nitrogenous organic base. The organic base can be an aliphatic amine, an alkanolamine or a cyclic amine such as morpholine or an N-alkylmorpholine, and is added in an amount sufficient to adjust the pH of the fluid to from 7 to 9. Apart from the pH adjustment, there is no suggestion that the organic base performs any other function. The hydraulic fluids of Belgian Patent No. 771150 suffer from the disadvantage that the phosphate

esters are subject to hydrolysis in aqueous systems, forming acids, which can lower the pH, and increase the risk of corrosion. In addition, the partial phosphate esters disclosed, and more particularly phosphates produced by hydrolysis of the phosphate esters tend to form insoluble precipitates with calcium and magnesium ions that are naturally present in sea water. Many hydraulic systems have very small diameter holes and channels which can be easily obstructed by solids. Precipitates formed by hydrolysis of the partial phosphate esters can render the hydraulic fluid out of specification.

A further disadvantage of the use of phosphate esters is that the loss of the active constituent (the phosphate ester) by hydrolysis will tend to degrade the lubricity of the hydraulic fluid. This effect is particularly important in hydraulic fluids intended to be suitable for use at high temperatures, as the rate of hydrolysis increases rapidly with temperature.

OBJECT OF THE INVENTION

It is apparent from the above that there is a need for a water-based hydraulic fluid having improved long term thermal stability, in particular long term stability to temperatures of the order of 180 degrees C, a low rate of corrosion of metals wetted by the fluid, good VPI activity, and good buffering against pH drop, for example, which may be caused by glycollic acid formation.

BRIEF SUMMARY OF THE INVENTION

According to the invention, it has been found that the addition of certain analogues of morpholine can provide hydraulic fluids with substantially improved properties.

In a first aspect, the invention provides the use in a water-based hydraulic fluid of an N-alkyl morpholine or a salt thereof as a vapour phase corrosion inhibitor.

In a second aspect, the invention provides a fluid controlled apparatus wherein there is used a water-based hydraulic fluid comprising an N-alkyl morpholine or a salt thereof as a vapour phase corrosion inhibitor.

In a further aspect, the invention provides a water-based hydraulic fluid comprising an N-alkyl morpholine or a salt thereof and an acid other than a partial phosphate ester, the hydraulic fluid having a pH of 7 or more.

In a still further aspect, the invention provides a fluid controlled apparatus wherein there is used a water-based hydraulic fluid comprising an N-alkyl morpholine or a salt thereof and an acid other than a partial phosphate ester, the hydraulic fluid having a pH or 7 or more.

DETAILED DESCRIPTION OF THE INVENTION

Preferred N-alkyl morpholines for use in the present invention are those with alkyl groups comprising from 1

to 10 carbon atoms in the N-alkyl chain, more preferably from one to six carbon atoms, for example, N-methyl morpholine, N-ethyl morpholine and N-propyl morpholine. Substituted N-alkyl morpholines wherein one or more of the methylene groups in the morpholine ring carry alkyl substituents can also be used. These N-alkyl morpholines have been found to provide a substantial improvement over other nitrogenous organic bases such as alkanolamines, in that they have significant volatility, making them excellent vapour phase inhibitors. They also have improved thermal stability and corrosion inhibition properties over morpholine-containing hydraulic fluids.

Preferably the N-alkyl morpholine is present in an amount of greater than 0.1% W/W, more preferably in an amount of from 1 to 15 %W/W.

The hydraulic fluids of the invention preferably also comprise an acid (other than a partial phosphate ester), more preferably an organic acid, and especially a carboxylic acid. Suitable carboxylic acids for use in the invention include, for example, aliphatic and aromatic mono- and di-carboxylic acids. Preferred carboxylic acids are aliphatic carboxylic acids, comprising up to 22 carbon atoms in the alkyl chain, for example, higher aliphatic carboxylic acids comprising 7 to 22 carbon atoms in the alkyl chain for example, heptanoic acid, octanoic acid, nonanoic acid, decanoic acid and

undecanoic acid. Particularly preferred aliphatic carboxylic acids include branched chain aliphatic carboxylic acids, such as, for example, isodecanoic acid. Other carboxylic acids which can be used include substituted aryl carboxylic acids, such as, for example, benzene N-methylsulphonamido hexanoic acid and toluene sulphonamido hexanoic acid. Preferably the carboxylic acid is present in an amount of from 5 to 15 %W/W. One or more carboxylic acids can be used, as desired.

Suitable salts of the N-alkyl morpholines which can be used include, for example, salts with carboxylic acids, and particularly with aliphatic and aromatic mono- and di-carboxylic acids. Aliphatic carboxylic acids are especially preferred, and very good results have been obtained with aliphate carboxylic acids comprising up to 22 carbon atoms in the alkyl chain, for example, N-methyl morpholine acetate and N-methyl morpholino isodecanoate. The N-alkyl morpholine salts are preferably present in an amount of from about 5 to 25 %W/W, for example, about 15 %W/W.

For improved low temperature stability, the hydraulic fluids of the invention can comprise a freezing point depressant, for example, a glycol, such as ethane 1,2 diol. The freezing point depressant is preferably present in an amount of from 20 to 60 %W/W, depending on

the temperature performance required, more preferably from 20 to 40 %W/W.

Preferably the hydraulic fluid of the invention has a pH of 7 or greater, more preferably from 7 to 10, more preferably from 7 to 8.5. It has been found that the rate of corrosion of, for example, aluminium, increases at pH values over about 8.5, and for many applications becomes unacceptably high at pH values over 10. A particularly preferred pH is around 8.2.

The pH of the hydraulic fluid can be adjusted by increasing the amount of the N-alkyl morpholine present, but usually it is preferred to add a quantity of a cheaper alkali, for example, an alkali metal hydroxide such as potassium hydroxide. Where the alkali metal hydroxide is added to a salt of the N-methyl morpholine and a carboxylic acid, this can also result in the liberation of the free amine.

Although not essential to the invention, other conventional additives may be included in the hydraulic fluid, for example, other lubricants, corrosion inhibitors, defoaming agents and dyes.

The hydraulic fluids of the invention are preferably substantially free from morpholine and hydroxy alkyl amines.

The invention is illustrated by the following Example:

EXAMPLE

Fluids were prepared as follows:

Composition %W/W

Example	1	2	3	4	5
	AMP 75	TEA 85	Morpholine	NMM	NEM
Amine	3.8	5.6	2.8	3.4	3.7
Hostacor H Liquid	4.1	4.1	4.1	4.1	4.1
MEG	40	40	40	40	40
Demineralised Water	52.1	50.3	53.1	52.5	52.2

AMP 75 Amino Methyl propanol 75% - Product of Angus

TEA 85 Triethanolamine 85% W/W commercial quality

NMM N-methyl morpholine

NEM N-ethyl morpholine

MEG Ethane 1,2 Diol

Hostacor H Benzene, N-methylsulphonamido hexanoic acid (Product of HOECHST-CELANESE, USA)

Some properties were determined as follows:

Example	1	2	3	4	5
pH	10.2	8.8	9.2	8.1	8.3
Specific gravity (20°C)	1.059	1.068	1.062	1.060	1.060
Vapour Phase Corrosion Inhibition	*x*	*y*	*x*	*x*	*x*
Liquid Corrosion	Nil	Nil	Nil	Nil	Nil

x = pass *y* = fail

The vapour corrosion test is for VPI activity, and is conducted as follows:

- Heat 100ml fluid to 60°C in wide neck conical flask
- Place clean mild steel plate over mouth and allow to stand for 15 minutes, check for spots of rust every three minutes.

For examples 1,3,4,5 there was no rust after 15 minutes, which is a PASS.

For example 2, rust was evident after three minutes, FAIL.

The liquid corrosion test is the "iron chip" test according to Institution of Petroleum method 287. All fluids passed.

Further corrosion testing was done with a Galvanic Corrosion Analyser.

Tests performed using the BK Technology Galvanic Corrosion Flow Test Cell Analyser using 5Kg fluid at 25°C with a flow rate of 5 litres/minute. Where appropriate the test was conducted in accordance with IP329.

IP = Institute of Petroleum.

Galvanic Corrosion Analyser

Example	1	2	3	4	5
ALL					
Aluminium	3011	1190	629	3.2	1.1
Copper	-2222	-466	-261	-46.6	-8.6
Brass	-1879	-371	-72.9	10.7	-71
Steel	-639	-383	-180	-2.3	-15
Zinc	624	36.4	56.9	44.9	175
Cast Iron	-877	-659	-365	-8.1	-33
Cadmium	26.6	26.6	2.0	2.0	2.0
Couples					
Aluminium	1584	879	553	0	-2.1
Steel	-1865	-1014	-610	-26.7	-63
Zinc	254	91.3	22.5	40.4	90
Brass	-62.2	-12.9	-25.7	25.7	21
Cast Iron	-30.2	10.4	16.3	-10.4	-8.1
Copper	2.3	2.3	2.3	2.3	2.3
Cadmium	2.0	2.0	2.0	2.0	2.0
Brass	137	6.4	0	32.2	30
Steel	0	9.3	3.5	0	-3.5
Cast Iron	-47.6	-8.1	0	-11.6	-8.1

Negative numbers imply cathodic protection and correspond to an insignificant or zero rate of corrosion. The positive numbers are corrosion rates in microns per year calculated from the observed anodic current densities.

It can be seen that examples 4,5 show overall lower corrosion rates, particularly on aluminium.

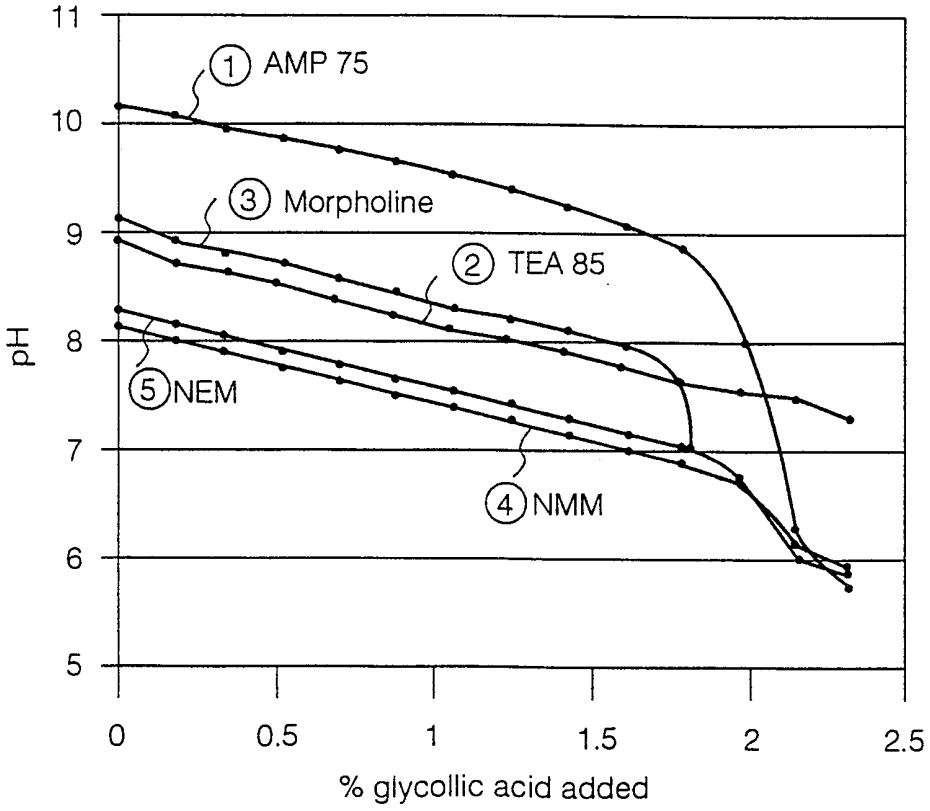
For many purposes, a corrosion rate in this test of less than 100 microns per year is regarded as acceptable, and using this criterion only the N-alkyl morpholines give acceptable rates on all the metals tested.

BUFFERING

100 grams of each fluid was titrated with 70% glycollic acid and the pH determined after each 0.2ml aliquot.

The results are expressed graphically below:

pH buffer curves for alkanolamines and morpholine derivatives



It can be seen that the N-alkyl morpholines provide excellent buffering characteristics, in particular having a relatively low starting pH. Withouth wishing to be bound by any particular theory, it is believed that the low starting pH may explain the low corrosion rate of the fluids of Examples 4 and 5 on aluminium, which is an amphoteric metal.

THERMAL STABILITY

The Fluids were tested for thermal stability by being heated in an autoclave at 220°C for 14 days. 220°C was selected as the test temperature to give an acceleration of ageing compared to an operating temperature of 180°C.

Following the period at high temperature the fluid was examined at 20°C for visible change.

Fluid

1. Considerable quantity of liquid insoluble in fluid ie separate phase.

2. Significant quantity of liquid insoluble in fluid.

3. As 2.

4. Very slight opalescence only.

5. Very slight opalescence only.

Fluids 4,5 are considered to have acceptable thermal stability, for exposure up to 180°C and certainly far superior in this respect to fluids 2,3 which themselves are better than fluid 1.

Fluids 1,2,3 are considered to have insufficient thermal stability for operation at 180°C.

the invention also provides the possibility of providing a hydraulic fluid for offshore oil applications where the fluid can be discharged into the sea at the control valve (which may be 10 - 20 kilometres from the platform). This avoids the need to provide a return line with the consequent loss of power (back pressure) and the cost of the line. A suitable water based hydraulic fluid in accordance with the invention for this application can comprise 15 %W/W N-methyl morpholino isodecanoate, 25-40 %W/W ethane 1,2 diol, and sufficient potassium hydroxide to give a pH of 8.2. In tests, this fluid gave similar results to those of Examples 4 and 5 above.

The reader's attention is directed to all papers and documents which are filed concurrently with or previous to this specification in connection with this application and which are open to public inspection with this specification, and the contents of all such papers and documents are incorporated herein by reference.

All of the features disclosed in this specification (including any accompanying claims, abstract and drawings), and/or all of the steps of any method or process so disclosed, may be combined in any combination, except combinations where at least some of such features and/or steps are mutually exclusive.

Each feature disclosed in this specification (including any accompanying claims, abstract and drawings), may be replaced by alternative features serving the same, equivalent or similar purpose, unless expressly stated otherwise. Thus, unless expressly stated otherwise, each feature disclosed is one example only of a generic series of equivalent or similar features.

The invention is not restricted to the details of the foregoing embodiments. The invention extends to any novel one, or any novel combination, of the features disclosed in this specification (including any accompanying claims, abstract and drawings), or to any novel one, or any novel combination, of the steps of any method or process so disclosed.

CLAIMS

1. Use in a water based hydraulic fluid of an N-alkyl morpholine or a salt thereof as a vapour phase corrosion inhibitor.

2. Use according to Claim 1, wherein the N-alkyl morpholine comprises an N-alkyl group having from 1 to 10 carbon atoms in the alkyl chain.

3. Use according to Claim 1 or 2, wherein the N-alkyl morpholine comprises an N-alkyl group having from 1 to 6 carbon atoms in the alkyl chain.

4. Use according to any one of the preceding claims, wherein the N-alkyl morpholine is N-methyl morpholine.

5. Use according to any of claims 1 to 3, wherein the N-alkyl morpholine is N-ethyl morpholine.

6. Use according to any one of the preceding claims, wherein the N-alkyl morpholine is present in an amount of from 1 to 15 %W/W.

7. Use according to any one of the preceding claims, wherein the hydraulic fluid also comprises an aliphatic or aromatic carboxylic acid.

8. Use according to claim 7, wherein the carboxylic acid is an aliphatic carboxylic acid, comprising up to 22 carbon atoms in the alkyl chain.

9. Use according to claim 8, wherein the aliphatic carboxylic acid, is heptanoic acid, octanoic acid, nonanoic acid, decanoic acid or undecanoic acid.

10. Use according to claim 8, wherein the aliphatic carboxylic acid, is isodecanoic acid.

11. Use according to claim 8, wherein the aliphatic carboxylic acid, is a substituted aryl carboxylic acid.

12. Use according to claim 11, wherein the substituted aryl carboxylic acid is benzene N-methylsulphonamido hexanoic acid.

13. Use according to any one of the preceding claims, wherein the salt of the N-alkyl morpholine is a salt thereof with a carboxylic acid.

14. Use according to claim 13, wherein the salt of the N-alkyl morpholine is a salt thereof with an aliphatic carboxylic acid.

15. Use according to claim 14, wherein the salt of the N-alkyl morpholine is N-methyl morpholine acetate or N-methyl morpholino isodecanoate.

16. Use according to any one of claims 13 to 15, wherein the N-alkyl morpholine salt is present in an amount of from about 5 to 25 %W/W.

17. Use according to any one of the preceding claims, wherein the hydraulic fluid also comprises a freezing point depressant.

18. Use according to claim 17, wherein the freezing point depressant is a glycol.

19. Use fluid according to claim 18, wherein the glycol is ethane 1,2 diol.

20. Use according to any one of the preceding claims, wherein the hydraulic fluid has a pH of from 7 to 10.

21. Use according to any one of the preceding claims, wherein the hydraulic fluid has a pH of from 7 to 8.5.

22. Use according to any one of the preceding claims, wherein the hydraulic fluid also comprises an alkali metal hydroxide.

23. Use according to claim 22, wherein the alkali metal hydroxide is present in an amount sufficient to give a pH of from 7 to 8.5.

24. Use according to claim 22 or 23, wherein the alkali metal hydroxide is potassium hydroxide.

25. Use according to any one of the preceding claims, wherein the hydraulic fluid is substantially free from morpholine and hydroxy alkyl amines.

26. Use of an N-alkylmorpholine or a salt thereof in a water based hydraulic fluid according to any one of the preceding claims, substantially as described in the Example.

27. Use of a water based hydraulic fluid according to any one of the preceding claims, substantially as hereinbefore described.

28. A water-based hydraulic fluid comprising an N-alkyl morpholine or a salt thereof and an acid other than a partial phosphate ester, the hydraulic fluid having a pH of 7 or more.

29. A water based hydraulic fluid according to Claim 28, wherein the N-alkyl morpholine comprises an alkyl group having from 1 to 10 atoms in the alkyl chain.

30. A water based hydraulic fluid according to Claim 28 or 29, wherein the N-alkyl morpholine comprises an alkyl group having from 1 to 6 carbon atoms in the alkyl chain.

31. A water based hydraulic fluid according to any one of Claims 28 to 30, wherein the N-alkyl morpholine is N-methyl morpholine.

32. A water based hydraulic fluid according to any one of Claims 28 to 31, wherein the N-alkyl morpholine is N-ethyl morpholine.

33. A water based hydraulic fluid according to any one of Claims 28 to 32, wherein the N-alkyl morpholine is present in an amount of from 1 to 15 %W/W.

34. A water based hydraulic fluid according to any one of Claims 28 to 33, wherein the acid comprises an aliphatic or aromatic carboxylic acid.

35. A water based hydraulic fluid according to Claim 34, wherein the carboxylic acid is a higher aliphatic carboxylic acid, comprising from about 7 to 22 carbon atoms in the alkyl chain.

36. A water based hydraulic fluid according to Claim 35, wherein the higher aliphatic carboxylic acid, is heptanoic acid, octanoic acid, nonanoic acid, decanoic acid or undecanoic acid.

37. A water based hydraulic fluid according to claim 35, wherein the higher aliphatic carboxylic acid, is isodecanoic acid.

38. A water based hydraulic fluid according to claim 35, wherein the higher aliphatic carboxylic acid, is a substituted aryl carboxylic acid.

39. A water based hydraulic fluid according to claim 38, wherein the substituted aryl carboxylic acid is benzene N-methylsulphonamido hexanoic acid.

40. A water based hydraulic fluid according to any one of Claims 28 to 39, wherein the salt of the N-alkyl morpholine is a salt thereof with a carboxylic acid.

41. A water based hydraulic fluid according to claim 40, wherein the salt of the N-alkyl morpholine is a salt thereof with an aliphatic carboxylic acid.

42. A water based hydraulic fluid according to claim 41, wherein the salt of the N-alkyl morpholine is N-methyl morpholino isodecanoate.

43. A water based hydraulic fluid according to any one of claims 40 to 42, in which the N-alkyl morpholine salt is present in an amount of from about 5 to 25 %W/W.

44. A water based hydraulic fluid according to any one of Claims 28 to 43, which also comprises a freezing point depressant.

45. A water based hydraulic fluid according to claim 44, wherein the freezing point depressant is a glycol.

46. A water based hydraulic fluid according to claim 45, wherein the glycol is ethane 1,2 diol.

47. A water based hydraulic fluid according to any one of Claims 28 to 46, which has a pH of from 7 to 10.

48. A water based hydraulic fluid according to any one of Claims 28 to 47, which has a pH of from 7 to 8.5.

49. A water based hydraulic fluid according to any one of Claims 28 to 48, which also comprises an alkali metal hydroxide.

50. A water based hydraulic fluid according to claim 49, wherein the alkali metal hydroxide is present in an amount sufficient to give a pH of from 7 to 8.5.

51. A water based hydraulic fluid according to claim 49 or 50, wherein the alkali metal hydroxide is potassium hydroxide.

52. A water based hydraulic fluid according to any one of Claims 28 to 51, substantially free from morpholine and hydroxy alkyl amines.

53. A water based hydraulic fluid according to any one of Claims 28 to 52, substantially as described in the Example.

54. A water based hydraulic fluid according to any one of Claims 28 to 53, substantially as hereinbefore described.

55. A fluid controlled apparatus wherein there is used a water based hydraulic fluid comprising an N-alkyl morpholine or a salt thereof as a vapour phase corrosion inhibitor.

56. A fluid controlled apparatus according to claim 55, wherein there is used a water based hydraulic fluid according to any one of claims 28 to 53.

57. A sub-sea oil production system which comprises a fluid controlled apparatus according to claim 55 or 56.

58. Use according to any one of claims 1 to 27, of a water based hydraulic fluid in the control of hydraulically operated valves sited below the sea, and associated with oil production.

INTERNATIONAL SEARCH REPORT

national Application No
PCT/GB 98/03805

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C10M173/02 //(C10M173/02,133:50,129:32,129:40,129:48,135:10, 125:10,129:08),C10N10:02,30:12,40:08

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C10M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 061 823 A (BASF WYANDOTTE CORP) 6 October 1982 see page 1, line 2-3 see page 13, line 1-23 see page 15, line 1-15 see page 15, line 32 - page 16, line 3 ---	1-6,25, 27,55
X	US 4 493 780 A (SCHWARTZ ELLEN S ET AL) 15 January 1985 see abstract see column 1, line 12-14 see column 2, line 42-46 see column 7, line 41-55 see column 8, line 22-31 see column 8, line 59-62 see column 9, line 15-33 --- -/--	1-58

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"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 when the document is taken alone

"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

Date of the actual completion of the international search	Date of mailing of the international search report
16 April 1999	26/04/1999

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Perakis, N

2

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

:national Application No
PCT/GB 98/03805

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 414 125 A (KEIL DECEASED HANS S H ET AL) 8 November 1983 see abstract see column 1, line 56 - column 2, line 16 see column 3, line 11-31 see column 4, line 19-39 see column 12, line 41-51	1-58
X	US 4 379 063 A (WILLIAMS MARK A) 5 April 1983 see abstract see column 1, line 4-7 see column 2, line 24-42 see column 3, line 48 - column 5, line 3	1-58
A	FR 2 101 027 A (NAPHTACHIMIE SA) 31 March 1972 see page 1, line 1-19 see page 2, line 3-7 see page 2, line 28 see page 3, line 28 - page 4, line 2 see page 4, line 23 see claims 1,5,6	1-58
A	GB 603 320 A (E.I. DU PONT DE NEMOURS AND COMPANY) 14 June 1948 see page 1, line 54 - page 2, line 14 see page 2, line 57-58	1-58

2

INTERNATIONAL SEARCH REPORT

Information on patent family members

national Application No
PCT/GB 98/03805

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0061823 A	06-10-1982	AT 13689 T	15-06-1985
		AU 546230 B	22-08-1985
		AU 7978482 A	07-10-1982
		BR 8200371 A	23-11-1982
		DK 30682 A	02-10-1982
		GR 76105 A	03-08-1984
		JP 57167397 A	15-10-1982
US 4493780 A	15-01-1985	US 4390439 A	28-06-1983
		CA 1173021 A	21-08-1984
		EP 0061693 A	06-10-1982
US 4414125 A	08-11-1983	DE 2948503 A	11-06-1981
		EP 0029892 A	10-06-1981
US 4379063 A	05-04-1983	AU 528432 B	28-04-1983
		AU 7552881 A	30-09-1982
		BE 492427 A	
		BR 8200885 A	28-12-1982
		CA 1203527 A	22-04-1986
		DE 3144013 A	16-09-1982
		DK 74082 A,B,	21-08-1982
		FR 2500473 A	27-08-1982
		FR 1000337 A	12-02-1952
		GB 652024 A	
		GB 2093478 A,B	02-09-1982
		JP 1378730 C	28-05-1987
		JP 57139193 A	27-08-1982
		JP 61046039 B	11-10-1986
		NL 75199 C	
		NL 78078 C	
		NL 184119 C	
		NL 8104816 A,B	16-09-1982
		SE 451377 B	05-10-1987
		SE 8106860 A	21-08-1982
		US 2602075 A	01-07-1952
		US 4452710 A	05-06-1984
		ZA 8108722 A	24-11-1982
FR 2101027 A	31-03-1972	BE 771101 A	09-02-1972
		DE 2139892 A	16-03-1972
		LU 63685 A	14-12-1971
		NL 7110935 A	14-02-1972
GB 603320 A		NONE	